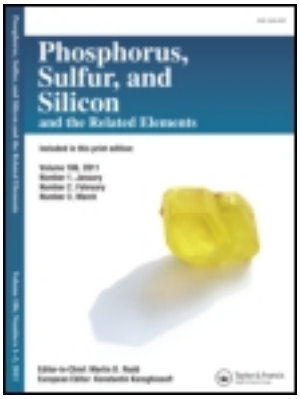

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Triphenylphosphine-Mediated Serendipitous Synthesis of Alkyl Cinnamates Through the Reaction of 3-Hydroxy-4-Methoxybenzaldehyde and Dialkyl Acetylenedicarboxylates

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Version of record first published: 19 Aug 2006

To cite this article: Issa Yavari, Hoorieh Djahaniani, Logman Moradi & Farough Nasiri (2005): Triphenylphosphine-Mediated Serendipitous Synthesis of Alkyl Cinnamates Through the Reaction of 3-Hydroxy-4-Methoxybenzaldehyde and Dialkyl Acetylenedicarboxylates, Phosphorus, Sulfur, and Silicon and the Related Elements, 180:9, 2149-2153

To link to this article: http://dx.doi.org/10.1080/104265090917664

Phosphorus, Sulfur, and Silicon, 180:2149–2153, 2005

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/104265090917664

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Triphenylphosphine-Mediated Serendipitous Synthesis of Alkyl Cinnamates Through the Reaction of 3-Hydroxy-4-Methoxybenzaldehyde and Dialkyl Acetylenedicarboxylates

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Alkyl cinnamates are formed in fairly good yields from the reaction of dialkyl acetylenedicarboxylates and 3-hydroxy-4-methoxybenzaldehyde in the presence of triphenylphosphine.

Keywords 3-Hydroxy-4-methoxybenzaldehyde; alkyl cinnamates; dialkyl acetylenedicarboxylates; triphenylphosphine

α, β-Unsaturated esters are useful chemical entities which are accessible through condensation reactions involving aldehydes, viz. (i) Knoevenagel condensations of active methylene esters with aldehydes,[1] (ii) condensation of alkyl acetates with aldehyde followed by dehydration,[2] and (iii) Hornet, Wadsworth-Emmons olefination of carbonyl compounds.[3] The Knoevenagel condensation route, particularly for cinnamic esters, involves two separate steps, i.e., (1) the preparation of cinnamic acid (2) followed by its esterification and Reformatsky reaction, which has the limitation of not being suitable for the preparation of cinnamic acids with halo, phenoxy, or nitro substituents on the aromatic moiety.[4]

We have recently described[5] the synthesis of functionalized coumarine derivatives from the reaction of triphenylphosphine, dimethyl acetylenedicarboxylate (DMAD), and phenols using an intramolecular Wittig reaction. With the purpose of preparing coumarine derivatives that have a methoxy group at position 8 and a carbaldehyde

Received November 4, 2004; accepted February 12, 2005.
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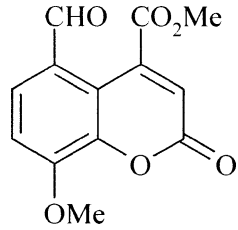
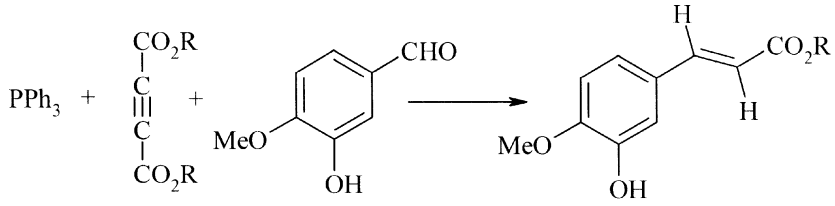


SCHEME 1

group at position 5, **1** (Scheme 1), 3-hydroxy-4-methoxybenzaldehyde was treated with DMAD and triphenylphosphine. However, the coumarine derivative **1** was not observed and methyl 3-hydroxy-4-methoxycinnamate **4a** was isolated instead in 60% yield (Scheme 2).

The reaction of 3-hydroxy-4-methoxybenzaldehyde with dialkyl acetylenedicarboxylates in the presence of triphenylphosphine in CH_2Cl_2 at room temperature proceeded smoothly and produced alkyl (*E*)-(3-hydroxy-4-methoxyphenyl)-2-propenoates (alkyl cinnamates, **4**) in moderate yields (see Scheme 2). These products were separated by column chromatography. The structures of compounds **4a–4d** were deduced from their ^{1}H NMR and ^{13}C NMR spectroscopic data.

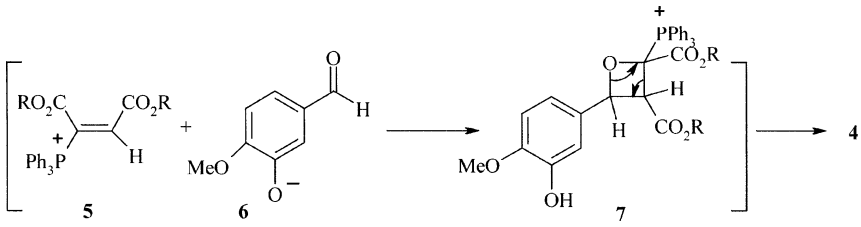
The ^{1}H NMR spectrum of **4a** exhibited two single sharp lines readily recognized as arising from methoxy ($\delta = 3.78$ and 3.90 ppm) group and an AX pattern for the vinylic protons ($\delta = 6.30$ ppm, $^3J_{HH} = 16$ Hz; and $\delta = 7.57$ ppm, $^3J_{HH} = 16$ Hz), together with an AXM pattern for the aromatic protons ($\delta = 6.82$ ppm, $^3J_{HH} = 8.2$ Hz; $\delta = 7.01$ ppm, $^3J_{HH} = 8$ Hz, and $^4J_{HH} = 2$ Hz; and $\delta = 7.12$ ppm, $^4J_{HH} = 2$ Hz). The proton-



2 **3** **4**

	R		R	% Yield
2a	Me	**4a**	Me	60
2b	Et	**4b**	Et	65
2c	*i*-Pr	**4c**	*i*-Pr	75
2d	*t*-Bu	**4d**	*t*-Bu	65

SCHEME 2



SCHEME 3

decoupled ^{13}C NMR spectrum of **4a** showed 11 distinct resonances in agreement with the proposed structure. The ^{1}H and ^{13}C NMR spectra of **4b–4d** are similar to those for **4a** except for the ester moieties, which give rise to characteristic signals in the aliphatic region of the spectra. Partial assignment of these resonances is given in the Experimental section.

The plausible way of formation of the product is proposed in Scheme 3. On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[5–13] it is reasonable to assume that compound **4** results from the nucleophilic addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the reactive 1:1 adduct by 3-hydroxy-4-methoxybenzaldehyde. Then the positively charged ion undergoes a [2 + 2] cycloaddiotion reaction with the aldehyde carbonyl group to produce the oxetane **7**. The alkyl cinnamates **4** are presumably produced by fragmentation of **7**.

In conclusion, the reaction of dialkyl acetylenedicarboxylates and 3-hydroxy-4-methoxybenzaldehyde in the presence of triphenylphosphine provides a simple one-pot entry into the synthesis of alkyl (*E*)-3-(3-hydroxy-4-methoxyphenyl)-2-propenoates. This procedure has the advantages of mild reaction conditions and simple experimental and work-up conditions.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. These results agreed favorably with the calculated values. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker DRX-500 AVANCE instrument with $CDCl_3$ as solvent at 500.1 and 125.7 MHz, respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. 3-Hydroxy-4-methoxybenzaldehyde, dialkyl

acetylenedicarboxylates, and triphenylphosphine were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

Preparation of Methyl (*E*)-3-(3-hydroxy-4-methoxyphenyl)-2-propenoate (4a)

To a stirred solution of 3-hydroxy-4-methoxybenzaldehyde (0.30 g, 2 mmol) and DMAD (0.28 g, 2 mmol) in CH_2Cl_2 (10 mL) was added drop wise at $-10^{\circ}C$ over 10 min a solution of triphenylphosphine (0.52 g, 2 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was then allowed to warm up to room temperature and stand for 24 h. The solvent was removed under reduced pressure and product **4a** was separated by silica gel column chromatography (Merck 230–400 mesh) using *n*-hexane-EtOAc as eluent. White powder; yield: 0.12 g (60%), mp 119–120°C. IR (KBr) (ν_{max}/cm^{-1}): 3395 (OH), 1693 (C=O). ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 3.78$ (3 H, s, OMe), 3.90 (3 H, s, OMe), 5.80 (1 H, br s, OH), 6.30 (1 H, d, $^3J_{HH} = 16$ Hz, CH), 6.82 (1 H, d, $^3J_{HH} = 8$ Hz, CH), 7.01 (1 H, dd, $^3J_{HH} = 8$ and $^4J_{HH} = 2$ Hz, CH), 7.12 (1 H, d, $^4J_{HH} = 2$ Hz, CH), 7.59 (1 H, d, $^3J_{HH} = 16$ Hz, CH). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 51.6 (OMe), 56.00 (OMe), 110.5, 113.0, 115.8, 121.8 (4 CH), 128.0 (C), 144.7 (CH), 145.9 (C–O), 148.6 (C–O), 167.7 (C=O).

Ethyl (*E*)-3-(3-hydroxy-4-methoxyphenyl)-2-propenoate (4b)

Yellow oil, yield: 0.14 g, (65%). IR (KBr) (ν_{max}/cm^{-1}): 3385 (OH), 1690 (C=O). ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.20$ (3 H, t, $^3J_{HH} = 7.1$ Hz, Me), 3.79 (3 H, s, OMe), 4.13 (2 H, q, $^3J_{HH} = 7$ Hz, O–CH_2), 5.58 (1 H, br s, OH), 6.15 (1 H, d, $^3J_{HH} = 16$ Hz, CH), 6.71 (1 H, d, $^3J_{HH} = 8$ Hz, CH), 6.90 (1 H, dd, $^3J_{HH} = 8$ and $^4J_{HH} = 2$ Hz, CH), 7.01 (1 H, d, $^4J_{HH} = 2$ Hz, CH), 7.45 (1 H, d, $^3J_{HH} = 16$ Hz, CH). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.2$ (Me), 56.0 (OMe), 60.4 (CH_2), 110.5, 113.0, 116.4, 121.8 (4 CH), 128.2 (C), 144.4 (CH), 145.9 (C–O), 148.5 (C–O), 167.3 (C=O).

iso-Propyl (*E*)-3-(3-hydroxy-4-methoxyphenyl)-2-propenoate (4c)

Yellow oil, yield: 0.17 g, (75%). IR (KBr) (ν_{max}/cm^{-1}): 3390 (OH), 1687 (C=O). ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.31$ (6 H, d, $^3J_{HH} = 7$ Hz, 2 Me), 3.76 (3 H, s, OMe), 5.09 (1 H, heptet, $^3J_{HH} = 7$ Hz , OCH), 5.50 (1 H, br s, OH), 6.27 (1 H, d, $^3J_{HH} = 16$ Hz, CH), 6.89 (1 H, d, $^3J_{HH} = 8$ Hz, CH), 6.91 (1 H, dd, $^3J_{HH} = 8$ and $^4J_{HH} = 2$ Hz, CH), 6.97 (1 H, d, $^4J_{HH} = 2$ Hz, CH), 7.59 (1 H, d, $^3J_{HH} = 16$ Hz, CH). ^{13}C NMR (125 MHz,

$CDCl_3$): $\delta = 21.6$ (Me), 55.9 (OMe), 67.3 (CH), 110.4, 113.3, 115.4, 121.4 (4 CH), 127.8 (C), 144.2 (CH), 145.7 (C—O), 148.1 (C—O), 167.8 (C=O).

tert-Butyl (*E*)-3-(3-hydroxy-4-methoxyphenyl)-2-propenoate (4d)

Yellow oil, yield: 0.16 g, (65%). IR (KBr) (ν_{max}/cm^{-1}): 3390 (OH), 1695 (C=O). ^1H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.49$ (9 H, s, CMe_3), 3.78 (3 H, s, OMe), 5.67 (1 H, br s, OH), 6.34 (1 H, d, $^3J_{HH} = 16$ Hz, CH), 6.86 (1 H, d, $^3J_{HH} = 8$ Hz, CH), 7.0 (1 H, dd, $^3J_{HH} = 8$ and $^4J_{HH} = 2$ Hz, CH), 6.90 (1 H, d, $^4J_{HH} = 2$ Hz, CH), 7.62 (1 H, d,$^3J_{HH} = 16$ Hz, CH). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 28.3$ (CMe_3), 55.8 (OMe), 81.5 (O—*C*Me_3), 110.5, 113.3, 115.3, 121.6 (4 CH), 127.9 (C), 144.9 (CH), 145.8 (C—O), 148.1 (C—O), 168.0 (C=O).

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