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Antimony trichloride ($SbCl_3$) catalyzed solvent free one-pot synthesis of benzoxanthenes

Sugat Kirti[1], Dhanraj T.Masram[1]*, Ram Singh[2]*

Department of Chemistry, University of Delhi, Delhi – 110007, (INDIA).

Department of Applied Chemistry, Delhi Technological University, Delhi – 110042, (INDIA)

E-mail: dhanraj_masram27@rediffmail.com; singh_dr_ram@yahoo.com

ABSTRACT

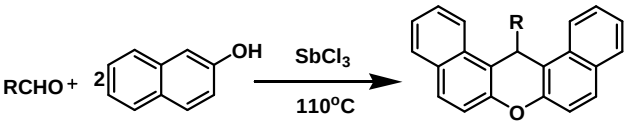
The synthesis of various 14-aryl-14-H-dibenzo[a,j]xanthenes has been carried out in high yields and high purity by one pot, solvent free cyclocondensation of an aldehyde and β-naphthol using antimony trichloride ($SbCl_3$) as catalyst. The method provides excellent isolated yield, short reaction time and easy work up procedure.

KEYWORDS

Aldehydes;
Antimony trichloride;
β-Naphthol;
Solvent free synthesis;
Xanthenes.

INTRODUCTION

Xanthene and their derivatives are versatile biologically active molecules[1-4]. These molecules are useful in photodynamic therapy[2], laser technologies[3], and as pH-sensitive fluorescent materials for biomolecular visualization[4]. Different methods have been reported for the synthesis of benzoxanthene scaffolds[1]. The condensation of 2-naphthol with aldehydes under acidic condition have been widely explored. Some of the catalyst used for the reaction are AcOH"H_2SO_4 in acidic medium[5], *p*-TSA[6], sulfamic acid[7], molecular iodine[8], tungsten heteropoly acid[9], silica sulfuric acid[10], amberlyst-15[11], wet cyanuric chloride[12], $K_5CoW_{12}O_{40}.3H_2O$[13], heteropoly acids (HPAs)[14], boric acid[15] and ionic liquids[16]. Most of the catalysts are used in different traditional solvents. Solvent free reactions are always appreciated over classical procedures making them more clean, safe, and easy to perform[17]. To make the synthesis of benzoxanthenes more environmental friendly and milder under solvent free condition, we have studied catalytic effect of the antimony trichloride ($SbCl_3$) for the one-pot synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes **(3)** under normal heating condition (Scheme 1). Antimony trichloride ($SbCl_3$) is easily commercially available, inexpensive and easy to handle[18-20].



1 2 3(a-m)

Scheme 1 : $SbCl_3$ catalysed synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes

EXPERIMENTAL

General information

All reagents were of analytical reagent grade and purified wherever necessary. The purities of the compounds were determined on silica-coated Al plates (Merck). All melting points have been determined on a

Thomas Hoover Capillary melting point apparatus and are uncorrected. The spectral data have been recorded on standard instruments from reputed companies.

General procedure

A mixture of β-naphthol (2 mmol), aldehyde (1 mmol) and $SbCl_3$ (0.2 mmol) was heated in an oil bath at 110°C with stirring for the time as indicated in Table 3. Progress of the reaction was monitored by TLC using hexane & ethyl acetate (4:1) as mobile phase. After completion of the reaction, the reaction mixture was cooled to room temperature. Further, methanol (10 mL) was added to the semisolid reaction mixture and stirred for 10 minutes. The solid so obtained was filtered off. The crude product solid was diluted with dichloromethane and filtered. The filtrate was concentrated in vacuum and the residue purified by crystallization with ethyl alcohol.

RESULTS AND DISCUSSION

The synthesis of selected 14-aryl-14H-dibenzo[a,j]xanthenes **(3)** have been achieved by one-pot solvent free cyclocondensation of an aldehyde **(1)** and β-naphthol **(2)** using antimony trichloride ($SbCl_3$) as catalyst (Scheme 1) in 80-95% yields. To study the feasibility of $SbCl_3$ as catalyst in this condensation reaction, the reaction of benzaldehyde with 2-naphthol has been selected as the model reactant under different reaction conditions. Initially, the reaction has been performed in both solvent and solvent free condition to check the feasibility (TABLE 1). The reaction has been performed in both protic and aprotic organic solvents and in solvent free condition taking antimony trichloride ($SbCl_3$) as lewis acid catalyst (TABLE 1). The best result has been observed under solvent free condition (Entry 6-9, TABLE 1). This may be attributed to the stability of catalyst in protic solvents and low boiling point of aprotic solvents. Also, the reaction temperature has been optimised at 110°C (Entry 8, TABLE 1).

The optimization for the catalyst concentration has been carried out using different amount of $SbCl_3$ keeping the amount of reactants constant (TABLE 2). In the absence of catalyst, the product formation was not observed. At lower amount of catalyst (entry 2, 3 & 4, TABLE 2) low yield was found and higher amount of catalyst (entry 6 & 7, TABLE 2) did not affect the yield. The optimum result was achieved at 0.2 mmol of $SbCl_3$ for 1 mmol of benzaldehyde and 2 mmol of β-naphthol.while on increasing the catalyst loading (entry 6 & 7, TABLE 2) did not affect the yield. So we concluded that optimum loading of catalyst is 0.2 mmol for this reaction. The reaction has also been performed using different catalyst such as $BiCl_3$, $InCl_3$ and $FeCl_3$. The best result was observed with $SbCl_3$ at 0.2 mmol for 1 mmol aldehyde and 2 mmol 2-naphthol. To check the feasibility of the reaction under above optimized conditions, we carried out this reaction using different aromatic aldehydes (TABLE 3).

TABLE 1 : Effect of solvent, reaction time and temperature*

Entry	Solvent	Time (mins)	Temperature (°C)	Isolated Yield (%)
1	H_2O	1440	Reflux	5
2	CH_3OH	1440	Reflux	36
3	CH_3CH_2OH	1440	Reflux	40
4	$CHCl_3$	1440	Reflux	55
5	CH_2Cl_2	1440	Reflux	58
6	Solvent Free	30	80	70
7	Solvent Free	30	90	83
8	Solvent Free	30	110	91
9	Solvent Free	30	120	90

***β-naphthol 2 mmol; aldehyde 1 mmol, $SbCl_3$ 0.2 mmol**

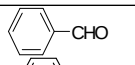
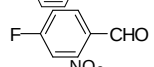
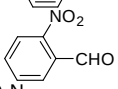
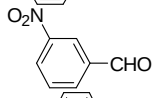
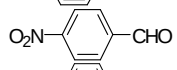
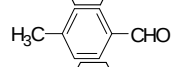
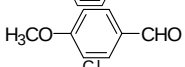
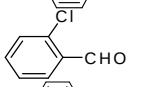
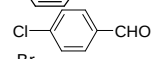
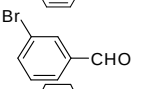
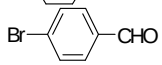
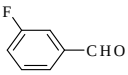
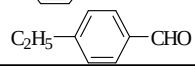
TABLE 2 : Catalyst optimization at 110°C for 30 mins under solvent free condition

Entry	Catalyst	Amount of Catalyst (mmol)	Isolated Yield (%)
1	$SbCl_3$	0	0
2	$SbCl_3$	0.025	10
3	$SbCl_3$	0.05	15
4	$SbCl_3$	0.1	40
5	$SbCl_3$	0.2	91
6	$SbCl_3$	0.4	91
7	$SbCl_3$	0.8	90
8	$BiCl_3$	0.2	88
9	$InCl_3$	0.2	76
10	$FeCl_3$	0.2	89

It has been found that the nature of the functional group on the aromatic ring of the aldehyde affects the reaction time and yield. The presence of electron withdrawing group at *para* position in comparison to the unsubstituted aromatic aldehyde shows increase of the

yield while the presence of an electron donating group decreases the yield. Though *meta* and *para* substituted aromatic aldehydes gave good results, *ortho*-substituted aromatic aldehydes (such as 2-nitrobenzadehyde) gave lower yields because of the steric effects[3]. $SbCl_3$ might be acting as the Lewis-acid catalyst for several stages of reaction. A conformation to the mechanism is in progress.

TABLE 3 : $SbCl_3$ catalysed synthesis of 14-aryl-14H-dibenzo[a,j] xanthenes

Comp No.	RCHO	Time (Mins)	Isolated Yield (%)	Mp. °C (Lit)[ref]
3a		30	91	182 (185)[21]
3b		35	93	237 (239)[21]
3c		45	85	294 (293)[7]
3d		35	91	212 (211)[21]
3e		45	94	312 (310)[21]
3f		35	83	227 (229) [21]
3g		30	80	205 (204)[21]
3h		60	87	214 (215)[21]
3i		30	95	288 (289)[21]
3j		45	90	190 (190)[21]
3k		40	92	295 (297)[21]
3l		40	90	260 (257)[21]
3m		35	80	151(152)[22]

CONCLUSIONS

We have developed an efficient and convenient one-pot solvent free synthesis of 14-aryl-14H-dibenzo[a,j] xanthenes using $SbCl_3$ as catalyst. The reaction takes place through the condensation of aldehyde or substituted aldehyde with β-naphthol in 1:2 molar ratio at 110°C under solvent free condition with excellent yield in short reaction time.

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