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Polyvinylpolypyrrolidone-supported boron trifluoride (PVPP-BF_3): Mild and efficient catalyst for the synthesis of 14-aryl-14*H*-dibenzo [a,j] xanthenes and bis(naphthalen-2-yl-sulfane) derivatives

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A B S T R A C T

A convenient and an efficient method for the synthesis of 14-aryl-14*H*-dibenzo [a,j] xanthenes and bis(naphthalen-2-yl-sulfane) derivatives is described. The reaction proceeded via condensation of aldehydes with 2-naphthol or 2-thionaphthol in the presence of polyvinylpolypyrrolidone-supported boron trifluoride. These reactions were studied under different conditions. In terms of reaction time and yield, it was found that optimum results were obtained for the synthesis of 14-aryl-14*H*-dibenzo [a,j] xanthenes under solvent free technique at 120 ^{O}C and for preparation of bis(naphthalen-2-yl-sulfane) derivatives in 1,2-dichloroethan under reflux conditions. Clean methodologies, easy workup procedure, high yield and simple preparation of the catalyst are some advantages of this work.

1. Introduction

Replacing oxygen by sulfur in a functional group does not just correspond to a small step in the periodic table, but may well lead to another world of chemistry. The differences in chemical reactivity and stability can be explained by the change in atomic radii, in electronegativity, and in polarizability between oxygen and sulfur [1]. The protection of carbonyl groups as dithioacetals is a common and popular practice in organic chemistry [2]. The importance of thioacetals is due in part to their inherent stability under usual acidic or basic conditions and because of their behavior as masked acyl anions or methylene functions [3]. In this view, there have been continued improvements in the methods of preparation of thioacetals [4–7]. Xanthenes are used in the fields of biology, pharmaceutical industry and sensitizers in photodynamic therapy [8–10]. They are also present or used in dyes [11], antagonists for the paralyzing action of Zoxazolamine [12], pH-sensitive fluorescent materials for visualization of biomolecules [13], and laser technologies [14]. The synthesis of xanthenes has been improved by condensing of aldehydes and 2-naphthol in the presence of an acid catalyst such as: AcOH–H_2SO_4 [15], sulfamic acid [16], *p*-TSA [17], Amberlyst-15 [18], silica sulfuric acid [19], $HClO_4$–SiO_2 [20], I_2 [21], heteropoly acid [22], Yb(OTf)$_3$ [23], montmorillonite K-10 [24], ionic liquids [25,26] and cellulose sulfuric acid [27].

However, some of these methods suffer from at least one of the following disadvantage: strongly acidic wastes, high cost and toxicity of the reagent, tedious work-up procedures, unsatisfactory yields, harsh conditions and nonrecyclable reagents. Therefore, it seems that the major task of current research is more acceptable methods based on improved stable and recoverable catalyst for the synthesis of 14-aryl-14*H*-dibenzo [a,j] xanthenes and bis(naphthalen-2-yl-sulfane) derivatives. Substantial investigations have been done to introduce novel supported catalysts and chemical reagents. These include dispersing catalysts on inorganic supports such as metal oxide, alumina, silica, and zeolite. There are a number of advantages in using polymer supported catalysts over the conventional catalysis. The reactions can be performed under mild condition and purification of the product is simplified because of the use of an insoluble solid support. Polymer supported catalysts can also be recycled after use [28]. Poly (vinyl pyrrolidone) displays a strong binding affinity toward small molecules. Furthermore, its iodine complex, povidon-iodine, is widely used as an anti-infective agent in clinical treatments [29]. Recovery of boron trifluoride from

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the reaction however results in the formation of large amounts of waste, which on an industrial scale is environmentally unacceptable. The use of a heterogenous BF_3 system would offer ease of catalyst recovery and minimize the production of waste currently formed during BF_3 recovery. However, a suitable replacement supported system must also exhibit activities and selectivity comparable to the existing homogenous route. In spite of boron trifluoride etherate, polyvinylpolypyrrolidone-supported boron trifluoride is non-corrosive and stable solid catalyst elevated Lewis acid property. Following our interest in the used of polyvinylpolypyrrolidone-boron trifluoride (PVPP-BF_3) for amidation of benzhydrol and *tert*-butyl acetate with nitriles via Ritter reaction [30,31], acylation of alcohols, phenols and trimethylsilyl ethers [32], synthesis of 4-methyl coumarins via the Pechmann reaction [33] and chemoselective oxygenation of sulfides to sulfones [34], herein, we found that PVPP-BF_3 could be use for the synthesis of 14-aryl-14*H*-dibenzo [a,j] xanthenes and bis(naphthalen-2-yl-sulfane) derivatives in excellent yields (Scheme 1).

2. Experimental

All chemicals were purchased from Merck chemical company. Melting points were recorded on an electro thermal melting point apparatus. The NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a Bruker Avance DRX 400 MHz spectrometer. IR spectra were determined on a SP-1100, P-UV-Com instrument. Products were separated by simple filtration, and identified by comparison of FT-IR, and ^1H NMR spectra, with those reported for authentic samples.

2.1. Catalyst preparation

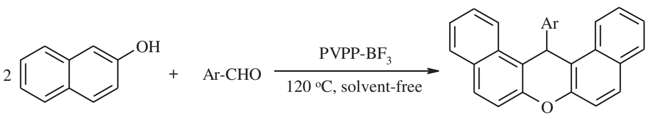
In this method boron trifluoride etherate was immobilized on polyvinylpolypyrrolidone to give a stable polymeric Lewis acid reagent according to our previous article [31].

2.2. Synthesis of 14-aryl-14H-dibenzo [a,j] xanthenes: general procedure

A mixture of 2–naphthol (2 mmol), aromatic aldehyde (1 mmol) and PVPP-BF_3 (0.05 g) was stirred at 120 °C for the appropriate time, as shown in Table 1. Completion of the reaction was indicated by TLC monitoring. The reaction mixture was cooled to ambient temperature, EtOAc was added and the PVPP-BF_3 was filtered off. The filtrate was concentrated to dryness, and the crude solid residue was recrystallized from ethanol to afford pure crystals of the proper 14-aryl-14*H*-dibenzo [a,j] xanthenes in 92–98% yields. The products were characterized by FT-IR, ^1H NMR and physical constants.

2.3. Synthesis of bis(naphthalen-2-yl-sulfane) derivatives: general procedure

A mixture of 2–thionaphthol (2 mmol), aromatic aldehyde (1 mmol) and PVPP-BF_3 (0.05 g) was stirred at reflux condition in the 1,2-dichloroethan for the appropriate time, as shown in Table 2. Completion of the reaction was indicated by TLC monitoring. The reaction mixture was cooled to ambient temperature, and the PVPP-BF_3 was filtered off. The filtrate was concentrated to dryness, and the crude solid residue was recrystallized from ethanol to afford pure crystals of the proper bis(naphthalen-2-yl-sulfane) derivatives in 86–98% yields. The products were characterized by FT-IR, ^1H NMR, ^{13}C NMR, electron ionization mass spectrometry and physical constants.



Scheme 1. The reaction of 2-naphthol with aldehydes catalyzed by PVPP-BF_3.

Table 1
Synthesis of 14-aryl-14*H*-dibenzo [a,j] xanthenes via condensation of aldehydes and 2–naphthol catalyzed by PVPP-BF_3.[a]

Entry	Aldehyde	Time/h	Yield %[b]	Mp. °C	
				Found	Lit [35]
1	Benzaldehyde	1/5	94	184–185	183–185
2	4-Bromobenzaldehyde	1/5	98	298–299	298–300
3	4-Chlorobenzaldehyde	1/5	98	290–292	289–291
4	2-Chlorobenzaldehyde	1/5	97	215–216	213–215
5	4-hydroxybenzaldehyde	2	92	140–142	141–143
6	4-Fluorobenzaldehyde	2	92	239–241	238–240
7	2-Methoxybenzaldehyde	1/5	98	258–259	258–259
8	4-Methylbenzaldehyde	2	98	227–229	226–228
9	3-Nitrobenzaldehyde	1/5	95	211–212	210–211
10	2-Nitrobenzaldehyde	1/5	94	214–216	213–215
11	4-Nitrobenzaldehyde	2	96	312–313	310–312

[a] All entries were carried on 2-naphthol (2 mmol), benzaldehyde (1 mmol) and PVPP-BF_3 (0.05 g) at 120 ^{O}C under solvent-free conditions.
[b] All yields refer to isolated products after recrystallization.

2.4. The spectral data of new products

2.4.1. (Phenylmethylene) bis(naphthalen-2-yl-sulfane) (Table 2, entry 1)

m.p. 135–138 °C. IR (KBr): (υ_{max}, cm^{-1}) 3049, 2966, 1652, 1581, 1533, 1494, 1450, 1340, 1263, 1128, 1070, 946, 811, 738. ^1H NMR ($CDCl_3$): δ = 5.68 (s, 1H), 7.29–7.87 (m, 19 H)ppm.^{13}C NMR δ = 60.53, 126.4, 126.5, 127.6, 127.7, 127.9, 127.9, 128.2, 128.6, 129.6, 131.7, 131.8, 132.6, 133.5, 139.6. EI-MS (*m/z*): 408 ($M^+ + H$).

2.4.2. (4-bromophenylmethylene) bis(naphthalen-2-yl-sulfane) (Table 2, entry 2)

m.p. 110–112 °C. IR (KBr): (υ_{max}, cm^{-1}) 3047, 1652, 1539, 1506, 1477, 1394, 1340, 1068, 1008, 811, 736. ^1H NMR ($CDCl_3$): δ = 5.60 (s, 1H), 7.31–7.85 (m, 18 H) ppm. ^{13}C NMR δ = 59.92, 122, 126, 127.6, 127.7, 128.5, 129.6, 131.28, 131.7, 132, 132.7, 133.5, 138.7. EI-MS (*m/z*):487 ($M^+ + H$).

2.4.3. (4-chlorophenylmethylene) bis(naphthalen-2-yl-sulfane) (Table 2, entry 3)

m.p. 108–110 °C. IR (KBr): (υ_{max}, cm^{-1}) 3049, 2916, 1622, 1579, 1539, 1488, 1404, 1240, 1186, 1049, 813, 742. ^1H NMR ($CDCl_3$):

Table 2
Synthesis of bis(naphthalen-2-yl-sulfane) derivatives via condensation of aldehydes and 2–thionaphthol catalyzed by PVPP-BF_3.[a]

Entry	Aldehyde	Time/h	Yield%[b]
1	Benzaldehyde	3/5	92
2	4-Bromobenzaldehyde	3	98
3	4-Chlorobenzaldehyde	3/5	98
4	4-Methylbenzaldehyde	2/5	97
5	3,5-Dichlorobenzaldehyde	3	92
6	2-Methoxybenzaldehyde	2/5	86
7	3-Methoxybenzaldehyde	3	95
8	4-Methoxybenzaldehyde	3	98
9	3-Nitrobenzaldehyde	4	92
10	2,4-Dichlorobenzaldehyde	3/5	94
11	Naphtalen-2-carbaldehyde	3	91

[a] All entries were carried on 2-thionaphthol (2 mmol), aldehyde (1 mmol) and PVPP-BF_3 (0.05 g) under reflux conditions in DCE solvent.
[b] All yields refer to isolated products after recrystallization.