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Doped Cobalt Iron Tartrates As Efficient Catalyst in Synthesis of 3,3 Arylindene Bis (4-Hydroxy Coumarin) Derivatives

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Abstract: *The catalyst need to be green in the recent time hence in this search doped cobalt iron tartrates is a very efficient, water soluble and reusable catalyst for synthesis of 3,3 Arylindene Bis (4-hydroxycoumarin) through a one-pot condensation with various aromatic aldehydes. Catalyst used under solvent-free conditions and can be recovered by simply evaporation. Compared with other synthetic methods, this new method has advantages such as milder reaction conditions, good to excellent yields, short reaction times, and environmentally benign procedure.*

Keywords: Doped Cobalt Iron Tartrates; 3, 3 Arylindene Bis (4-hydroxycoumarin); Water Soluble Catalyst Reusable Catalyst.

I. INTRODUCTION

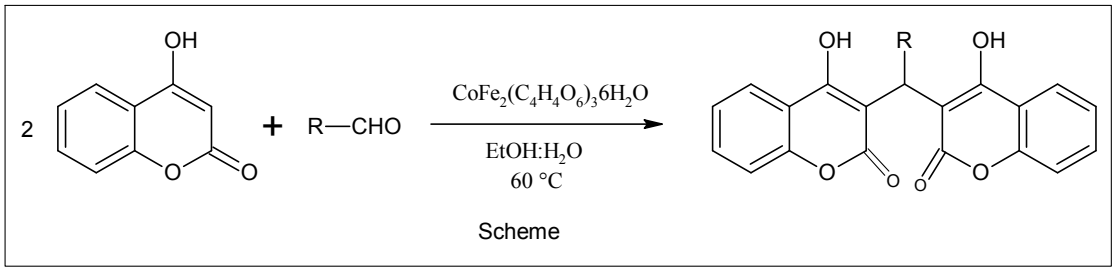
Amongst the heterocyclic compounds Triazoles, thiadiazoles, pyrazoles, oxadiazoles, Xanthene, coumarin attracted a tremendous attention, as they are full of many ramifications especially in the biological and industrial applications. In this chapter we have given a short introduction of these compounds. In view of the general observation that the biological activities are invariably associated with a large variety of heterocyclic systems such as 3,3-arylidene bis(4-hydroxycoumarin) a large number of their new derivatives have been synthesized and extensively studied for various pharmacological properties. Recently many xanthenes were prepared from various doped metal tartrates.[1-5]

The procedures for its synthesis have been extensively studied and such studies have been stimulated by various promising applications, especially in the case of highly substituted 4-hydroxycoumarin derivatives. In fact, certain substituted chromene are used as antimicrobial, anticancer, anti-inflammatory, antidepressant, anticonvulsant, antihyperglycemic, antipyretic, antibacterial, antifungal activities, fungicidal, anti-arthritic activities[6]. The knowledge of such applications has pointed out that substituted 4-hydroxycoumarin are important target to be prepared to our interest on synthesis and molecular structure determination of some types of 4-hydroxycoumarin[7].

Herein work we developed some new synthetic protocols for carrying out different organic transformations using catalysts which are the tools of synthesis to minimize the byproduct waste formation without using hazardous regents.

II. RESULT AND DISCUSSION

In this scheme, efficient method was tried to be proposed for the condensation of aldehydes with 4-hydroxycoumarin, which led to the corresponding 3,3-arylidene bis-(4-hydroxycoumarin) and different aldehydes in the presence of doped cobalt iron tartrates ($CoFe_2(C_4H_4O_6)_3.6H_2O$) is an efficient and reusable catalyst for the synthesis. Doped cobalt iron tartrates is found to be a good catalyst for the preparation of 3,3-arylidene bis(4-hydroxycoumarin).



Scheme

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Initially, the systematic evaluation of different solvents for the model reaction of 3-nitro benzaldehyde and 4-hydroxycoumarin in the presence of doped cobalt iron tartrates in water at reflux was focused on. Attempts were made to study and optimize the reaction conditions in order to show that performing the reaction in H_2O with low yield while using the amounts of EtOH in the media produced satisfactory results. These results revealed that the highest yield was obtained with the water/ethanol (1:1) solvent system.

In order to check the viability of this protocol in obtaining a series of 3,3-arylidene bis(4-hydroxycoumarin) derivatives. As can be seen in Table 2, a range of dicoumarols was synthesized using different aldehydes and 4-hydroxycoumarin under the standardized reaction. The results are summarized in Table 1. Regardless of the nature of the substitution (electron donating and electron withdrawing) of the aromatic aldehydes, the products were obtained in good to excellent yields. In these reactions, there was no need for the column purification of the products. The obtained solid products were just filtered off from the reaction mixture, dissolved in hot ethanol, refiltered to separate any contaminated catalyst with the product and finally recrystallized from the filtrate to obtain pure dicoumarols.[8]

According to the proposed mechanism, the formation of 3,3-arylidene bis(4-hydroxycoumarin) could be rationalized. From the Knoevenagel condensation of aromatic aldehydes with 4-hydroxycoumarin in the presence of Doped cobalt iron tartrates and followed by Michele addition of the second 4-hydroxycoumarin (Scheme). To show the advantage of the present work in comparison with the reported results in the literature, the results of Doped cobalt iron tartrates with reflux in ethanol or acetic acid, iodine, DBU, SDS, TBAB and SiO_2/Cl were compared in terms of the synthesis of biscoumarin derivatives.

Table 1: Synthesis of 3,3-arylidene bis(4-hydroxycoumarin) by condensation of aldehydes and 4-hydroxycoumarin using $CoFe_2(C_4H_4O_6)_3.6H_2O$ as catalyst.

Entry	R	Product	Time (min)	% Yield	M.P(^{0}C)	
					Found	Reported
1	H	2p	45	96	232-234	230-232[9]
2	4-OMe	2q	45	95	249-251	246-248[9]
3	4-Cl	2r	45	92	258-260	256-258[9]
4	4-NO_2	2s	45	90	237 - 240	232-234[9]
5	3-NO_2	2t	45	92	256-258	254-258[9]
6	2-OH	2u	45	90	212-215	212-214[9]

III. EXPERIMENTAL

The melting points were determined on an electrothermal apparatus and the temperature was not calibrated. IR spectra were recorded as thin films on KBr using the Spectrum 400 spectrophotometer. The ^{13}CNMR spectra were recorded on a Bruker AVANCE NEO 500 MHz NMR spectrometer. The sample solution was prepared in DMSO containing tetramethylsilane (TMS) as an internal reference. Mass spectra were recorded on a Water S, Q-TOF MICROMASS (ESI-MS) at 70 eV. All chemical reagents were commercially available and purified with standard methods before use. Solvents were dried in routine ways and redistilled.

3.1 General Procedure for the Synthesis of 3,3-Arylidene bis(4-hydroxycoumarin) Derivatives.

A mixture of 4-hydroxycoumarin (2 mmol, 0.324 g), substituted benzaldehydes (1 mmol, 0.106 g), and $CoFe_2(C_4H_4O_6)_3.6H_2O$ (10 mol%) was stirred at reflux in 5 ml ethanol-water mixture (1:1). The progress of the reaction was monitored by TLC. After the reaction completion and upon its cooling, the solid material was precipitated from the solution. The precipitates were filtered off, washed with water, and were recrystalized from EtOH to obtain pure 3,3- arylidenebis(4-hydroxy-*2H*chromen-2-ones) derivatives as yellow-white solids.[10]

IV. CONCLUSION

In conclusion, $CoFe_2(C_4H_4O_6)_3.6H_2O$ 4 was demonstrated a new efficient catalyst for the synthesis of dicoumarols, prepared via the condensation reaction of aromatic aldehyde and 4-hydroxycoumarin using $CoFe_2(C_4H_4O_6)_3.6H_2O$ as a homogeneous catalyst under aqueous media. These conditions had advantages such as shorter reaction time, simpler work-up, inexpensive and non-toxic catalysis, environmental benignity and excellent yields. The protocol described herein is

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advantageous in terms of preclusion of hazardous organic solvents, catalytic amount of reagents, shorter reaction time, good yields, recovery and reusability of catalyst.

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