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COMPARATIVE STUDY OF VARIOUS SYNTHESIS METHOD OF 7-HYDROXY-4-METHYL COUMARINSVIA PECHMANN REACTION

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Abstract

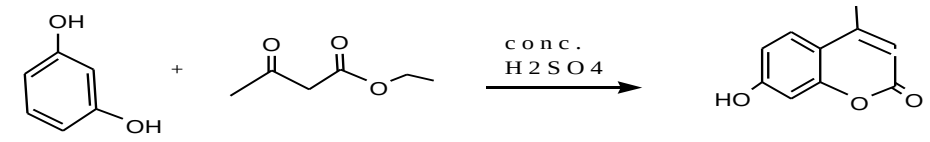
Resorcinol condensed with Ethyl acetoacetate (EAA) via pechmann condensation to form 7-hydroxy-4-methyl coumarin in various reaction conditions. Present paper is comparative study of synthesis of 7-hydroxy-4-methyl coumarin with respect to yield, reaction time and reaction condition. All products are characterized by spectral data and elemental analysis.

Keyword- *Coumarin, Pechmann Condensation, Comparative study.*

INTRODUCTION-

Coumarins are naturally occurring compound and found in various plants in large quantities. Coumarins arebiologically active compound used in various aspects like cosmetics, medicines and pharmaceutical industries. Coumarin molecules are recently used in anti- tuberculosis and anti- AIDS]as active drugs. So it is interesting tostudy the molecule and its derivatives. It is well known that the Coumarin derivatives represent an important class of oxygen containing heterocyclic compounds. They are widely used as additives in foods, perfumesand in thepreparation of optical Brighteners as well as laser dyes. Coumarins have been synthesized by several routes including Pechmann, Perkins, Knovengeals, Reformatskys, and Witting reaction. Among the methods applied, Pechmann reaction is the most widelyapplied methods for synthesizing Coumarins. Pechmann involves the condensation of phenols with β- keto esters inthe presence of variety of acids. Various acid types like Lewis, Protic, Solid acids, acid anhydrides ,and in different ionic liquids], as well as solvent free condition].In continuation of our interest, the current work represents the comparative study of synthesis of 7-hydroxy-4-Methyl Coumarin by Pechmann condensation using different procedures and its influence with various aspects likeyield, reaction time and conditions.

REACTION SCHEME-



Resorcinol EAA 7-hydroxy-4-Methyl Coumarin

The melting points of the compounds were determined in open head capillary and are uncorrected. The IR spectra ofthe compounds were recorded in the region of 4000-400 cm-1 by using KBr pallet on FT-IR Perkin spectrophotometer.H1 NMR spectra were recorded on a DRX-300 Bruker FT- NMR spectrophotometer in CDCl3.The values of chemical shift are expressed in δ ppm as a unit. All the compounds were checked for purity by thinlayer chromatography (TLC). The sonicator was used with 100 wattspower of 230 V AC suppliers.

A) Synthesis of 7-hydroxy- 4-methyl Coumarinby conventional method with Conc. Sulfuric acid as Catalyst:-

A solution of 1.1 gm. of resorcinol and 1.3 gm. of EAA was added drop wise with stirring to 10 ml of conc. H2SO4.So that the temperature of reaction mixture did not raise above the 10^0Cthe reaction on complete addition mixture was kept at ambient temperature for 18 hr. and then poured with vigorous stirring to the mixture of ice and water. The precipitated was filter off and washed with cold water then dried under reduced pressure to afford the crude solid mass.On recrystallized from aqueous alcohol gives final compound.

B) Synthesis of 7-hydroxy-4-Methyl Coumarin by Infra-Red lamp heating method:

Equimolar amount of solution of Resorcinol and EAA was mixed with a glass rod for few minute containing 1 ml of Conc. H2SO4 and heated with medicinal Infra Red lamp (250watts) for 8-10 hours, the temperature of the reaction mixture did not exceed above 75 0C . After completion of reaction (TLC) poured to ice-water mixture then filter it off and recrystallized from aqueous alcohol.

C) Synthesis of 7-hydroxy-4-Methyl Coumarin by conventionalmethod 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 TLC, the reaction mixture was cooled and poured to cold water,

obtained solid was washed with cold water and finally solid mass was recrystallized from aqueous alcohol to afford a pure product.

D) Synthesis of 7-hydroxy- 4-Methyl Coumarin by simple grinding technical method:

To an equimolar mixture of resorcinol and Ethyl aceto acetate was added TsOH in a mortar and ground it well with a pestle at room temperature. The Mixture was heated at 60 0C for 10 min., after cooling, water was added to the reaction mixture and obtained solid products were collected by filtration to give 7-hydroxy- 4-Methyl Coumarin in very good yield. The crude crystals thus obtained were recrystallized by ethanol to afford pure colorless prisms.

Table No.1. Table showing reaction condition, time,temperature and yield of compound-

Sr.no.	Compound	Time with temp.	Yield	Reaction condition
1	A)	Overnight at RT	80 %	Conc.H2SO4, addition 0^{O}C,overnight at RT.
2	B)	9-10 Hrs.at 250 ^{0}C watts	45 %	IR lamp heating.
3	C)	15 min at 180^{O}C	85 %	Without any catalyst and any solvent.
4	D)	15 min at 60^{O}C	90 %	Simple grinding technique at RT,then 60 ^{0}C for 15 min.

CONCLUSION-

In conclusion, here we reported comparative study of preparation of Coumarin by various methods. Among which this study prove that green synthetic method (4) is most efficient via by simple grinding Technique obtain product within few minutes.

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