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Perlite-SO_3H nanoparticles: a novel and efficient catalyst for the synthesis of 14-aryl 14*H*-dibenzo[*a,j*]xanthenes under microwave conditions

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Perlite-SO_3H nanoparticles efficiently catalyze the one-pot, two-component reaction of aryl aldehydes and 2-naphthol under solvent free microwave conditions to afford the corresponding 14-aryl 14*H*-dibenzo[*a,j*]xanthene derivatives. The present approach offers several advantages such as shorter reaction times, good yields, low cost, and mild reaction conditions.

Key words: perlite-SO_3H nanoparticles, catalyst, 14-aryl 14*H*-dibenzo[*a,j*]xanthenes, microwave conditions

INTRODUCTION

The preparation of benzoxanthenes is important due to their broad spectrum of biological and therapeutic properties such as antiviral [1], antibacterial [2], and anti-inflammatory [3] activities and efficiency in photodynamic therapy [4] and in antagonism of the paralyzing action of zoxazolamine [5]. Further, these compounds can be employed as dyes [6], pH sensitive fluorescent materials for visualization of biomolecules [7] and in laser technologies [8]. As a result of their importance from industrial, biological and synthetic points of view, many synthetic methods have been reported for the synthesis of xanthenes such as cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone [9], cyclodehydrations [10] and intramolecular phenyl carbonyl reaction of aldehydes with β-naphthol by dehydration [11]. Very recently several catalysts have been used for this reaction including sulphamic acid [12], iodine [13], aluminium hydrogen sulphate [14], dipyridine cobalt chloride [15], selectflour [16], sodium hydrogen sulphate [17], ytterbium triflates [18], 1,3-dibromo-5,5-dimethylhydantoin [19], trifluoromethanesulfonic acid [20], zinc oxide nanoparticles [21] and alum [22]. However, some of these methods suffer from one or more drawbacks such as strong acidic condition, long reaction times, low yield of the products, tedious work-up, and need to use excess amounts of reagents. Thus, there is a need to develop a simple, efficient and rapid procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes (see Table 1).

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Table 1. **Comparative study of catalytic potential perlite-SO_3H nanoparticles with other reported catalysts for the synthesis of 14-phenyl-14*H*-dibenzo[*a,j*] xanthene (3h) under microwave irradiation**

Entry	Catalysts	Time, min	Yields[a], %
1	Sulfamic acid	2.5	95[12]
2	n-Bu_4NBr	4	94[23]
3	Methanesulfonic acid	2	86[24]
4	LiBr	4	83[25]
5	Perlite-SO_3H nanoparticles	8	86[b]

[a] References.

[b] Present work.

The use of heterogeneous catalysts [26–28] has received considerable importance in organic synthesis because of their ease of handling, enhanced reaction rates, greater selectivity, simple work-up, and recoverability of catalysts. Among various heterogeneous catalysts, particularly perlite nanoparticles have advantages of eco-friendly catalysts, low cost, ease of preparation and catalyst recycling [29]. Perlite is an amorphous volcanic glass that has a relatively high water content, typically formed by the hydration of obsidian. Because of its low density and relatively low price, many commercial applications for perlite have been developed. In the construction and manufacturing fields, it is used in lightweight plasters and mortars, insulation and ceiling tiles. There are few reports about using perlite as a suitable support for catalytic applications [30–33].

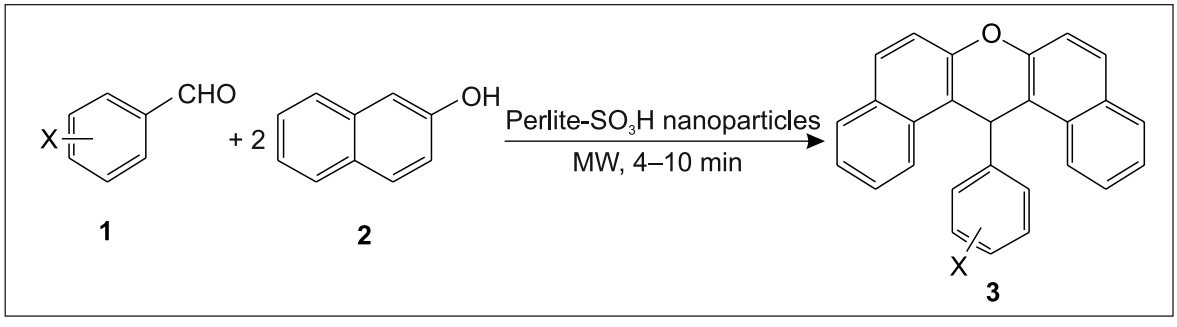
Microwave irradiation as a new technology has been widely used in various organic reactions, such as substitution [34], addition [34], dehydration [35], rearrangement [36] and redox [37]. Solvent-free procedures could avoid the use of auxiliary reagents that may be toxic or flammable, and also simplify the follow-up operation. The synthesis without a solvent under microwave irradiation has been of growing interest as an efficient, economic, and clean procedure [38].

To the best of our knowledge, there has been no report available on the synthesis of 14-aryl 14*H*-dibenzo[*a,j*]xanthenes derivatives (**3**) using perlite-SO_3H nanoparticles. Herein, we demonstrate a green, efficient and convenient method for the synthesis of 14-aryl 14*H*-dibenzo[*a,j*]xanthenes derivatives (**3**) using Perlite-SO_3H nanoparticles as a catalyst through one-pot condensation reaction of aromatic aldehydes (**1**) with β-naphthol (**2**) (Scheme 1). We think that our work is in good agreement with the principles of green chemistry [39–42] such as prevention of the formation of waste materials, possessing very high atom economy, avoiding hazardous products, designing safer products, using natural volcanic rock as a catalyst, energy economy with operating reaction under microwave conditions and elimination of chemical stages with one-pot reaction.

RESULTS AND DISCUSSION

As shown in Scheme 1 and Table 2, the reaction was carried out by adding the two components, β-naphthol and aryl aldehyde, to perlite-SO_3H nanoparticles. The mixture was irradiated for 4–10 minutes which afforded the corresponding 14-aryl 14*H*-dibenzo[*a,j*]xanthenes (82–97%). The structures of all products were unequivocally confirmed spectroscopically (FT-IR) and by physical data.

Benzaldehyde was selected as a representative aldehyde along with β-naphthol and perlite-SO_3H nanoparticles which reacted under microwave conditions at 700 W in order to optimize the reaction conditions. The condensation of a mixture of benzaldehyde (**1h**) (1 mmol) with β-naphthol (**2**) (2 mmol) in the presence of perlite-SO_3H nanoparticles (0.2 g) was carried out at 700 W for 8 minutes under microwave conditions. The reaction proceeded smoothly and gave the corresponding 14-aryl 14*H*-dibenzo[*a,j*]xanthenes (**3h**) as the sole product in 86% isolated yield (Table 2). Furthermore, the catalytic potential of perlite-SO_3H nanoparticles was compared with other reported catalysts for the synthesis of 14-phenyl-14*H*-dibenzo[*a,j*]xanthene (**3h**) under microwave irradiation (see Table 1). It is evident from Table 1 that Perlite-SO_3H nanoparticles have demonstrated a relatively comparable catalytic efficiency with others (Table 1,



Scheme 1. Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes

Table 2. **Synthesis of 14-aryl 14*H*-dibenzo[*a,j*]xanthenes (3) with perlite-SO_3H nanoparticles as a catalyst under microwave conditions**

Product[a]	Aldehyde	Time, min	Yield[b], %	Mp, °C	
				Found	Reported
a	4-$NO_2C_6H_4$	5	96	308–310	308–310 [22]
b	4-$MeOC_6H_4$	8	93	200–202	200–202 [45]
c	3-BrC_6H_4	8	87	187–188	186–188 [45]
d	4-OHC_6H_4	6	82	139–141	140 [46]
e	2,6-$Cl_2C_6H_3$	8	92	267–269	267–268 [46]
f	4-ClC_6H_4	4	97	288–289	289–290 [47]
g	3-ClC_6H_4	10	92	209–210	209–211[47]
h	C_6H_5	8	86	184–186	184–185 [48]
i	4-MeC_6H_4	4	4	225–226	227–228 [48]
j	2-ClC_6H_4	10	82	214–215	214–215 [48]
k	2,3-$Cl_2C_6H_3$	4	92	284–286	–
l	4-BrC_6H_4	8	92	297–298	297–298 [48]
m	2-$NO_2C_6H_4$	7	90	215–216	214–215 [48]
n	3-$NO_2C_6H_4$	8	92	209–210	210–211 [48]

[a] All known compounds were characterized by comparing their spectral data (FT-IR) and physical data with those reported.

[b] Isolated yields.

entries 1–4) while it can be considered as a better catalyst than n-Bu_4NBr, methanesulfonic acid, LiBr, sulfamic acid and other similar catalysts [43] for the synthesis of **3h** under solvent-free microwave conditions because of eco-friendly properties, low cost, ease of preparation, ease of handling, simple work-up and recoverability of the catalyst.

Data of NMR spectra for compound (**3k**) as a new compound have been provided: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.59 (2H, d, *J* = 8.5 Hz), 7.75 (2H, d, *J* = 7.9 Hz), 7.81 (2H, d, *J* = 8.8 Hz), 7.60 (2H, t, *J* = 7.5 Hz), 7.56 (2H, d, *J* = 8.8 Hz), 7.47 (2H, t, *J* = 7.4 Hz), 7.23 (1H, d, *J* = 8.6 Hz), 7.20 (1H, s), 6.83 (1H, d, *J* = 6.8 Hz), 6.79 (1H, s) ppm; ^{13}C NMR ($CDCl_3$): δ = 149.1, 1 421.9, 133.0, 132.6, 131.1, 131.0, 130.6, 129.7, 129.2, 128.7, 128.2, 127.5, 124.3, 122.8, 118.7, 117.4, 34.8 ppm; IR (KBr, cm^{-1}): 3 054, 2 922, 1 620, 1 597, 1 559, 1 515, 1 459, 1 405, 1 241, 1 210, 1 138, 1 101, 1 048, 961, 865, 836, 808, 748, 703, 609.

In order to demonstrate the generality of the process, some examples illustrating the present method for the synthesis of 14-aryl 14*H*-dibenzo[*a,j*]xanthenes (**3**) were studied (Table 2). The reaction of β-naphthol (**2**) with various aromatic aldehydes (**1**) bearing electron withdrawing groups (such as nitro, halo) and electron releasing groups (such as methyl and methoxy) was carried out in the presence of perlite-SO_3H nanoparticles as a catalyst. In all cases, clean and complete conversion resulted in the formation of the corresponding 14-aryl 14*H*-dibenzo[*a,j*]xanthenes (**4a–4n**) in shorter reaction times (4–10 min).

EXPERIMENTAL

General

All reagents were obtained from Merck (Germany) and Fluka (Switzerland) and used without further purification. Infrared spectra were recorded on a Jasco 6300 FTIR spectrometer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The microwave-assisted procedures were carried out in a Milestone Microwave Oven operating at 1 600 W. ^{1}H- and ^{13}C-NMR spectra were measured ($CDCl_3$) with a BRUKER DRX-400 AVANCE spectrometer at 400.0 and 100.0 MHz, respectively. Scanning electron microscopy (Philips XL-30 SEM) with an acceleration voltage of 17 kV was used to investigate the size and morphology of the nanoparticles.

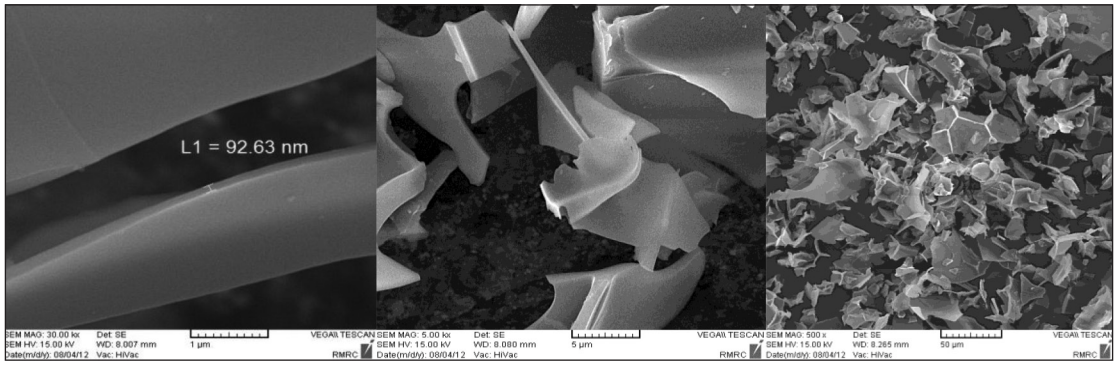
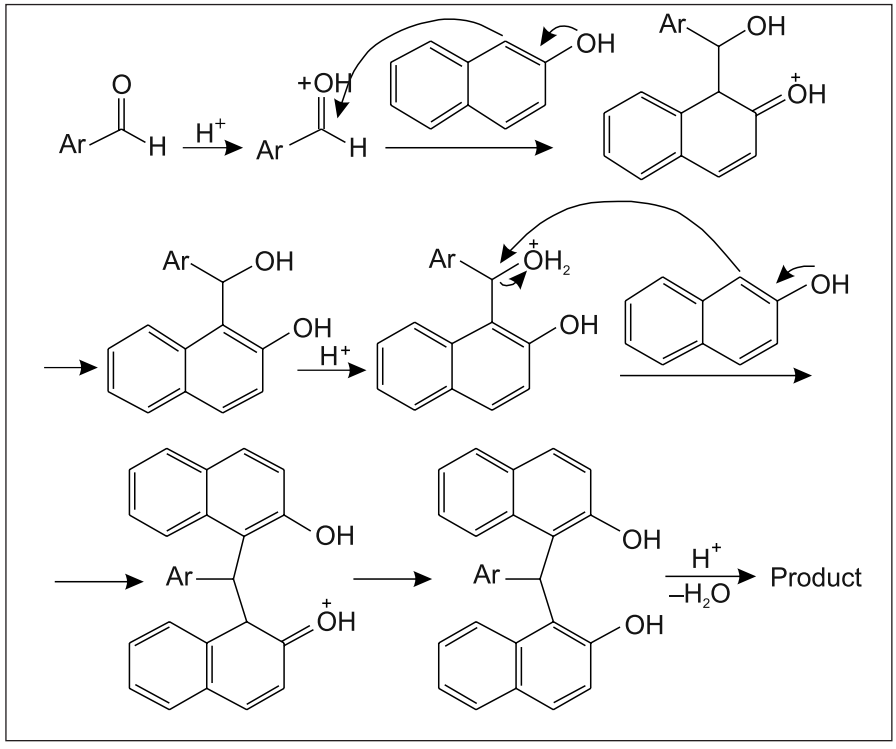


Figure. SEM of the synthesized perlite nanoparticles



Scheme 2. Proposed mechanism for the synthesis of 14-aryl 14*H*-dibenzo[*a,j*]xanthenes

Preparation of perlite nanoparticles

Perlite nanoparticles were prepared from perlite mineral powder according to the preparation of silica nanoparticles from organic laboratory waste of the silica gel HF_{254} method [44]. The morphology and grain size of the perlite nanoparticles were investigated by SEM (Figure).

Preparation of perlite-SO_3H nanoparticles

A 250 mL suction flask was equipped with a constant pressure dropping funnel containing chlorosulfonic acid (11.6 g, 0.1 mol) and a gas inlet tube for conducting HCl gas over an adsorbing solution, i. e. H_2O. Then 30.0 g of perlite nanoparticles were charged in to the flask. Chlorosulfonic acid was added dropwise over a period of 30 min at room temperature. After the addition was complete, the mixture was shaken for 30 min. Perlite-SO_3H nanoparticles were obtained as a white solid.

General procedure for the one-pot synthesis of 14-aryl 14*H*-dibenzo[*a,j*]xanthenes

The mixture of aromatic aldehyde (1 mmol), β-naphthol (2 mmol) and perlite-SO_3H nanoparticles (0.2 g) was taken in a 50 ml Borosil beaker. The reaction mixture was mixed properly with the help of a glass rod and then irradiated in a microwave oven operating power (700 W) for 4–10 min. The progress of reaction was monitored by TLC after completion of the reaction; the hot ethanol was added to the reaction mixture and the heterogeneous catalyst was isolated from the mixture of the reaction by simple filtration. In continuation of work up, the filtrate ethanol solution was concentrated. The aqueous ethanol 15% was added to the crude product, the precipitate was separated and then recrystallized using aqueous ethanol 15% for two times. The desired pure product(s) was characterized by comparison of the spectroscopic data (FT-IR) and physical data with those of known benzoxanthenes.

The possible mechanism for the formation of product (**3**) is shown in Scheme 2.

CONCLUSIONS

In conclusion, we have investigated the perlite-SO_3H nanoparticles as a mild and efficient catalyst for the synthesis of substituted 14-aryl-14*H*-dibenzo[*a,j*]xanthenes under solvent-free conditions using microwave irradiation. The remarkable advantages offered by this method are as follows: the catalyst is inexpensive, non-toxic, and easy handling; simple work-up procedure, short reaction time, high yields of the product with better purity and green aspect by avoiding a toxic catalyst and a hazardous solvent.

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PERLITO-SO_3H NANODALELĖS: NAUJAS IR EFEKTYVUS KATALIZATORIUS 14-ARIL 14*H*-DIBENZO[*A,J*]KSANTENŲ SINTEZEI MIKROBANGINIO ŠVITINIMO SĄLYGOMIS

S a n t r a u k a

Perlito-SO_3H nanodalelės efektyviai katalizuoja vienastadijinę dvikomponentę reakciją tarp arilaldehidų ir 2-naftolo. Reakcija vykdoma be tirpiklio švitinant mikrobangomis. Dėl sintezės gaunami atitinkami 14-aril 14*H*-dibenzo[*a,j*]ksantenų dariniai.