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Short Communication

A Facile synthesis of Coumarin derivatives from Readily available Precursors and Mild acid catalysts

Bahule B.B.[1]*, Patil B.K.[2] and Kalaskar S.B.[3]
Department of Chemistry, Nowrosjee Wadia College, Pune-411001, Maharashtra, India
bharatbahule@gmail.com

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Abstract

The present paper reveals the synthesis of a lactone ring of coumarin derivatives of suitable phenolic precursors and lewis acids.The reactions are facile and the products are obtained in high yield.The lewis acids which are common and the reaction follows green route.The products are characterised by ^{1}H NMR spectroscopy and IR spectroscopy.

Keywords: Lactone ring, Lewis acid, FTIR and ^{1}H NMR Spectroscopy.

Introduction

As per the structure biological activity correlation, the presence of lactone ring in coumarin has a vital importance[1]. Substituted coumarin derivatives are known to possess the antibacterial, ant proliferative activity[2]. The presence of polar group in coumarin derivatives may bind to the protein molecules via hydrogen bonding. The chromone ring is also important in flavones structures, which are biosynthesised via Chalcones. The lead compound, dicoumarole is found in moldy hay and was responsible for the deaths of cattle in 1920 also has chromone ring as its structural feature[4]. The lactone ring was modified to lactums and the biological activity was assessed by Ahmed A. Hussain Al-amiery in his research article[5]. In case of cancer patients, the application of many ant proliferative drugs is associated to high toxicity and non-specificity.

The discovery of new drugs with less toxicity and high efficiency remains top priority task. The laboratory synthesis of chromone nucleus of the drug is an important aspect towards this work. The present article highlights the simple, efficient and ecofriendly method for the synthesis of coumarin derivatives. The substituted 2H-benzopyran-2one derivatives were tested positive for their antibacterial and invitro antioxidant activity[6]. Coumarins are known for their various biological activities such as anticoagulant, antimicrobial, anti-inflammatory, analgesic, antioxidant, anticancer, antiviral, antimalarial etc.[7].

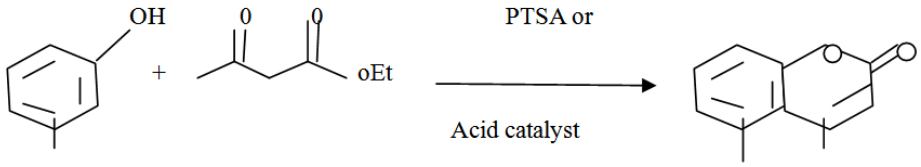
Materials and Methods

The organic solvents were purified and dried prior to use. The reactions were monitored by TLC and UV light. The crude products thus formed are purified by column chromatographic techniques. The products are characterised by IR and ^{1}H NMR spectroscopic methods.

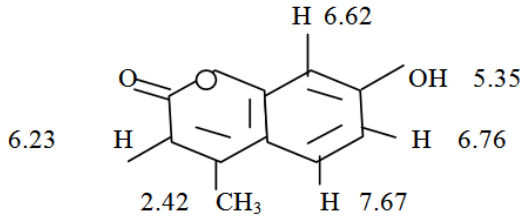
General Procedure for the Synthesis of Chromone Ring of Coumarin Derivatives: A mixture of resorcinol 1gm (9 mmoles), ethylacetoacetate 1.3 gm (10 mmoles) were taken in a 50 ml round bottom flask equipped with a reflux condenser. The mild acid catalyst 0.1gm was added the reaction mixture was refluxed for 2 hrs. The course of the reaction was monitored by TLC and UV light. After the completion of the reaction, the solvent was removed and the reaction mixture was cooled, which upon cooling yield a solid product. The crude product was purified using neutral alumina column and was subjected to the IR and ^{1}H NMR spectral characterisation. The same process was applied to the other phenolic substrates like o/m/p cresol, hydroquinone etc.

Table-1
Synthesis of Chromone Ring of Coumarin Derivatives

Substrate	Catalyst	% yield
Resorcinol	PTSA	90
o-cresol	PTSA	91
m-cresol	PTSA	89
p-cresol	PTSA	88
o-chlorophenol	PTSA	86
p-chlorophenol	PTSA	85
m-chlorophenol	PTSA	83
hydroquinone	PTSA	80



IR of compound 1: 3063, 2811, 1879, 1852, 1670, 1614, 1227, 1180 cm-1
^{1}H NMR of compound 1:(∂,$CDCl_3$) :7.5 d,7.0 s,6.87 d,6.16 s,4.146 s,1.8 d bs



Scheme-1
General Procedure for the Synthesis of Chromone Ring of Coumarin Derivatives

The lewis acids which were employed for the above conversion were PTSA, Na-S zeolite, H-y zeolite, cation exchange resins such as Amberlyst, Tulsion, Indion etc. The catalysts except PTSA can be removed from reaction mixture merely by simple filtration through the Whatmann filter papers. The work up process for PTSA catalysed reaction is as follows.

The reaction mixture was neutralised by aq. $NaHCO_3$ and then the organic layer was subjected to the evaporation. The removal of solvent yielded the crude product. The yields of products are very high and the conversion is complete. The PTSA and other acid catalysts are highly selective and useful for the cyclisation reaction in this case.

Result and Discussion

Coumarin belongs to benzoalpha pyrones and flavanoids belong to benzo-gama-pyrones. Coumarins comprise a very large class of compounds found through the plant kingdom. They have remarkable biological activity and the various derivatives of coumarins are therefore vital. The present paper suggests the simple lucid pathway for the synthesis of coumarins. The lewis acid catalysed method is very important since it is according to green chemistry norm.

Conclusion

The present method is simple and can be easily executed. The yield of the coumarin derivatives are high and reaction follows green route. Beside PTSA the other reagents like Na-S zeolite, H-S zeolite, cation exchange lesius such as amberlyst, Tulsion, Indion can be used effectively.

Acknowledgement

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