β-Cyclodextrain sulfonic acid as a biodegradable solid catalyst in benzoxanthenes synthesis

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Abstract- A new and efficient synthesis of benzoxanthene drivatives from the three-component condensation reaction ofaryl aldehydes and β-naphthol under solvent-free conditions in the presence of β-cyclodextrin sulfonic acid, as an efficient heterogeneous solid acid catalyst with excellent yields and short reaction time is presented.

Keywords: benzoxanthene; β-cyclodextrain sulfonic acid; solvent-free conditions; β-naphthol; aryl aldehydes

Introduction

A multicomponent reaction (MCR) is a process in which three or more easily accessible components are combined together in a single reaction vessel to produce a final product displaying features of all inputs and thus offers greater possibilities for molecular diversity per step with a minimum of synthetic time and effort. Solvent-free organic reactions have attracted much interest particularly from the viewpoint of green chemistry.

The solid-state reaction (or solvent-free reaction) has many advantages such as: reduced pollution, low costs, and simplicity in process and handling [1]. The possibility of performing multicomponent reactions under solvent-free conditions with a hetrogeneous catalyst could enhance their efficiency from an economic as well as ecological point of view [2].

Xanthenes and benzoxanthenes have recently received great attention because of their wide range of therapeutic and biological properties, such as antibacterial [3], antiviral [4], and anti-inflammatory activities [5].

Furthermore, these compounds have emerged as sensitizers in photodynamic therapy, a well known method of controlling the localized tumors [6]. The other useful applications of these heterocycles are as dyes [7] and in laser technologies [8].

Many procedures are disclosed to synthesize xanthenes and benzoxanthenes like cyclodehydrations [9], trapping of benzynes by phenols [10], alkylations ɣ to the heteroatoms [11], and cyclo condensation between 2-hydroxy aromatic aldehydes and 2-tetralone [12]. Furthermore, 14Hdibenzo[a,j]xanthenes and its analogous are prepared by reaction of 2-naphthol with 2-naphthol-1-methanol [13], formamide [14], and carbon monoxide [15].

In spite of potential utility of aforementioned routes for the synthesis of xanthene derivatives, many of these methods involve expensive reagents, strong acidic conditions, long reaction times, low yields, use of excess of reagents/catalysts and use of toxic organic solvents. Therefore, to avoid these limitations, the discovery of a new and efficient catalyst with high catalytic activity, short reaction time, recyclability and simple work-up for the preparation of xanthenes under neutral, mild and practical conditions is of prime interest.

Experimental

All commercially available chemicals were purchased from Fluka and Merck companies and use without furtherpurification. IR spectra were recorded on a BOMEM MB-series 1998 FT-IR spectrophotometer. Reaction monitoring was accomplished by TLC on silica gel polygram SILG/UV 254 plates.

preparation of β-Cyclodextrain sulfonic acid

A 50 ml suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution of alkali trap. β-cyclodextrin (1.5 g) was charged in the flaskwhere chlorosulfunic acid (2.5ml) and CCl_4 (5 ml) were added dropwise and the mixture was shaken over a priod of 1 h at room temperature. The residual HCl was eliminated by suction. Thenthe mixture was washed with excess dried CCl_4.

General procedure for the preparation of 14-aryl-14H-dibenzo[a,j]xanthenes

A mixture of β-naphthol (2 mmol), aromatic aldehyde (1 mmol) and β-cyclodextrin sulfonic acid (0.05 g) was heated on the oil bath at 80^{o}C(Scheme1). After completion of reaction (monitored by TLC n-hexan/ethylacetate, 2/5) the reaction mass was cooled at room temperature and hot ethanol was added. The product was filtered and recrystallized from ethanol to give compounds in high yields.

The spectral data of some dibenzo [a,j] xanthenes

14-(2-Chlorophenyl)-14H-dibenzo[a.j]xanthene: IR (KBr,)□:3056, 1620, 1592, 1514, 1459, 1429, 1402, 1254, 1032, 964, 828, 810, 749, 739 cm^{-1}.

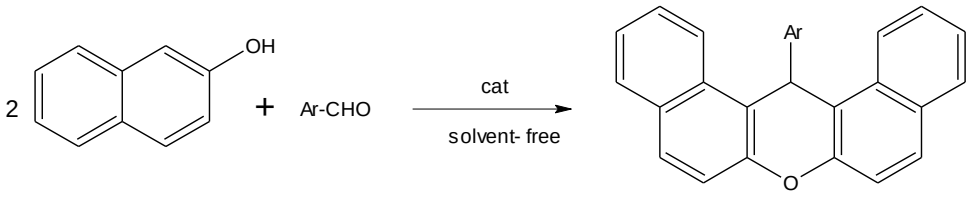
14-(3-Nitrophenyl)-14H-dibenzo[a.j]xanthene: IR (KBr,)□:3080, 1621, 1592, 1529, 1458, 1430, 1401, 1347, 1251, 1140, 1081, 964, 825, 808, 744 cm^{-1}.

14-(4-Methoxyphenyl)-14H-dibenzo[a.j]xanthene: IR (KBr)□:3072, 2833, 1591, 1457, 1430, 1399, 1248, 1177, 1027, 961, 830, 808, 741 cm^{-1}.

14-(4-Methylphenyl)-14H-dibenzo[a.j]xanthene: IR (KBr,)□:3019, 2901, 1620, 1590, 1508, 1457, 1429, 1401, 1247, 961, 808, 739, 609 cm^{-1}.

Results and discussion

(β-CDSA/SiO_2), was easily prepared by simple mixing of β-cyclodextrin and chlorosulfonic acid in CCl_4 at room temperature. This reaction is easy and clean, because the only by products of the reaction is HCl gas which is evolved from the reaction vessel immediately. We began to study this condensation reaction by examining the amount of catalyst for the reaction involving 3-nitrobenzaldehyde and β-naphthol to afford the product under solvent-free conditions at 80°C. We found that 0.05 g of β-cyclodextrin sulfonic acid seems to be the optimum amount of catalyst and increasing amount of catalyst did not improve the yields while decreasing the amount of catalyst decreased the yield.



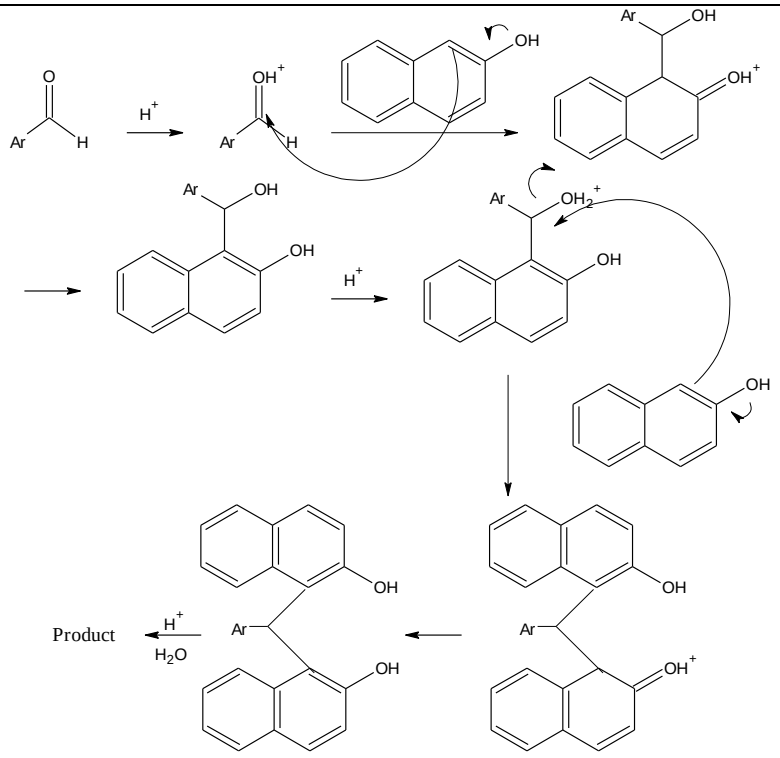
Scheme 1. The preparation of 14-aryl -14H-dibenzo[a,j]xanthenes usingβ-cyclodextrin sulfonic acid

High yields wereobtained using aromatic aldehydes carrying electron donating or electron-withdrawing substituents in 5-40min (Table1), and many problems which may associate with using solvent such as cost, handling, safety and pollution havebeen avoided. The suggested mechanism for the reaction catalyzed by β-cyclodextrin sulfonic acid is shown in (Scheme 2). Finally, it should be mentioned when reactions were carried out in the absence of catalyst for long period of time(7-8h) and in solvent-free condition at 80 °C the yields of products were low (<30%).

Table 1. Synthesis of 14-aryl -14H-dibenzo[a,j]xanthenes derivatives in presence of β-cyclodextrin sulfonic acid as catalyst from β-naphthol and aromatic aldehydes under thermal (80°C) and solvent-free conditions

Entry	Product	Time(min)	Yield(%)	Mp (oC)

				Found	Reported
1	Benzaldehyde	30	80	183-184	185
2	2-Chlorobenzaldehyde	20	72	214-215	215
3	4-Bromobenzaldehyde	15	70	297-298	297
4	2-Nitrobenzaldehyde	20	80	213-214	213
5	3-Nitrobenzaldehyde	5	83	210-211	210-211
6	4-methoxybenzaldehyde	40	76	202-203	204
7	4-Methylbenzaldehyde	10	83	227-228	229
8	Cinnamaldehyde	180	No	-	-
9	2,4-Dimethylbenzaldehyde	35	Reaction	196-197	-
10	4-Cyanobenzaldehyde	5	93	291-293	291-292
			70		



Scheme 2. Proposed mechanism for the preparation of 14-aryl-14*H*-benzo[a,j]xanthene.

Conclusion

We have developed a simple, efficient and green methodology for the synthesis of xanthenes using β-cyclodextrin sulfonic acid under solvent-free conditions. This method offers several advantages including high yields, applicarion of an inexpensive catalyst, short reaction times, easy workup and performing multicomponent reaction under solvent free conditions that is considered to be relatively environmentally benign.

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