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Short communication

Heteropolyacid: An efficient and eco-friendly catalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene

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Abstract

A simple and efficient catalytic procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene is reported. Tungsten heteropoly acid catalysts are used both in bulk or supported on silica gel under solvent-free conditions at 100 °C. Good yields and short reaction time are advantages of this new method.

Keywords: Heteropolyacid; Xanthene; Solvent-free; Naphthol; Recyclable catalyst

1. Introduction

Xanthenes and benzoxanthenes have been reported to posses diverse biological and therapeutic properties such as antibacterial [1], antiviral [2], and anti-inflammatory activities [3], as well as photodynamic therapy [4] and for antagonism of the paralyzing action of zoxazolamine [5]. The other useful applications of this heterocycles are as dyes [6], fluorescent materials for visualization of biomolecules [7], and in laser technologies [8]. Various routes are available in literatures to synthesis xanthenes, including the reactions of aryl oxomagnesium halides with triethylortoformate [9], cyclohydration [10], trapping of benzynes by phenols [11], cyclization of polycyclic aryltriflate esters [12] and cyclo condensation between 2-hydroxy aromatic aldehydes and 2-teralone [13]. In addition,14*H*-dibenzo[*a*,*j*]xanthenes and related products are prepared by reaction of 2-naphthol with formamide [14], 2-naphthol-1-methanol [15], carbon monoxide [16] and aldehyde acetals [17]. Recently, several improved procedures were reported including reaction of 2-naphthol with aldehydes under various conditions using Lewis acids as well as protic acid promoters [18] for the synthesis of 14*H*-dibenzo[*a*,*j*]xanthene.

Due to the super acidic properties of solid heteropolyacid (HPAs), in the last three decades, heteropolyacids have found numerous applications as useful and versatile acid catalyst for some acid-catalyzed reactions [19]. They are usually solids that are insoluble in non-polar solvents but highly soluble in polar ones. They can be used in bulk or supported forms in both homogeneous and heterogeneous systems. Furthermore, heteropolyacids have several advantages, including high flexibility in modification of the acid strength, ease of handling, environmental compatibility, and non-toxicity and experimental simplicity [19].

In spite of potential utility of aforementioned routes for the synthesis of 14*H*-dibenzo[*a*,*j*]xanthene, 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 14*H*-dibenzo[*a*,*j*]-xanthene under neutral, mild and practical conditions is of prime interest. The aim of this study is to utilized the silica gel supported Keggin and Well–Dawson tungsten heteropolyacids as catalysts for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]-xanthene.

2. Experimental

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an

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ionization potential of 70 eV. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz, respectively. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer.

2.1. Preparation of the supported catalyst

The silica gel supported $H_6P_2W_{18}O_{62}\cdot 24H_2O$ (WD acid) or $H_3PW_{12}O_{40}\cdot 6H_2O$ (PW acid) was prepared by mixing silica gel (1.5 g, Merck grade 60, 230–400 mesh) with a solution of WD acid (0.30 g) or PW acid (0.30 g) in distilled water (10 ml). The resulting mixture was stirred for 30 min. After removal of water in a rotary evaporator, the solid powder was dried at 70 °C for 3 h.

2.2. General procedure for the preparation of aryl-14H-dibenzo[a,j]xanthenes 3

(a) A mixture of 2-naphthol (2 mmol), aldehyde (1 mmol) and WD acid (1 mol%, 0.05 g) or PW acid (2 mol%, 0.06 g) was heated at 100 °C for an appropriate time (TLC). After cooling, the reaction mixture was washed with $CHCl_3$ (10 ml). The solvent was evaporated and the crude product recrystallized from EtOH to afford the pure product.

(b) A mixture of 2-naphthol (2 mmol), aldehyde (1 mmol) and silica gel supported WD acid (0.2 g) or silica gel supported PW acid (0.15 g) was heated at 100 °C for an appropriate time (TLC). After cooling, the reaction mixture was washed with $CHCl_3$ and filtered to recover the catalyst. The solvent was evaporated and the crude product recrystallized from EtOH to afford the pure product. The recovered catalysts dried for 2 h at 70 °C for investigation of the recyclability of the catalysts.

All the products are known compounds and were characterized by IR and NMR spectroscopic data and their melting points are compared with reported values.

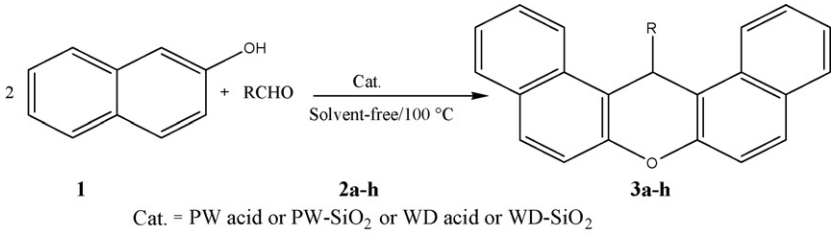
*Spectral data for compound **3c***: mp 286–288 °C; IR (KBr) (ν_{max}, cm^{-1}): 3033, 1618, 1580; ^{1}H NMR ($CDCl_3$): δ_H 6.48 (1H, s, CH), 7.10–8.34 (16H, m, Arom.); ^{13}C NMR ($CDCl_3$): δ_c 37.37, 116.73, 118.02, 122.40, 124.37, 126.92, 128.64, 128.91, 129.09, 129.49, 131.04, 131.24, 132.07, 143.46, 148.66. MS (*m/z*, %): 392 (25), 281 (100), 252 (45), 75 (34).

3. Results and discussion

In continuation of our interest on the application of heteropolyacid catalysts for development of useful synthetic methodology [20], we wish to report a simple, efficient and practical approach for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene using two tungsten heteropolyacids, $H_3PW_{12}O_{40}\cdot 6H_2O$ (PW acid) and $H_6P_2W_{18}O_{62}\cdot 24H_2O$ (WD acid) in bulk or silica gel supported forms as eco-friendly catalysts with high catalytic activity under solvent-free conditions at 100 °C (Scheme 1).

We started to study this condensation reaction by examining the amount of catalysts for the reaction involving 4-chlorobenzaldehyde **2c** (1 mmol) and 2-naphthol **1** (2 mmol) to afforded the product **3c** under solvent-free conditions at 100 °C. As can be seen from Fig. 1, best results was obtained with a 2 mol% of PW acid and 1 mol% WD acid or low catalyst concentration for supported (see Section 2) under solvent-free conditions and gave 14-(4-chloro-phenyl)-14*H*-dibenzo[*a*,*j*]-xanthene **3c** in high yield (Fig. 1).

$H_3PW_{12}O_{40}\cdot 6H_2O$ (PW acid) and $H_6P_2W_{18}O_{62}\cdot 24H_2O$ (WD acid) as environmentally benign and solid protic acids catalyzed the condensation of 2-naphtol and a wide range of aromatic aldehydes under solvent-free conditions at 100 °C and reaction completed within 0.5–1.5 h. As indicated in Table 1, in all cases the reaction gives the products in good yields and prevents problems which many associate with solvent use such as cost, handling, safety and pollution. Reduced reaction times



Scheme 1.

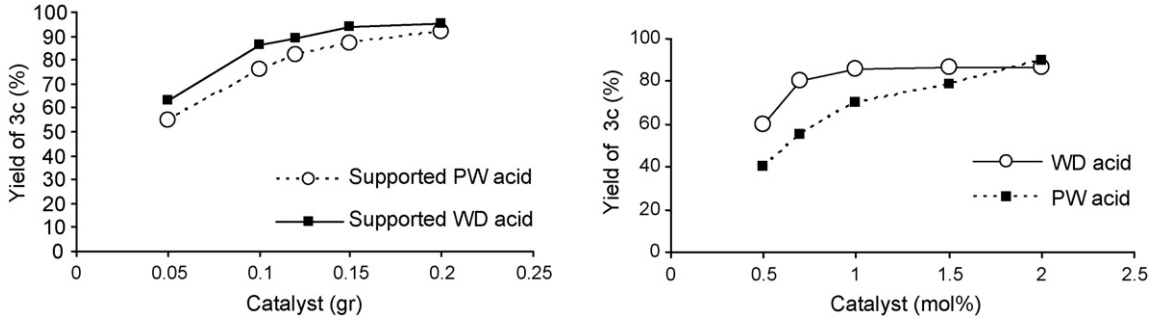


Fig. 1. Effect of amount of catalyst on the synthesis of **3c** (reaction conditions: 100 °C, 1.5 h). mol% = (mol cat./mol of compound **2**) × 100.