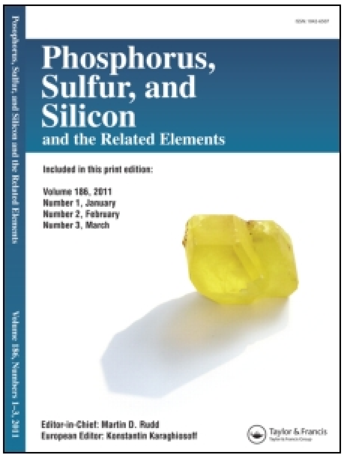


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# Microwave-Assisted Pechmann Reaction on P 2 O 5 /Molecular Sieves. Application to the Preparation of 4-Substituted Coumarins

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# MICROWAVE-ASSISTED PECHMANN REACTION ON $P_2O_5$/MOLECULAR SIEVES. APPLICATION TO THE PREPARATION OF 4-SUBSTITUTED COUMARINS

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*4-Substituted coumarins were efficiently and rapidly synthesised via Pechmann condensation of phenols with ethyl acetoacetate catalyzed by $P_2O_5$/molecular sieves in satisfactory yields.*

*Keywords:* Microwave irradiation; molecular sieves; Pechmann reaction; $P_2O_5$



Coumarins stand in special place in the realm of synthetic organic chemistry and natural products. Coumarins are common in nature and used as intermediates in the synthesis of pharmaceuticals,[1] insecticides,[2] fluorescent brightness,[3] and anticoagulant agents.[4]

Coumarins have been synthesized by many different routes,[5] including Pechmann reaction.[6] In this reaction, substituted phenols are condensed with $\beta$-ketonic esters in acidic media to afford coumarins. Various acidic media have been used to carry out this reaction.[7] These methods have their own merits and advantages. In some methods the reactions need several hours or even days to be completed as should be heated above 150°C. In addition some undesired products such as chromones are reported to be formed during the reaction.[8] Some methods also suffer from having tedious work-up procedure.

The microwave enhanced chemical reactions in solventless system have gained popularity[9] as they can be conducted efficiently and rapidly to afford pure products in quantitative yields.

Although we did not have any accident using $P_2O_5$ in microwave oven, it is highly recommended that the reaction should be carried out in an efficient hood.

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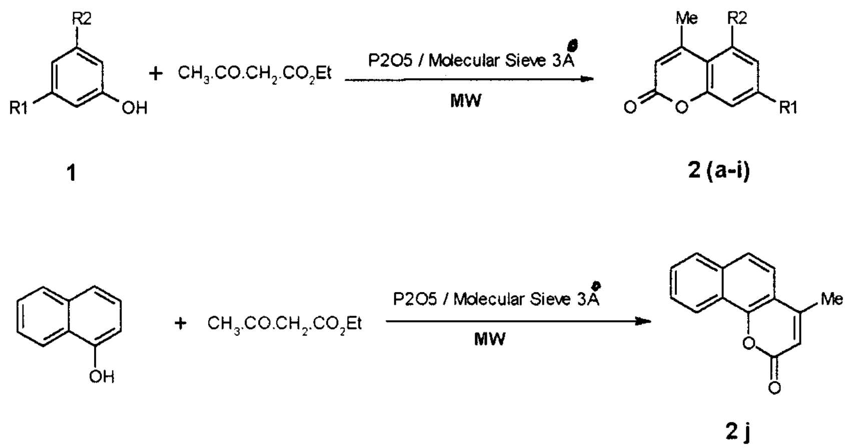
In this communication we report on the synthesis of coumarins via Pechmann condensation of phenols and ethyl acetoacetate using $P_2O_5$/molecular sieves 3 Å under microwave irradiation in a solventless system.

Surprisingly, a survey of the literature revealed that the synthesis of coumarins via Pechmann condensation of phenols with ethyl acetoacetate using solid support and microwave irradiation has received little attention in the past. In best of our knowledge there are two methods for the preparation of analogs of **2** that have been reported. Acceleration of the Pechmann reaction by microwave irradiation using concentrated $H_2SO_4$ has been reported by Kad et al.[10] In another procedure developed by Li et al.,[11] montmorillonite clay has been used as a catalyst in a thermal reaction.

In view of the current emphasis on solid state synthesis[12] and on green chemistry[13] there is a merit developing a solventless preparation of coumarins using an inexpensive and nonpolluting catalyst. We recently have used 3 Å molecular sieve as promoting agent in regioselective synthesis of syn-oximes.[14] In continuation of our interest in conducting of organic synthesis in solventless system under microwave irradiation[15] we report an alternative method for the preparation of coumarins **2** using $P_2O_5$ supported on molecular sieve 3 Å under microwave irradiation (Scheme 1).




**SCHEME 1**

The reaction is conducted by exposure of a mixture of phenolic compounds, $P_2O_5$ and molecular sieve 3 Å to microwave irradiation.

Most of the phenolic compound disappeared within the first 4 min as determined by TLC. It is nothworthy to mention that in the absence of molecular sieve 3 Å the reactions are slugish and considerable amounts of starting materials are recovered unchanged even ofter prolonged exposure to microwave irradiation. Other types of solid supports were also used in this procedure but molecular sieve 3 Å were found to give the best yields.

It is also worthwhile to mention that in any cases no undesired products like chromans in addition to coumarins were detected.

In conclusion, we have developed an alternative procedure for the fast and releatively eco-friendly preparation of coumarins. This method features mild reaction condition, high yields and easy work-up procedurs. We beleive this strategy will find utility in organic synthesis.

## EXPERIMENTAL SECTION

Molecular sieves 3 Å power was purchased from Merck chemical company. MP(s) were recorded on Stuart scientific apparatus and are uncorrected. $^1$H-NMR spectra were recorded on 60 MHz Bruker using TMS as an internal standard and IR spectra were obtained from Perkin-Elmer model 543 using KBr disc.



### General Procedure

An appropriate phenol (14 mmol), ethyl acetoacetate (14.5 mmol), $P_2O_5$ (14 mmol) and molecular sieve 3 Å (2 g) were mixed throughly using a spatula in a beaker. The beaker was placed in an house hold microwave oven. The progress of reaction was monitored by TLC. The residue was taken up in hot ethanol:acetone 50:50 and filtered. The filtrate was evaporated to dryness and the crude was crystallized from suitable solvent (Table I).

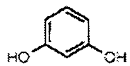
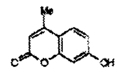
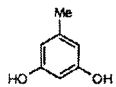
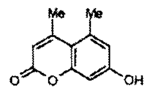
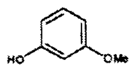
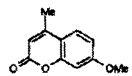
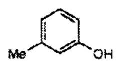
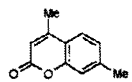
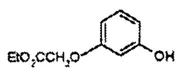
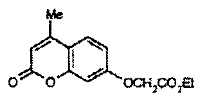
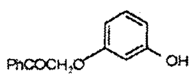
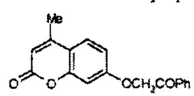
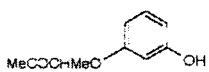
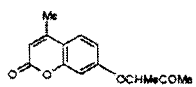
#### *Selective Spectroscopic Data for 2a*

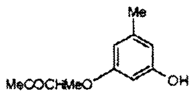
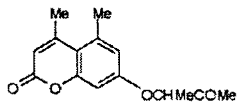
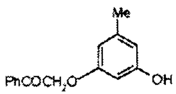
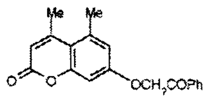
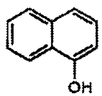
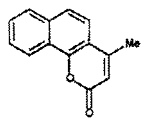
$^1$H-NMR $\delta$ (DMSO $d_6$): 2.65 (s, 3H, Me), 6.4 (s, 1H, olefinic CH), 6.9–7.7 (m, 3H, aromatic protons), OH is unobserved, IR, $\nu$ (KBr disc): up to 3000 (OH broad), 1690 $cm^{-1}$.

#### *Selective Spectroscopic Data for 2b*

$^1$H-NMR $\delta$ (DMSO $d_6$): 2.6 (s, 3H, Me), 2.95 (s, 3H, Me), 6.35 (s, 1H, olefinic CH), 6.8–7.6 (m, 2H, aromatic protons), OH is unobserved, IR, $\nu$ (KBr disc): up to 3000 (OH broad), 1685 $cm^{-1}$.

**TABLE I** Preparation of Coumarins by Using $P_2O_5$ Supported onto Molecular Sieve 3 Å under Microwave Irradiation in Solventless System

| Entry | Substrate | Product | Time (min) | Yield (%) | Product m.p. (°C) | Recryst. solv. |
|---|---|---|---|---|---|---|
| a |  |  | 4 | 79 | 186 | Ethanol (95%) |
| b |  |  | 4.5 | 72 | 258–260 | Ethanol (60%) |
| c |  |  | 3 | 82 | 157–158 | Diethyl ether |
| d |  |  | 5 | 65 | 131 | Ethanol (70%) |
| e |  |  | 4 | 60 | 98–100 | Ethanol (85%) |
| f |  |  | 4.5 | 59 | 173–174 | Acetone |
| g |  |  | 5 | 65 | 232 | Ethanol |

| | | | | | | |
|---|---|---|---|---|---|---|
| h |  |  | 4.5 | 71 | 108–110 | Ethanol |
| i |  |  | 4 | 68 | 175–176 | Acetone |
| j |  |  | 4.5 | 71 | 154–156 | Methanol |

### Selective Spectroscopic Data for 2c

$^1$H-NMR $\delta$ ($CDCl_3$): 2.59 (s, 3H, Me), 4.2 (s, 3H, OMe), 6.5 (s, 1H, olefinic CH), 7–7.5 (m, 3H, aromatic protons), IR, $\nu$ (KBr disc): 1685 $cm^{-1}$.

### Selective Spectroscopic Data for 2d

$^1$H-NMR $\delta$ ($CDCl_3$): 2.62 (s, 3H, Me), 2.8 (s, 3H, Me), 6.4 (s, 1H, olefinic CH), 7.1–7.6 (m, 3H, aromatic protons), IR, $\nu$ (KBr disc): 1685 $cm^{-1}$.

### Selective Spectroscopic Data for 2e

$^1$H-NMR $\delta$ ($CDCl_3$): 1.7 (t, 3H, Me), 2.5 (s, 3H, Me), 4.3 (q, 2H, $OCH_2$), 6.45 (s, 1H, olefinic CH), 7.2–7.8 (m, 3H, aromatic protons), IR, $\nu$ (KBr disc): 1730, 1650 $cm^{-1}$.

### Selective Spectroscopic Data for 2f

$^1$H-NMR $\delta$ ($CDCl_3$): 2.65 (s, 3H, Me), 5.5 (s, 2H, $CH_2$), 6.5 (s, 1H, olefinic CH), 7–8.2 (m, 8H, aromatic protons), IR, $\nu$ (KBr disc): 1700, 1630 $cm^{-1}$.

### Selective Spectroscopic Data for 2g

$^1$H-NMR $\delta$ ($CDCl_3$): 1.9 (d, 3H, Me), 2.6 (s, 3H, Me), 2.9 (s, 3H, Me), 5.1 (q, 1H, aliphatic CH), 6.6 (s, 1H, olefinic CH), 7.1–7.8 (m, 3H, aromatic protons), IR, $\nu$ (KBr disc): 1730, 1690 $cm^{-1}$.

### Selective Spectroscopic Data for 2h

$^1$H-NMR $\delta$ ($CDCl_3$): 1.8 (d, 3H, Me), 2.6 (s, 3H, Me), 2.9 (s, 3H, Me), 3.1 (s, 3H, Me), 5.1 (q, 1H, aliphatic CH), 6.6 (s, 1H, olefinic CH), 7.1–7.8 (d, 1H, aromatic CH), 7.6 (d, 1H, aromatic CH), IR, $\nu$ (KBr disc): 1730, 1685 $cm^{-1}$.

### Selective Spectroscopic Data for 2i

$^1$H-NMR $\delta$ ($CDCl_3$): 2.6 (s, 3H, Me), 2.8 (s, 3H, Me), 5.7 (s, 2H, $CH_2$), 6.3 (s, 1H, olefinic CH), 7.1–8.4 (m, 7H, aromatic protons), IR, $\nu$ (KBr disc): 1710, 1685 $cm^{-1}$.

### Selective Spectroscopic Data for 2j

$^1$H-NMR $\delta$ ($CDCl_3$): 2.71 (s, 3H, Me), 6.5 (s, 1H, olefinic CH), 7.5–8.9 (m, 6H, aromatic protons), IR, $\nu$ (KBr disc): 1690 $cm^{-1}$.

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