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GRINDSTONE CHEMISTRY: ACID-CATALYZED FACILE SYNTHESIS OF COUMARINS

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Abstract: Mild acid-catalyzed Pechmann reaction using Grindstone Chemistry is used as an efficient and rapid method for the condensation of a phenol with a beta-keto ester for the facile synthesis of coumarin. The reaction proceeds under solventless conditions, affording a high yield of the product. This approach works well with various phenols and beta-keto esters.

Keywords: Phenols, Beta-keto esters, Grindstone chemistry, Coumarins

Introduction:

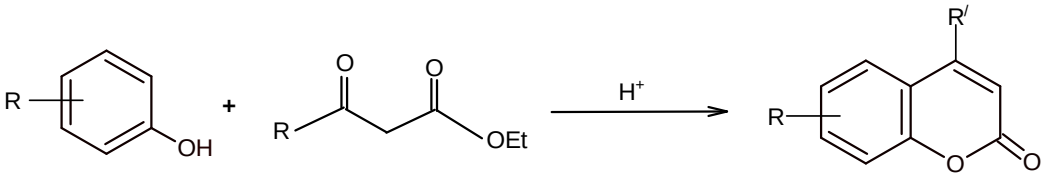
Coumarins have diverse biological activities. The Peachmann reaction is widely used for the preparation of coumarins.[1]This reaction describes a process in which a phenol reacts with a beta-keto ester in the presence of strong sulphuric acid and produces coumarin.
In recent years, it has been discovered that many reactions can be performed successfully in the absence of a solvent. Moreover, reactions can be conducted rapidly by Grindstone chemistry which involves frictions among the reactants.[2]We report herein a new solventless Peachmann reaction for the synthesis of coumarins using Grindstone chemistry.

Results and Discussion:

A chemical reaction without solvent minimizes toxicity and reduces pollution of the environment. Many researchers have demonstrated green methods such as sonochemical[3], microwave irradiation[4], and mechanochemistry[5] for the preparation of diverse compounds. Importantly, chemical reaction is performed by frictional force following mechanochemistry. During the course of our research on sustainable green chemistry, synthesis of coumarins following mechanochemistry was conducted.
Diverse resorcinol derivatives and beta-keto-esters were used for the preparation of coumarins with great success (**Scheme 1**). Cyclic beta-keto-esters produced products with lower yields (about 80%) compared to the yield with linear beta-keto-esters (about 90%). Bismuth nitrate

and p-toulenesulfonic acid were proven to be excellent acid promoters for this reaction (**Table 1**). A few other acidic inorganic salts and organic acids were used for this purpose. For example, calcium nitrate, bismuth sulphate, bismuth iodide, ferric chloride, copper nitrate and magnesium sulphate were examined. However, bismuth nitrate was the most efficient. Acetic acid, benzoic acid and citric acid were not effective.

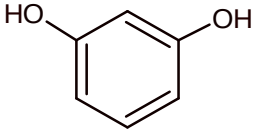
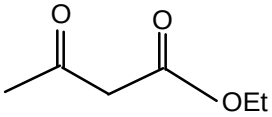
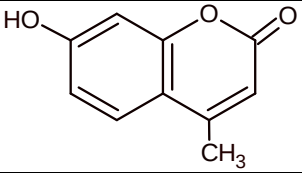
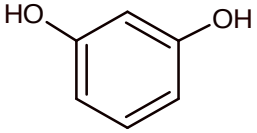
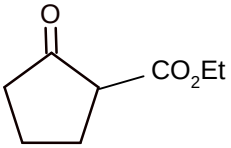
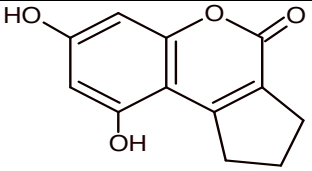
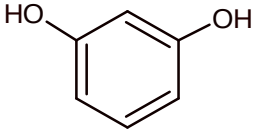
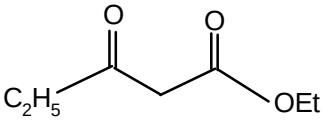
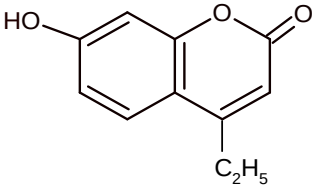
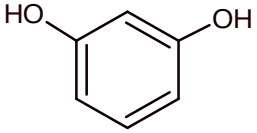
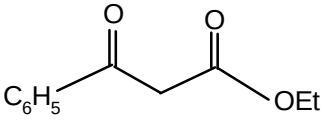
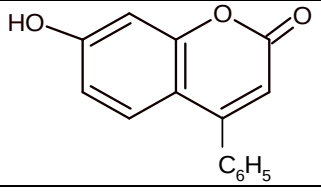
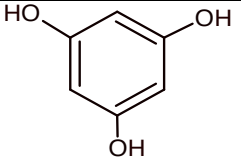
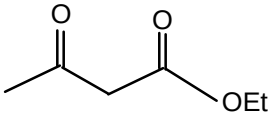
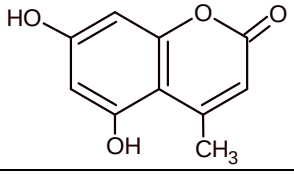
Bismuth nitrate can liberate nitric acid in the reaction media due to high friction. It can also coordinate with the dicarbonyl compound using its vacant d-orbital. This type of coordination, in principle can promote the nucleophilic attack by the phenol. It seems p-toluenesulfonic acid promotes this reaction as well.

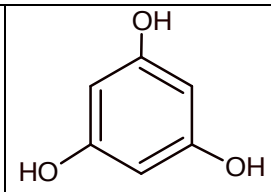
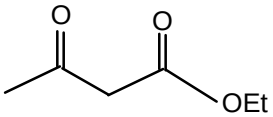
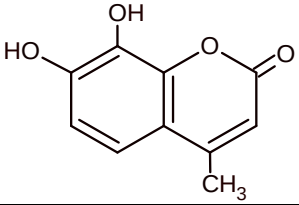
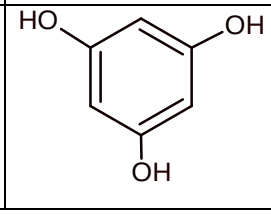
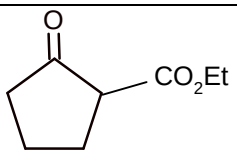
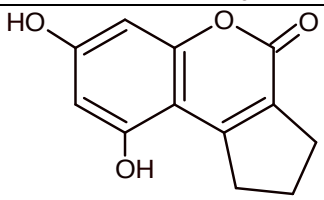


Scheme 1: Synthesis of coumarins by Grindstone method in the presence of bismuth nitrate or p-toulenesulfonic acid.

Compounds with two or three phenolic groups were used for this investigation with success. Cyclic or acyclic beta-keto esters were effective (**Table 1**).

Table 1: Synthesis of Coumarins by Grindstone Method

Entry	Phenols	Beta-Keto Ester	Product	Yield (%)
1				**94**
2				**81**
3				**96**
4				**92**
5				**86**

6				**90**
7				**80**

Experimental:

Phenol, beta-keto ester and catalytic amounts of bismuth nitrate (or p-toluenesulfonic acid) were ground in a mortar and pestle. Specifically, resorcinol (25 mmol), ethyl acetoacetate (25 mmol) and p-toluenesulfonic acid (200 mg) [or bismuth nitrate (200 mg)] was ground for 15 minutes with a mortar and pestle. The reaction mixture became thicker and the temperature of the reaction mixture went up by a few degrees in the beginning. The reaction materials were stored for 30 minutes at room temperature. Water (100 mL) was added to the reaction mixture and stirred for 10 minutes. The resultant solid product was filtered, washed with water (10 mL) and dried. The white solid was crystallized from ethanol and it was identified as 7-hyddroxy-4-methylcoumarin (mp 185-186^{0}C).

Conclusions:

In summary, we have demonstrated a solvent-free Peachmann reaction for the synthesis of coumarins using catalytic amounts of bismuth nitrate or p-toluenesulfonic acid in a mortar-pestle. This simple procedure can be extended for the preparation of diverse organic compounds.

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Authors' Contributions

The final form of the manuscript was appraised by every author.

Human and Animal Rights

Not applicable.

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