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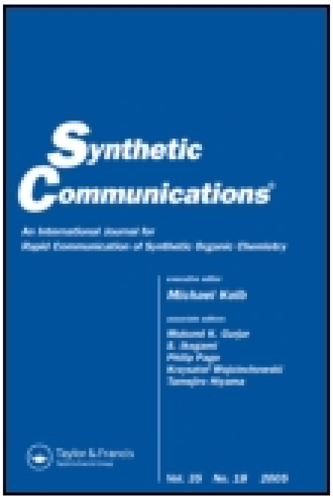

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SYNTHESIS OF COUMARINS CATALYZED BY ECO-FRIENDLY W/ZrO$_2$ SOLID ACID CATALYST

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SYNTHESIS OF COUMARINS CATALYZED BY ECO-FRIENDLY W/ZrO$_2$ SOLID ACID CATALYST

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ABSTRACT

Synthesis of substituted coumarins *via* reactions of resorcinol and substituted resorcinol with ethyl acetoacetate and ethyl α-methylacetoacetate (Pechmann reaction) are reported, in which the production of environmentally harmful waste streams is minimized by the use of a novel solid acid catalyst.

Progress towards environmentally responsible processing is marked by the elimination of waste and by-product generation and reduced dependence on hazardous chemicals. The use of large quantities of concentrated sulfuric acid as a condensing agent in the preparation of hydroxycoumarins by the von Pechmann reaction (i.e., condensation of phenols with malic acid or

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*Corresponding author.

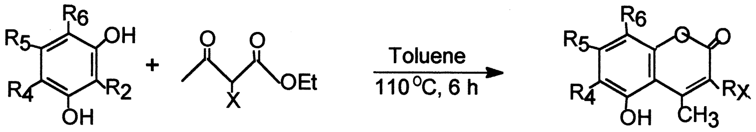
with β-keto esters) is an established fact in the literature.[1] Recent investigations for the Pechmann reaction employed various reagents such as zeolites, clays and sulfonic acid resins resulting in simplified product recovery and reduction of undesirable wasteful products.[2–4] However, the zeolite and clay based catalysts are highly susceptible to deactivation due to pore blocking and hydration. Application of cationic exchange resins as condensing agents results in better yields,[5] however, most of the cationic exchange resins are not resistant enough to high temperatures.

In this communication we report a new efficient ecofriendly W/ZrO_2 solid acid catalyst for the synthesis of substituted coumarins from resorcinol and substituted resorcinols with ethyl acetoacetate and ethyl-α-methylacetoacetate in good yields. The reaction of resorcinol with ethyl acetoacetate gives methylumbelliferone (4-methyl-7-hydroxycoumarin) a perfumery ingredient for the insecticide Hymecromone.[6] The tungstate modified zirconia solid acid catalyst possesses many advantages such as easy to handle, non-corrosive, low-cost, high activity, and high recycling capacity.

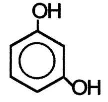
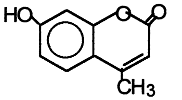
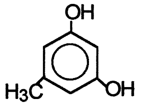
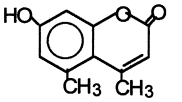
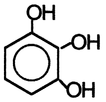
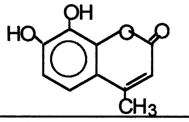
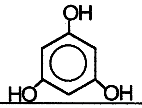
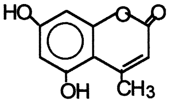
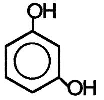
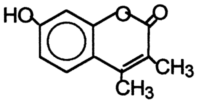
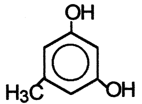
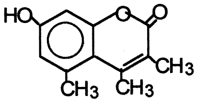
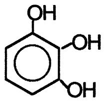
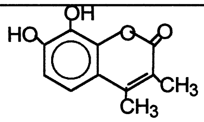
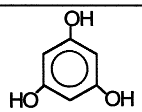
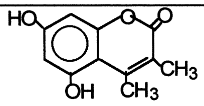
The sulfated zirconia solid superacid catalyst has attracted much attention recently because of its ability to catalyze many acid catalyzed reactions more effectively.[7] However, the SO_4^{2-}/ZrO_2 catalyst gets deactivated easily by loosing sulfate ions and thereby recycling of the catalyst is highly restricted. Very recent investigations reveal that molybdenum or tungsten doped ZrO_2 is an alternative catalyst[8–12] in reactions requiring stronger acid sites ($H_0 \leq -14.52$).[13] The major advantage of Mo-(or W-) modified ZrO_2 over sulfated catalyst is that they do not suffer from dopent loss during thermal treatments and also undergoes significantly less deactivation during catalytic runs. Although, solid superacids have been attempted in petrochemical industries, their application in synthetic organic chemistry remains unexplored.

The synthesis of substituted coumarins from resorcinol and substituted resorcinols with ethyl acetoacetate and ethyl-α-methylacetoacetate are presented in Table 1. From entries 1–4 the reaction is carried out with ethyl acetoacetate; and from entries 5–8 the reaction is carried out with ethyl-α-methylacetoacetate. As can be noted from Table 1, the catalytic activity of W/ZrO_2 was found to be more promising. Different mechanisms have been put forward to account for this reaction in the literature.[5] The resorcinol as a result of resonance has a center of high electron density at the position *ortho* to the hydroxyl group. Addition then takes place across the double bond in the enolic form of the β-keto ester and results in good yields. In case of orcinol, the position *para* to a methyl group is deactivated for an electrophilic reagent. The activity of orcinol will therefore be less than that of resorcinol. In case of pyrogallol, the third hydroxyl group deactivates the position *meta* to it for an electrophilic reagent resulting in less yield.

Table 1. W/ZrO$_2$ Solid Acid Catalyzed Synthesis of Substituted Coumarins



(R_2= OH, R_5= CH_3, OH, X= H, CH_3)

Entry	Substrate	Product	Yield[a] (%)	mp (°C)
1			80	188
2			70	262
3			65	243
4			56	286
5			67	256
6			65	249
7			60	274
8			50	290

[a] Isolated Yield.

Similarly, the decrease in the yield, in case of phloroglucinol can be attributed due to steric hindrance caused by third hydroxyl group. The substitution of hydrogen atom by methyl in case of β-keto ester is less active because of its lesser extent of the enolization.

Preparation of the Catalyst

To make the W/ZrO_2 solid acid catalyst, $Zr(OH)_4$ was prepared first from zirconium oxychloride by hydrolysis with dilute ammonia. In a typical experiment the required quantity of $ZrOCl_2.8H_2O$ (Loba Chemie, GR grade) was dissolved in doubly distilled water and the pH of the resulting solution was 2. To this clear solution dilute NH_4OH was added drop wise from a burette with constant stirring until the pH of solution reached 8. The obtained precipitate was washed several times until free from chloride ions and dried at 393 K for 48 h. To make 13 wt.% W/ZrO_2 catalyst, the requisite quantity of ammonium tungstate (J. T. Baker, England; GR grade) was dissolved in 1 M oxalic acid solution. To this clear solution the desired amount of finely powdered oven dried precipitate was added and the excess water was evaporated on a water bath. The resulting sample was oven dried again at 393 K for 48 h and calcined at 873 K for 6 h in a flow of oxygen. The X-ray powder diffraction analysis of the sample revealed the presence of XRD lines due to ZrO_2 tetragonal phase. The preferential formation and subsequent stabilization of the tetragonal zirconia was mainly attributed to the observed high acidity and activity of promoted zirconia solid acid catalysts.[8,11,14]

General Procedure for Substituted Coumarins Synthesis

In a typical reaction procedure (Table 1) a mixture of 1 : 1 molar amounts of reactants with the catalyst (0.3 g) in solvent toluene (20 ml) was refluxed for 6 h. After completion of the reaction the catalyst was filtered off when the reaction mixture is in hot condition and the wet catalyst was used for recycling. No appreciable change in the activity was noticed. The product was recovered from the filtrate. The isolated yields were obtained after recrystallization from aqueous methanol. NMR and mass spectrometric techniques were utilized along with their melting points for analyzing the products. In the controlled experiments, no reaction was observed in the absence of $W\text{-}ZrO_2$ catalyst in the reaction mixture.

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