

Synthesis of coumarin by Pechman reaction - A Review

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Abstract:

Phenol condensed with β -keto esters via Pechmann condensation to form derivatives of Coumarin in various reaction conditions by two ways. Present paper is comparative study of synthesis Coumarin with the yield of product, reaction time and reaction conditions.

Keywords: Coumarin, Pechman reaction, phenols, β -keto esters.

INTRODUCTION

Coumarin is of the benzopyrone so it is the basic particle that can be synthesis from them many more complex for the Coumarin derivatives that containing alkyl groups or hydroxy or benzyl as imitative totals [1] the Coumarin is within the important organic compounds And within the many uses of terms within the cosmetics, dyes and food added [2] Coumarin derivatives have been used in the medical field as anti-clotting blood pressure depressor muscles loosened and many others [3] as well as HIV and affecting the liver [4] one of the Industrial methods of preparing Coumarin is Pechman reaction, where they preparing a number of Coumarin derivatives by condensation alphenol or products with compounds beta - keto ester with sulfuric acid [5]

Reaction Mechanism

The Laboratory methods of the hetrogeneous compounds and Coumarin derivatives it is reaction of Beckman[6] a German chemist, Hans von Pechmann synthesized coumarins from the reaction a phenols with a carboxylic acid or ester

compounds containing the afunctional group β -carbonyl [7].

Pechmann Condensation Coumarin Synthesis

a coumarins synthesis from reaction the phenols compounds with compounds of β -keto esters by Pechmann Condensation

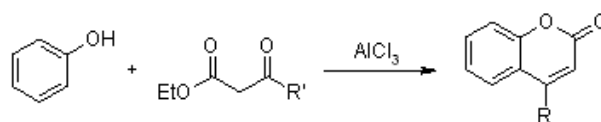


Figure -1

Mechanism of the Pechmann reaction

The reaction is conducted with a strong acid such as methanesulfonic acid or a Lewis acid such as $AlCl_3$. The acid catalyses transesterification as well as keto-enol tautomerisation

In figure -4 we show the Subsequent induced- acid elimination of H_2O gives the product. [8]

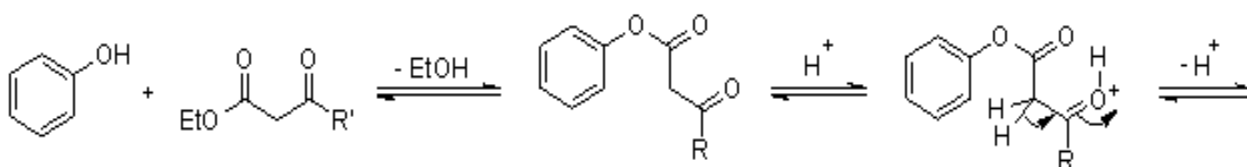


Figure -2

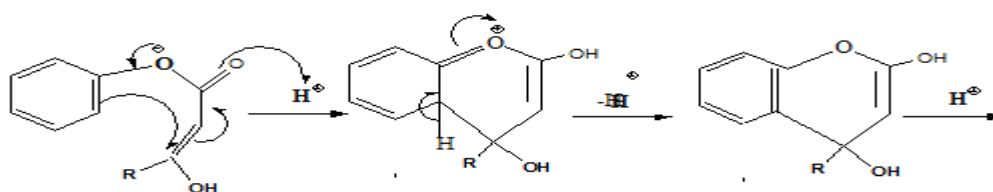


Figure -3

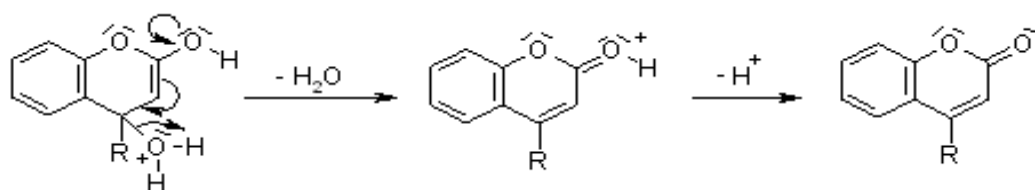


Figure -4

Different reaction and ways for Pechman reaction to synthesis coumarin

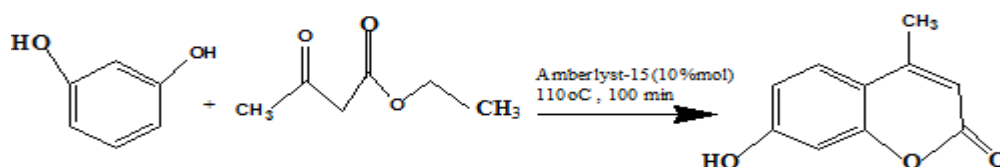
This reaction originally involves a reaction of a of phenols compounds with β -keto esters compound. All these types of compounds used in the Pechman reaction with different products and methods are discussed and comparative study of synthesis Coumarin

A-First way

Conventional methods (all Reaction conditions show in tabel-1)

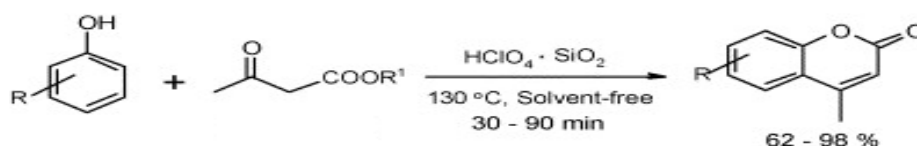
1- The coumarins synthesis from Pechmann condensation by use Amberlyst-15 catalyst:

The first time of reaction mixture (1 mmol) of resorcinol with (1.1 mmol) ethyl acetoacetate and added (10 mol%) Amberlyst-15 was catalyst, then stirred the reaction mixture in oil bath at 110°C for the desired time. The reaction was monitored by thin layer chromatography . After completed the reaction filtered mixture was to remove the heterogeneous catalyst, then filtrate was cooled to room temperature, after that, a hot methanol was added to cooled filtrate to result a solid that it was filtered and then was recrystallized with ethanol to obtain pure product.[9]



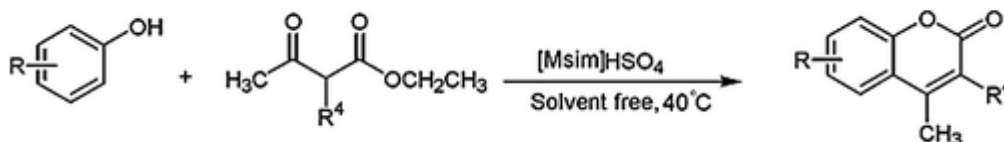
Scheme 1.

2- The coumarins synthesis from Pechmann condensation by use heterogeneous catalyst [10]



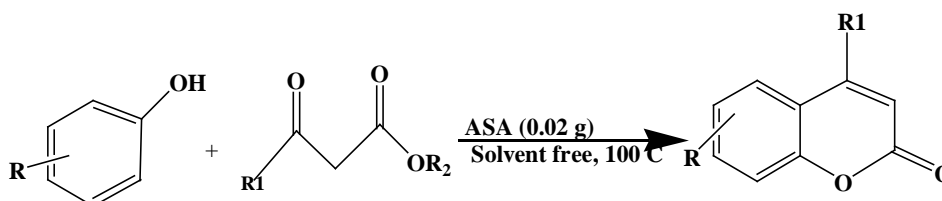
Scheme 2.

3- The coumarins synthesis from Pechmann reaction by use (ILi) onic liquid catalyzed [11]



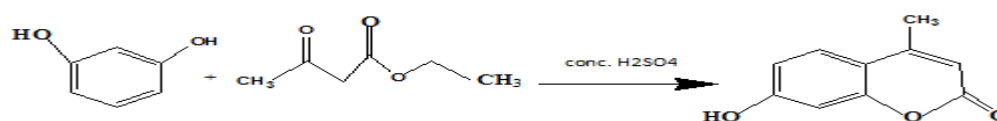
Scheme 3.

4 -The coumarins synthesis from Pechmann condensation by use Alumina Sulfuric Acid(ASA) catalyst [12]



Scheme 4.

5- The coumarins synthesis from Pechmann condensation by use H₂SO₄ acid catalyzed [13]



Scheme 5

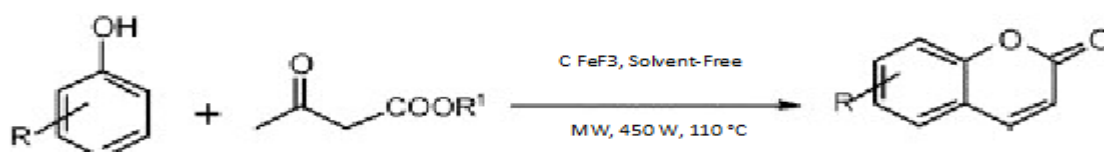
Table-1: Reaction conditions of the coumarins synthesis by Conventional methods of Pechman reaction

Synthesis	catalyst	Time [s]	Temp. [°C]	Yield [%]
1	Amberlyst-15	600	110	95
2	HClO ₄ ·SiO ₂	1800-3600	130	98
3	[Msim]HSO ₄	1320	60	96
4	alumina sulfuric acid (ASA)	1800	100	85
5	conc. H ₂ SO ₄	Overnight	R.T.	85

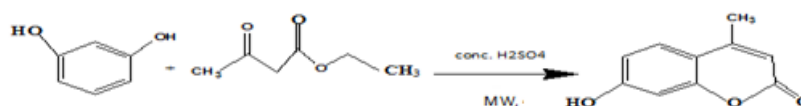
B-Second Part**The coumarins synthesis from Pechmann reaction by Assisted Microwave**

(all Reaction conditions show in tabel-2)

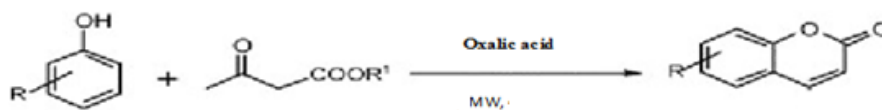
6- The coumarins synthesis from Pechmann Condensation by FeF₃ Catalyzed by Assisted Microwave the (1 mmol) resorsinol and (1 mmol) ethyl acetoacetate and (0.05 g) FeF₃ was ground in an open Pyrex beaker and the homogenized mixture was heated by microwave irradiation for about 7 min, [14]

**Scheme 6**

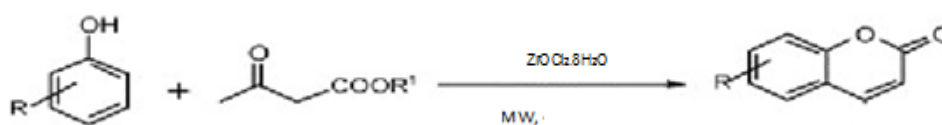
7- The coumarins synthesis from Pechmann Condensation by use conc. H₂SO₄ Catalyzed by Microwave Irradiation[15].

**Scheme 7**

8- The coumarins synthesis from Pechmann Condensation by use Oxalic acid Catalyzed in Microwave Irradiation [16]

**Scheme 8**

9- The coumarins synthesis from Pechmann Condensation by use ZrOCl₂·8H₂O Catalyzed in Microwave Irradiation [17]

**Scheme 9**

10- The coumarins synthesis from Pechmann Condensation by use piperidine Catalyzed in Microwave Irradiation [17]

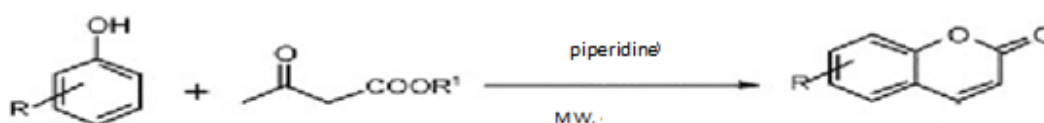
**Scheme 10**

Table -2: Assisted Microwave Reaction conditions of the coumarins synthesis by the Pechman reaction

Synthesis	catalyst	Time [s]	Temp. [°C]	Yield [%]
6	0.05 g FeF ₃	540	MW, 450 W, 110 °C	95
7	conc. H ₂ SO ₄ -1 ml	600	MW ,350 W,75 ⁰ C or less	95
8	Oxalic acid	500	MW ,700 W,110-140 ⁰ C	68
9	ZrOCl ₂ .8H ₂ O	3600	MW ,700 W,120 ⁰ C	86
10	piperidine	600	MW ,700 W,129 ⁰ C	89

C-third Part**11- The coumarins synthesis from Pechmann reaction Without any Catalyst.[18]****(Reaction conditions show in tabel-3)**

Synthesis of Coumarin sby conventional method without any catalyst: Equimolar amount of solution of Resorcinol and ethyl β- amino crotonate Enamine derivatives of (EAA) heated at 180 0C without any catalyst, after completion of reaction, monitor by Thin Layer Chromotography , the mixture product was cooled and poured to cold water, obtained solid was washed with cold water and finally solid mass was recrystallised from aqueous alcohol to afford a pure product.

Table-3: Reaction conditions of the coumarins synthesis by the Pechman reaction Without any Catalyst

Synthesis	Time [s]	Temp. [°C]	Yield [%]
11	1200	180	85

CONCLUSION:

Pechmann Reaction :Many routes are available for the synthesis of coumarins. Mony of these types for Pechmann reaction is considered to be one of the most important one as it requires simple starting materials With simple phenols and ester compounds containing compounds have β-carbonyl group .

on all reports discussed in this review methods of Synthesis of Coumarin Derivatives via Pechmann reaction hould catalysts have shown promising catalytic activity by Conventional and Microwave Irradiation methods than Without any Catalyst .

The results at these all methods We respect them were reported , the remarkable observations, high yield

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