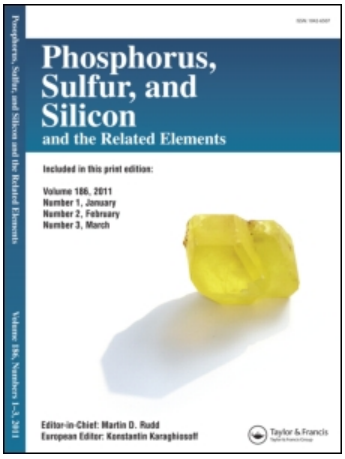

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Facile and One-Pot Synthesis of 2 H -Chromene Derivatives Mediated by Vinyl triphenylphosphonium Salt

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FACILE AND ONE-POT SYNTHESIS OF 2*H*-CHROMENE DERIVATIVES MEDIATED BY VINYL TRIPHENYLPHOSPHONIUM SALT

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An efficient process that converts 2-hydroxybenzaldehyde and their derivetives to chromene derivatives via intramolecular Wittig reaction is described.

Keywords: 2H-Chromene derivatives; dimethyl acetylene dicarboxylate (DMAD); vinyl triphenylphosphonium salt

Chromene (2*H*-1-benzopyran derivatives) are important hetrocyclic compounds in bioorganic chemistry[1–2] and have been employed widely as important intermediates in the synthesis of many natural products and medical agents.[3–4] There has been recent interest in the use of these common structural elements for a new family of potassium-channel activating drugs.[5] They also serve as the frame work of a range of tannins[6] which are becoming increasingly important because of their health-promoting effects found in teas, vegetables, fruits, fruit juices, and red wines.

Despite several existing methods for the synthesis of chromene derivatives[7] there still is a demand for general strategies which can efficiently produce these systems.

In this article we report a facile one-pot synthesis of dimethyl 2*H*-benzopyran-2,3-dicarboxylate and their derivatives in fairly high yields.

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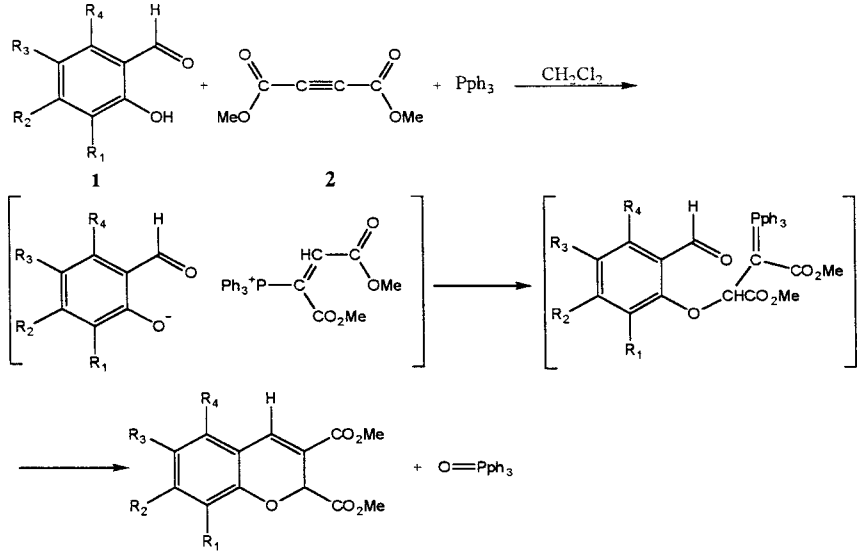
RESULTS AND DISCUSSION

A series of chromene derivatives (**3a–f**) was easily prepared in fairly high yields from readily available compounds substituted salicylaldehydes and DMAD (**2**).

Protonation of the products produced in the reaction between triphenylphosphine and dimethyl acetylene dicarboxylate by 2-hydroxy benzaldehyde and their derivatives leads to vinyl triphenylphosphonium salts, which undergo an intramolecular Wittig reaction to produce dimethyl-2-*H*-benzopyran-2,3-dicarboxylate and their derivatives. The result of our studies are summarized in Scheme 1.



Entry for **3**	R_1	R_2	R_3	R_4
a	H	H	H	H
b	H	H	NO_2	H
c	H	H	OMe	H
d	H	H	Br	H
e	OMe	H	H	H
f	H	OMe	H	H

SCHEME 1

The structure of compounds **3a–f** were deduced from their elemental analyses and their ^{1}H and ^{13}C NMR spectra. The mass spectra of these compounds displayed a molecular ion peak at appropriate m/e values.

EXPERIMENTAL

Melting points were measured with an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN—O-Rapid analyzer. The infrared spectra were recorded on a Philips PU9800 FT-IR spectrometer, ^{1}H and ^{13}CNMR spectra were measured with JEOL EX-90A spectrometer at 90 and 22.6 MHz respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Dimethyl acetylenedicarboxylate, 2-hdroxybenzaldehyde and their derivatives, and triphenylphosphine were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

Dimethyl12H-chromene-2,3-dicarboxylate (3a)

Yield 85%; m.p.: 81–82°C; ^{1}H NMR (90 MHz, δ, $CDCl_3$): 3.68 (3H, s, OCH_3), 3.7 (3H, s, OCH_3), 6.30 (1H, s, CH), 6.89 (1H, s, CH), 7.25–7.34 ($4H_{ar}$) ppm; ^{13}C NMR (22.6 MHz, δ, $CDCl_3$): 51.30 (OCH_3), 51.80 (OCH_3), 71.44 (C—O), 112.87 (CH), 119.73 (C), 120.121 (C), 121.25 (CH_{ar}), 126.62 (CH_{ar}), 126.70 (CH_{ar}), 129.79 (CH_{ar}), 154.61 (CO), 166.75 (CO_{ester}), 168.66 (CO_{ester}) ppm; Elemental analysis calculated for $C_{13}H_{12}O_5$; (MW: 248); C, 62.90; H, 4.87; O, 32.23 and found C, 62.87; H, 4.79; O, 31.93; ms (70 eV) m/z = 248.2.

Dimethyl6-nitro-2H-chromene-2,3-dicarboxylate (3b)

Yield 90%; m.p.: 99°C; ^{1}H NMR (90 MHz, δ, $CDCl_3$): 3.68 (3H, s, OCH_3), 3.7 (3H, s, OCH_3), 6.30 (1H, s, CH), 6.69 (1H, s, CH), 7.05–7.34 ($3H_{ar}$) ppm; ^{13}C NMR (22.6 MHz, δ, $CDCl_3$): 51.30 (OCH_3), 51.80 (OCH_3), 71.44 (C—O), 116.64 (CH_{ar}), 118.97 (C), 119.73 (C), 122.10 (CH_{ar}), 125.23 (CH_{ar}), 128.25 (CH_{ar}), 142.14 (C—N), 154.26 (CO), 166.75 (CO_{ester}), 168.66 (CO_{ester}) ppm; Elemental analysis calculated for $C_{13}H_{11}O_7N$: (MW: 293); C, 53.25; H, 3.78; O, 38.19; N, 4.78 and found C, 53.30; H, 3.80; O, 38.2; N, 4.69; ms (70 eV) m/z = 293.2.

Dimethyl6-methoxy-2H-chromene-2,3-dicarboxylate (3c)

Yield 80%; m.p.: 113°C; ^{1}H NMR (90 MHz, δ, $CDCl_3$): 3.66 (3H, s, OCH_3), 3.68 (3H, s, OCH_3), 3.70 (3H, s, OCH_3), 6.30 (1H, s, CH),

6.80 (1H, s, CH), 6.86–7.14 ($3H_{ar}$) ppm; ^{13}C NMR (22.6 MHz, δ, $CDCl_3$: 51.30 (OCH_3), 51.80 (OCH_3), 55.99 (OCH_3), 111.39 (CH_{ar}), 113.31 (CH_{ar}), 115.08 (CH_{ar}), 123.96 (CH), 127.61 (CH), 148.40 (C—O), 152.14 (C—O), 166.75 (CO_{ester}), 168.66 (CO_{ester}) ppm; Elemental analysis calculated for $C_{14}H_{14}O_6$: (MW: 278); C, 60.43; H, 5.07; O, 34.50 and found C, 60.40; H, 5.02; O, 34,30; ms (70 eV) m/z = 278.3.

Dimethyl6-bromo-2H-chromene-2,3-dicarboxylate (3d)

Yield 92%; m.p.: 139°C; ^1H NMR (90 MHz, δ $CDCl_3$): 3.68 (3H, s, OCH_3), 3.7 (3H, s, OCH_3), 6.30 (1H, s, CH), 6.99 (1H, s, CH), 7.05–7.36 ($3H_{ar}$) ppm; ^{13}C NMR (22.6 MHz, δ, $CDCl_3$): 51.30 (OCH_3), 51.80 (OCH_3), 71.44 (C—O), 110.38 (C—Br), 119.73 (C), 124.36 (CH_{ar}), 126.21 (CH_{ar}), 130.77 (CH_{ar}), 133.13 (CH_{ar}), 150.56 (CO), 166.77 (C═O), 168.66 (CO_{ester}) ppm; Elemental analysis calculated for $C_{13}H_{11}O_5$ Br: (MW: 327); C, 47.73; H, 3.39; O, 24.45; Br, 24.43 and found C, 47.51; H, 3.85; O, 24.30: Br, 24.48; ms (70 eV) m/z = 327.1.

Dimethyl8-methyoxy-2H-chromene-2,3-dicarboxylate (3e)

Yield 85%; m.p.: 66°C; ^1H NMR (90 MHz, δ, $CDCl_3$): 3.20 (3H, s, OCH_3), 3.68 (3H, s, OCH_3), 3.70 (3H, s, OCH_3), 6.24 (1H, s, CH), 6.25 (1H, s, CH), 7.12–7.20 ($3H_{ar}$) ppm; ^{13}C NMR (22.6 MHz, δ, $CDCl_3$): 51:30 (OCH_3), 51.80 (OCH_3), 55.99 (OCH_3), 118.89 (CH_{ar}), 119.73 (C), 120.16 (C), 121.24 (CH_{ar}), 121.96 (CH_{ar}), 127.61 (CH), 148.60 (C—O), 152.14 (C—O), 166.75 (CO_{ester}), 168.66 (CO_{ester}) ppm; Elemental analysis calculated for $C_{14}H_{14}O_6$: (MW: 278); C, 60.43; H, 5.07; O, 34.50 and found C, 60:30; H, 5.02; O, 34.60; ms (70 eV) m/z = 278.26.

Dimethyl2H-chromene-2,3-dicarboxylate (3f)

Yield 85%; m.p.: 168°C; ^1H NMR (90 MHz, δ, $CDCl_3$): 3.68 (3H, s, OCH_3), 3.7 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 6.30 (1H, s, CH), 6.50 (1H, s, CH), 7.19–7.34 ($3H_{ar}$) ppm; ^{13}C NMR (22.6 MHz, δ, $CDCl_3$): 51.30 (OCH_3), 51.80 (OCH_3), 55.64 (C—O), 71.44 (C—O), 98.47 (CH_{ar}), 107.38 (CH_{ar}), 118.36 (C), 119.73 (CH), 126.62 (CH), 129.99 (CH_{ar}), 158.17 (CO), 161.19 (CO), 166.75 (CO_{ester}), 168.66 (CO_{ester}) ppm; Elemental analysis calculated for $C_{14}H_{14}O_6$: (MW: 278); C, 60.43; H, 5.07; O, 34.50 and found C, 60.31; H, 4.97; O, 34.23; ms (70 eV) m/z = 278.3.

GENERAL PROCEDURE

To a magnetically stirred solution of triphenylphosphine (0.524 g, 2 mmol), and 2-hydroxybenzaldehyde (2 mmol) in 5 ml dichloromethane was added dropwise a mixture of dimethyl acetylen dicarboxylate (0.284 g, 2 mmol) in 2 ml of dichloromethane at -5°C over 10 min. The reaction was then allowed to warm to room temperature and stirred for 24 h. The solvent was removed under reduced pressure. After the removal of solvent and column chromatography on silicagel (10 g) eluted with a mixture of n-hexane:dimethyl ether (2:1) a pure product was obtained.

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