

# Reaction Between Dimethyl Acetylenedicarboxylate and Phenols in the Presence of Dipotassium Hydrogen Phosphate in Solvent-Free Conditions: An Efficient Environment-Friendly Method for the Synthesis of Aryl Vinyl Ethers

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**Abstract.** *A two-component condensation reaction between an electron-poor acetylenic ester and a phenol efficiently provides substituted aryl vinyl ethers in a one-pot reaction in the presence of dipotassium hydrogen phosphate in solvent-free conditions.*

**Keywords:** *Dipotassium hydrogen phosphate; Aryl vinyl ether; Acetylenic ester; Phenol; Solvent-free conditions.*

## INTRODUCTION

The environmentally friendly synthesis of organic compounds without using organic solvents has improved considerably in recent years [1]. Organic reactions using conventional organic solvents especially those using chlorinated hydrocarbons have posed a serious threat to the environment, owing to their toxic and volatile nature [1]. In this regard, solvent-free catalytic organic reactions have received tremendous attention in recent times [2].

For several years, acetylenic esters have been attracting the attention of organic chemists [3]. Acetylenic esters are reactive systems that take part in many chemical syntheses [3]. The compounds almost act as a Michael acceptor in organic reactions [4]. In recent years, there has been increasing interest in the application of acetylenic esters in multi-component synthesis [5-11]. Due to the atom economy, convergent character and simplicity of one-pot procedures, Multi-

component Condensation Reactions (MCRs) have an advantageous position over other reactions. The discovery and development of novel MCRs is receiving growing interest from industrial chemistry research groups, representing a new challenge for organic chemists, including a basic understanding of organic chemistry itself [12].

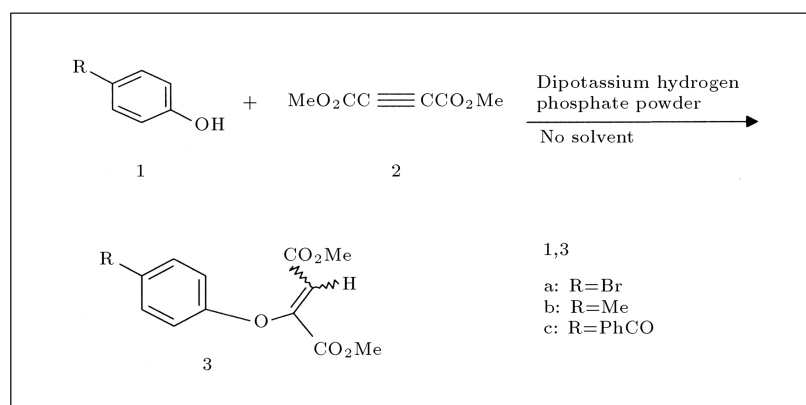
Aryl vinyl ether derivatives are important monomers with potentially useful properties in that they free-radically polymerize to produce organic polymers [13,14]. Several methods have been reported in the literature for the synthesis of aryl vinyl ethers whose protocols are multi-step in nature [13,14]. Few reliable and operationally simple examples have been reported for the one-pot synthesis of aryl vinyl ethers especially from readily available phenols, acetylenic esters and triphenylphosphine [15-21].

As an additive, dipotassium hydrogen phosphate promotes many condensation reactions under solvent-free conditions [22-26]. Following this interest in solvent-free synthesis [27], in this paper, a report is given on a hitherto unknown two-component reaction which, starting from simple and readily available precursors, affords functionalized aryl vinyl ethers in a one-pot reaction in the presence of dipotassium hy-

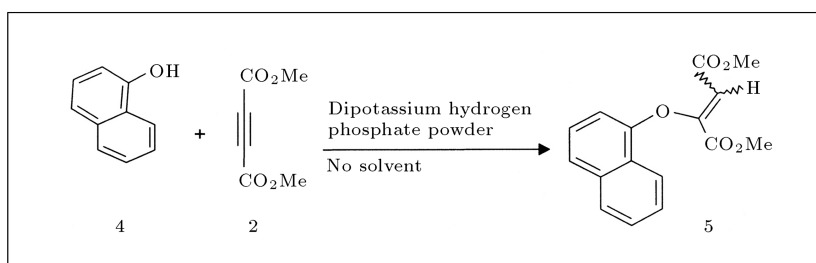
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Received 15 July 2007; received in revised form 12 December 2007; accepted 10 February 2008



**Scheme 1.** Preparation of *O*-vinyl ethers from 4-substituted phenol derivatives.



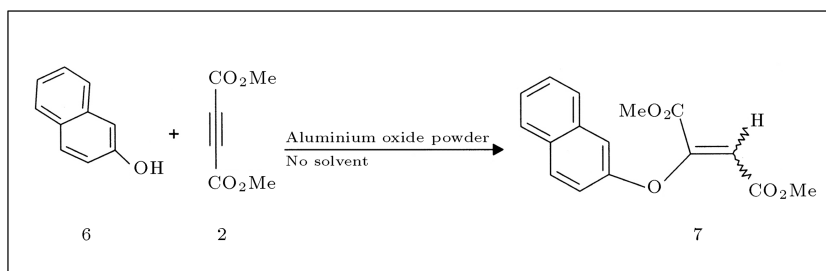
**Scheme 2.** Synthesis of *O*-vinyl ethers **5** from 1-naphthol and dimethyl acetylenedicarboxylate.

drogen phosphate powder under solvent-free conditions (Schemes 1 to 3 and Table 1).

## RESULTS AND DISCUSSION

In the presence of dipotassium hydrogen phosphate powder, phenols (**1**, **4** and **6**) and dimethyl acetylenedicarboxylate **2** undergo a smooth 1:1 addition reaction under solvent-free conditions to produce functionalized aryl vinyl ethers **3**, **5** and **7** (Schemes 1 to 3 and Table 1). The reaction proceeds smoothly and cleanly under mild conditions and no side reactions are observed. In the absence of solid inorganic catalyst powders, the phenols (**1**, **4** and **6**) did not react under reaction conditions with dimethyl acetylenedicarboxylate

**2** in the solvent-free system (Schemes 1 to 3 and Table 1). Also, the reaction did not occur in dichloromethane solutions after several days. TLC indicated the formation of compounds **3**, **5** and **7** on the solid catalyst surface. Compounds **3**, **5** and **7** are stable, due to staying at room temperature in solvent ( $\text{CHCl}_3$ ), neat or on the solid catalyst surfaces.  $\text{SiO}_2$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{NaHSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{KHSO}_4$ ,  $\text{MgO}$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{KAl}(\text{SO}_4)_2$ ,  $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ ,  $\text{ZnO}$ , and  $(\text{NH}_4)_2\text{HPO}_4$  have also been used in this reaction, but the yields of the products were very low and, in some cases, decomposition and several products were observed. However, in the case of product **7**, it was found that  $\text{Al}_2\text{O}_3$  is a suitable catalyst relative to  $\text{K}_2\text{HPO}_4$ . The mechanistic role of the catalysts was not



**Scheme 3.** Aluminium oxide catalyzed synthesis of *O*-vinyl ether **7** from 2-naphthol and dimethyl acetylenedicarboxylate.

**Table 1.** Synthesis of aryl vinyl ethers in solvent-free conditions.

Entry	Product	Thermal Conditions; Isolated Yield%	Microwave Conditions; Isolated Yield%	Inorganic Catalyst	Ratio of Z/E
1	<b>3a</b>	45°C, 90 min.; 58	0.8 KW, 3 min.; 64	K <sub>2</sub> HPO <sub>4</sub>	100/0
2	<b>3b</b>	30°C, 90 min.; 85	0.8 KW, 2 min.; 88	K <sub>2</sub> HPO <sub>4</sub>	73/27
3	<b>3c</b>	60°C, 45 min.; 84	0.8 KW, 2 min.; 85	K <sub>2</sub> HPO <sub>4</sub>	39/61
4	<b>5</b>	70°C, 45 min.; 62	0.8 KW, 2 min.; 67	K <sub>2</sub> HPO <sub>4</sub>	71/29
5	<b>7</b>	80°C, 50 min.; 60	0.8 KW, 2 min.; 62	Al <sub>2</sub> O <sub>3</sub>	11/89

investigated in this reaction. The <sup>1</sup>H NMR (CDCl<sub>3</sub>) spectra of compounds **3**, **5** and **7** show the presence of two stereoisomers (**E** and **Z**) for each *O*-vinyl ether. The relative population of **E** and **Z** isomers were determined via their <sup>1</sup>H NMR spectra (based on the relative intensities of the olefinic protons of **E** and **Z** isomers (=CH)) (see Table 1 and Experimental Section). <sup>1</sup>H NMR spectra show that the two stereoisomers (**E** and **Z**) are not in equilibrium. In each case, the relative population of **E** and **Z** isomers are not dependent on the reaction conditions (thermal and microwave conditions) (see Table 1).

The mechanism of the reaction between the phenols (1, 4 and 6) and dimethyl acetylenedicarboxylate **2** in the presence of solid inorganic catalysts under solvent-free conditions has not been established experimentally.

## CONCLUSIONS

It is believed that the reported method offers a mild, simple and efficient route for the preparation of substituted aryl vinyl ethers. The ease of work up, good yields and fairly short reaction time make it a useful addition to modern synthetic methodologies. Other aspects of this process are under investigation.

## EXPERIMENTAL

Starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Flash chromatography columns were prepared from Merck silica gel powder. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. A commercial oven Butane M245 was used for microwave irradiation. IR spectra were measured on a Shimadzu IR-460 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured (CDCl<sub>3</sub> solution) with a BRUKER DRX-250 AVANCE spectrometer at 250.0 and 62.5 MHz, respectively.

## General Procedure

A homogenous mixture of phenol (1 mmol), dimethylacetylenedicarboxylate (1 mmol) and powdered solid catalyst (0.7 g) were heated at the sealed vessel in a thermal oven (or in a microwave oven) and then over a column of silica gel (10 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:15) as eluent. The solvent was removed under reduced pressure and the products were obtained. The relative population of **E** and **Z** stereoisomers for the compounds **3**, **5** and **7** were determined via their <sup>1</sup>H NMR spectra. The characterization data of the products are given below.

### *Dimethyl(Z)-2-(4-Bromophenoxy)-2-Butenedioate(3a)*

White crystals, m. p. = 86.0-90.0°C. IR (KBr) ( $\nu_{max}$ , cm<sup>-1</sup>): 3093 (=C-H); 3008 (C-H, arom.); 2954 (C-H, aliph.); 1727 (C=O, ester); 1658 (C=C, alkene); 1581 and 1481 (C=C, arom.); 1252, 1203, 1010 (C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>) for **Z** stereoisomer;  $\delta_H$ : 3.72 and 3.76 (6 H, 2 s, 2 OCH<sub>3</sub>); 6.64 (1 H, s, =CH); 6.84 (2 H, d, <sup>3</sup>J<sub>HH</sub>=8.8 Hz, C2 and C6, arom.); 7.41 (2 H, d, <sup>3</sup>J<sub>HH</sub>= 8.8 Hz, C3 and C5, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for **Z** stereoisomer,  $\delta_C$ : 52.08 and 53.12 (2 OCH<sub>3</sub>); 115.82 (=CH); 115.84 and 117.87 and 132.58 and 149.51 and 155.31 (5 C); 162.82 and 164.10 (2 C=O, ester).

### *Dimethyl 2-(4-Methylphenoxy)-2-Butenedioate (3b)*

Colorless oil, IR(neat) ( $\nu_{max}$ , cm<sup>-1</sup>): 3100(=C-H); 3008 (C-H, arom.); 2951 (C-H, aliph.); 1735 (C=O, ester); 1658 (C=C, alkene); 1504 and 1442 (C=C, arom.); 1203 and 1103 (C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>) for **Z** stereoisomer,  $\delta_H$ : 2.30 (3 H, s, CH<sub>3</sub>); 3.71 and 3.73 (6 H, 2 s, 2 OCH<sub>3</sub>); 6.55 (1 H, s, =CH); 6.85 (2 H, d, <sup>3</sup>J<sub>HH</sub>=8.5 Hz, C2 and C6 arom.); 7.09 (2 H, d, <sup>3</sup>J<sub>HH</sub>= 8.5 Hz, C3 and C5, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for **Z** stereoisomer,  $\delta_C$ : 20.61 (CH<sub>3</sub>); 51.92 and 52.93 (2 OCH<sub>3</sub>); 114.51 (=CH); 115.97 (C2 and C6, arom.); 130.08 (C3 and C5, arom.); 132.88 (C4, arom.); 150.10 (O-C=); 154.46 (OC, arom.); 162.75 and 163.99 (2 C=O, ester). <sup>1</sup>H NMR (CDCl<sub>3</sub>) for **E** stereoisomer,  $\delta_H$ :

2.35 (3 H, s, CH<sub>3</sub>); 3.65 and 3.93 (6 H, 2 s, 2 OCH<sub>3</sub>); 5.11 (1 H, s, =CH); 6.99 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C2 and C6, arom.); 7.20 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C3 and C5, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for **E** stereoisomer, δ<sub>C</sub>: 20.82 (CH<sub>3</sub>); 51.65 and 53.04 (2 OCH<sub>3</sub>); 98.24 (=CH); 120.55 (C2 and C6, arom.); 130.64 (C3 and C5, arom.); 132.11 (C4, arom.); 150.90 (O-C=); 151.55 (OC, arom.); 163.55 and 164.95 (2 C=O, ester).

#### Dimethyl

#### 2-(4-Benzoylphenoxy)-2-Butenedioate (3c)

White crystals, m. p. = 96.0-98.0°C. IR(KBr) (*v*<sub>max</sub>, cm<sup>-1</sup>): 3026(=C-H); 3016 (C-H, arom.); 2923 (C-H, aliph.); 1735 (C=O, ester); 1650 (C=C, alkene); 1596 and 1442 (C=C, arom.); 1211 and 1025 (C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>) for **Z** stereoisomer, δ<sub>H</sub>: 3.74 and 3.79 (6 H, 2 s, 2 OCH<sub>3</sub>); 6.74 (1 H, s, =CH); 7.01-7.90 (9 H, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for **Z** stereoisomer, δ<sub>C</sub>: 52.24 and 53.33 (2 OCH<sub>3</sub>); 116.70 (=CH); 128.30, 129.86, 132.28, 132.36, 132.73 (5 CH, arom.); 134.50, 137.71, 148.91, 159.93 (4C); 162.18 and 163.53 (2C=O, ester); 193.11 (C=O, ketone). <sup>1</sup>H NMR (CDCl<sub>3</sub>) for **E** stereoisomer, δ<sub>H</sub>: 3.72 and 3.94 (6 H, 2 s, 2 OCH<sub>3</sub>); 5.35 (1 H, s, =CH); 7.01-7.90 (9 H, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for **E** stereoisomer, δ<sub>C</sub>: 52.03 and 53.28 (2 OCH<sub>3</sub>); 101.51 (=CH); 115.48, 120.29, 128.45, 129.97, 132.47 (5 CH, arom.); 135.36, 137.17, 156.39, 158.95 (4C); 162.90 and 165.52 (2 C=O, ester); 195.31 (C=O, ketone).

#### Dimethyl 2-(1-Naphthylloxy)-2-Butenedioate (5)

Viscous yellow oil, IR(neat) (*v*<sub>max</sub>, cm<sup>-1</sup>): 3061 (=C-H); 3015 (C-H, arom.); 2961 (C-H, aliph.); 1734 (C=O, ester); 1649 (C=C, alkene); 1587 and 1449 (C=C, arom.); 1279, 1217, 1047 (C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>) for **Z** stereoisomer, δ<sub>H</sub>: 3.68 and 3.69 (6 H, 2 s, 2 OCH<sub>3</sub>); 6.75 (1 H, s, =CH); 6.78-8.40 (7 H, m, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for **Z** stereoisomer, δ<sub>C</sub>: 52.06 and 53.08 (2 OCH<sub>3</sub>); 108.52 (=CH); 115.35, 122.15, 123.37, 125.22, 126.04, 126.83, 127.48 (7 CH, arom.); 120.40 and 125.54 (2 C, arom.); 150.24 (O-C=); 152.74 (OC, arom.); 162.77 and 164.13 (C=O, ester). <sup>1</sup>H NMR (CDCl<sub>3</sub>) for **E** stereoisomer, δ<sub>H</sub>: 3.65 and 4.03 (6 H, 2 s, 2 OCH<sub>3</sub>); 5.03 (1 H, s, =CH); 6.78-8.40 (7 H, m, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for **E** stereoisomer, δ<sub>C</sub>: 51.76 and 53.29 (2 OCH<sub>3</sub>); 98.45 (=CH); 120.4, 121.30, 121.67, 125.54, 125.86, 126.75, 128.02 (7 CH, arom.); 122.71 and 124.42 (2 C, arom.); 148.53 (O-C=); 151.63 (OC, arom.); 161.39 and 163.62 (2 C=O, ester).

#### Dimethyl 2-(2-Naphthylloxy)-2-Butenedioate (7)

Light yellow crystals, m. p. = 96.0-99.0°C. IR(KBr) (*v*<sub>max</sub>, cm<sup>-1</sup>): 3054 (=C-H); 3010 (C-H, arom.); 2923 (C-H, aliph.); 1727 (C=O, ester); 1627 (C=C, alkene);

1604 and 1465 (C=C, arom.); 1280, 1218, 1172 (C-O). <sup>1</sup>H NMR (CDCl<sub>3</sub>) for **Z** stereoisomer, δ<sub>H</sub>: 3.69 and 3.96 (6 H, 2 s, 2 OCH<sub>3</sub>); 6.7 (1 H, s, =CH); 7.09-7.84 (7 H, m, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for **Z** stereoisomer, δ<sub>C</sub>: 51.50 and 53.16 (2 OCH<sub>3</sub>); 109.50 (=CH); 109.91, 117.95, 126.34, 124.79, 127.13, 128.81, 130.02 (7 CH, arom.); 120.01 and 127.11 (2 C, arom.); 150.89 (O-C=); 154.75 (C1, arom.); 163.45 and 166.12 (2 C=O, ester). <sup>1</sup>H NMR (CDCl<sub>3</sub>) for **E** stereoisomer, δ<sub>H</sub>: 3.72 and 3.73 (6 H, 2 s, 2 OCH<sub>3</sub>); 5.13 (1 H, s, =CH); 7.09-7.84 (7 H, m, arom.). <sup>13</sup>C NMR (CDCl<sub>3</sub>) for **E** stereoisomer, δ<sub>C</sub>: 52.09 and 53.11 (2 OCH<sub>3</sub>); 115.55 (=CH); 117.73, 123.60, 126.34, 126.35, 127.75, 129.82, 134.60 (7 CH, arom.); 127.13 and 130.02 (2 C, arom.); 149.89 (O-C=); 153.36 (C1, arom.); 162.45 and 164.56 (2 C=O, ester).

#### ACKNOWLEDGMENTS

This work was done under the appreciated support of Zanjan University, Iran.

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