



Pentafluoropropionic Acid as a Efficient Catalyst for the One-Pot Synthesis of 14-aryl-14*H*-dibenzo[*a, j*] xanthenes Under Solvent Free Conditions

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ABSTRACT

Pentafluoropropionic acid was found to be highly efficient, and green catalyst for the synthesis of dibenzo[*a, j*] xanthenes by condensation reaction of β -naphthol with aryl aldehydes in good to high yields under solvent-free conditions. Present methodology offers several advantages, such as good yields, simple procedure with an easy work-up and the absence of any volatile and hazardous organic solvent.

Key words: Dibenzo[*a, j*] xanthenes, pentafluoropropionic acid, Solvent-free conditions, recyclable catalyst.

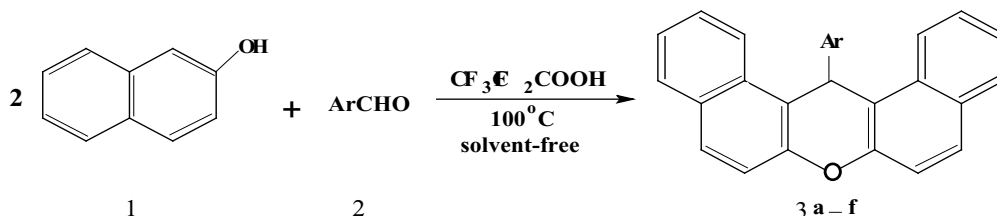
INTRODUCTION

Xanthenes and their derivatives are of considerable interest as they possess a wide range of biological properties, such as anti-inflammatory¹, antibacterial², antiviral³ activities, as well as their use in photodynamic⁴. Such compounds are also utilized for antagonism of the paralyzing action of zoxazolamine⁵. Moreover, xanthene derivatives such as 14-aryl-14*H*-dibenzo [*a, j*] xanthenes are of importance as they have various industrial, pharmaceutical and biological applications⁵⁻⁹. For example, these compounds have been applied as dyes in laser technology⁶, and as PH sensitive fluorescent materials for visualization of biomolecules⁸. Therefore, the development of new and efficient

methodologies for the synthesis of xanthene derivatives will be interesting in both synthetic organic and medicinal chemistry. Dibenzo xanthene derivatives are generally synthesized via one-pot reaction of an aryl aldehyde and 2-naphthol in the presence of several catalysts such as AcOH-H₂SO₄⁸, *P*-TSA^{10,11}, wet cyano chloride¹², molecular iodine^{13,14}, sulfamic acid¹⁵, heteropoly acid¹⁶, silica sulfuric acid¹⁷, cellulose sulfuric acid¹⁸, caro's acid-silica gel¹⁰, Sr(OTf)₂²⁰, Al(HSO₄)₃²¹, LiBr²², Cation-exchange resins²³, HClO₄-SiO₂²⁴, methanesulfonic acid²⁵, dowex-50w²⁶, NH₄H₂PO₄²⁷, Yb(OTf)₃²⁸, BF₃·SiO₂²⁹, potassium dodecatungstocobaltate trihydrate³⁰, NaHSO₄³¹, nano-TiO₂³², Amberlyst 15³³, InCl₃³⁴, TaCl₅³⁵ and Ionic Liquid³⁶. As a finding of our ongoing research projects on the synthesis of

heterocyclic compounds³⁷⁻³⁹, and in continuations of our previous works on the applications of organocatalyst in organic reactions, herein, we want to report a new and efficient synthesis of 14-

aryl-14*H*-dibenzo [*a*, *j*] xanthene derivatives in the presence of pentafluoropropionic acid (PFPA), as a Brønsted acidic organocatalyst under solvent-free conditions (Scheme 1).



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

EXPERIMENTAL

All of the chemical material used in this work were purchased from merck and without further purification. Melting points were recorded of Electrothermal type 9100 melting point apparatus. The IR spectra were obtained on a 4300-Shimadzu spectrophotometer in KBr disks. The ¹H NMR (500MHz) spectra were recorded on a Bruker-Ac-500 spectrometer.

General procedure for the synthesis of 14-aryl-14*H*-dibenzo [*a*, *j*] xanthenes (3a-f)

A mixture of β-naphthol (0.288g, 2 mmol), aryl aldehyde (1 mmol) and pentafluoropropionic acid (25 mol% based on aryl aldehyde) was heated on the oil bath at 100°C for the indicated time. The progress of the reaction was monitored by TLC. After completion of the reaction, mixture was cooled to room temperature and water was added. The precipitated solid was collected by filtration under suction, washed with cold water, and then recrystallized from ethanol to afford pure products 3a-f (Table 2) in good yields. All the products were identified by comparison of spectral data (IR, and ¹H NMR), and m.p. with those reported [8, 15, 34, 40].

RESULTS AND DISCUSSION

Solvent-free conditions are especially important for providing an eco-friendly system. One advantage of solvent-free reactions, in comparison to the reaction in molecular solvents, is that the compounds formed are often sufficiently pure to circumvent extensive purification using

chromatography. Due to the increasing demand in modern organic processes for avoiding expensive purification, we decided to investigate the efficiency of pentafluoropropionic acid as a catalyst in the synthesis of 14-aryl-14*H*-dibenzo [*a*, *j*] xanthene derivatives under solvent-free conditions. At first, the synthesis of compound 3a was selected as a model reaction to optimize the reaction conditions. Therefore, mixture of β-naphthol (2 mmol), and benzaldehyde (1 mmol), was heated on the oil bath at different temperatures in the presence of various amount of penta fluoropropionic acid as catalyst under solvent-free conditions (Table 1). As can be seen from this table, the yield of compound 3a is affected by the catalyst amount and reaction temperature. No product was obtained in the absence of the catalyst (Entry 1) or in the presence of the catalyst at room temperature (Entry 2) indicating that the catalyst and temperature are necessary for the reaction. Increasing the amount of the catalyst and reaction temperature up to 25 mol% and 100°C, respectively, increased the yield of the product 3a. Further increase in both catalyst amount and temperature did not increase the yield noticeably (Entries 8-11).

To evaluate the generality of this model reaction we then prepared a range of dibenzo [*a*, *j*] xanthenes under optimized reaction conditions. In all cases, aromatic aldehydes with substituents carrying either electron-donating or electron-withdrawing groups reacted successfully and gave the products in good yields. The type of aldehydes had no significant effect on the reaction. The results are summarized in table 2.

Table 1: Effect of penta fluoropropionic acid amount on the model reaction^a

Entry	Catalyst (mol%)	Temperature(°C)	Time (min)	Yield (%) ^b
1	-	100	300	-
2	25	R.T.	300	-
3	20	80	240	65
4	20	100	200	72
5	20	120	200	67
6	25	80	150	86
7	25	100	100	88
8	25	120	120	87
9	30	80	120	82
10	30	100	100	84
11	30	120	100	84

^a2mmol β -naphthol, 1mmol benzaldehyde in the presence of various amount of catalyst and temperature under solvent-free conditions. ^bIsolated yields.

Table 2: Synthesis of 14-aryl-14H-dibenzo [a, j] xanthenes 3a-f^a

Entry	Ar	Product ^b	Time(min)	Yield(%) ^c	m.p(°C)	
					Found	Reported
1	C ₆ H ₅	3a	100	88	185-187	183-187[15]
2	4-ClC ₆ H ₄	3b	100	85	285-289	289-290[34]
3	3-NO ₂ C ₆ H ₄	3c	125	83	214-215	213-214[40]
4	4-NO ₂ C ₆ H ₄	3d	120	86	307-310	308-310[8]
5	4-MeOC ₆ H ₄	3e	115	82	205-207	203-205[8]
6	4-MeC ₆ H ₄	3f	125	87	225-227	227-229[8]

^a 2mmol β -naphthol, 1mmol benzaldehyde and 25mol% penta fluoropropionic acid at 100°C under solvent-free conditions. ^bThe products were characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by reported procedures. ^c Isolated yields.

CONCLUSIONS

In conclusion we have successfully demonstrated the catalytic activity of penta fluoropropionic acid in the synthesis of 14-aryl-14H-dibenzo [a,j] xanthenes. Easy simple work-up, short reaction times and good yields are some advantages of this method.

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