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ORIGINAL

$BiVO_4$-NPs as a new and efficient nano-catalyst for the synthesis of 1,8-dioxo-octahydro xanthenes

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Abstract $BiVO_4$-NPs can be used as a new and efficient nano-catalyst for the promotion of the synthesis of 1,8-dioxo-octahydro xanthenes derivatives. The structures of the products were characterized by their physical properties, comparison with authentic samples and IR, ^1H NMR and ^{13}C NMR spectroscopy. Easy preparation of the catalyst, mild reaction conditions, easy work-up procedure, excellent yields and short reaction times are some of the advantages of this work.

Keywords $BiVO_4$-NPs · Nano-particles · 1,8-dioxo-octahydro xanthenes · Aldehyde · Reusable catalyst

Background

Xanthenes and their derivatives have received special attention due to their diverse array of biological activities such as anti-inflammatory, antibacterial and antiviral activities [1–3]. Furthermore, these compounds can be used as leuco dyes [4], in laser technology [5] and pH-sensitive fluorescent materials for the visualization of biomolecular assemblies [6]. Because of their wide range of synthetic, industrial and pharmacological applications, there are several reports in the literature for the synthesis of xanthene derivatives.

1,8-Dioxo-octahydro xanthene derivatives are among the most important types of xanthenes and for this reason several methods are reported for the synthesis of 1,8-dioxo-octahydro xanthenes using a variety of catalysts and reagents [7–17].

However, these methods suffer from one or more disadvantages such as: long reaction times, low yields, the use of toxic solvents, requirement of excess of reagents/catalysts and harsh reaction conditions. Therefore, it is important to find more efficient catalysts and methods for the synthesis of these types of compounds.

In recent years and because of the unique properties of nano-particles, synthetic chemists focused on the synthesis and characterization of these types of catalysts with lower dimensions named as nano-catalysts [18].

Results and discussion

In recent years, a considerable amount of our research program is focused on the development of new methods and use of new reagents for the synthesis of xanthenes derivatives [19–25]. In continuation of these studies, we have found that $BiVO_4$-NPs as a newly reported reagent [26] is efficiently able to catalyze the synthesis of 1,8-dioxo-octahydro xanthenes. All reactions are performed under mild reaction conditions in good to high yields.

At the first step and to optimize the reaction conditions, the prepared catalyst was used for the promotion of the condensation of benzaldehyde with dimedone, as a model reaction, and compared the effect of different solvents and solvent-free conditions and also the effect of the catalyst load on the reaction yield and time at thermal conditions

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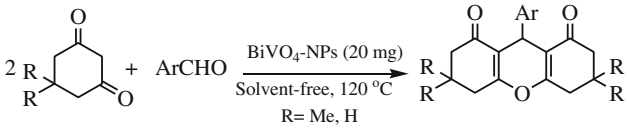
(Table 1). On the basis of these studies, we concluded that the best result can be obtained under the conditions showed in Scheme 1.

Table 1 The effect of different conditions on the model reaction

Entry	Conditions	$BiVO_4$-NPs (mg)	Time (min)	Conversion (%)[a]
1	EtOH (reflux)	20	60	100
2	H_2O (reflux)	20	60	0
3	Solvent-free (60 °C)	20	60	70
4	Solvent-free (100 °C)	20	45	90
5	Solvent-free (120 °C)	20	30 s	100
6	Solvent-free (120 °C)	10	15	80

Reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol)

[a] GC



Scheme 1 Synthesis of 1,8-dioxo-octahydro xanthenes

After optimization of the reaction conditions and to show the general applicability of the method, different types of aromatic aldehydes were subjected to the same reaction under the determined conditions. The obtained results showed that these conversions also were occurred with excellent yields during very short times (Table 2).

It seems that the electronic nature of the functional group on the ring of the aldehyde exerted a slight influence on the reaction time.

A plausible mechanism for the synthesis of 1,8-dioxo-octahydro xanthenes catalyzed by $BiVO_4$-NPs is shown in Scheme 2 [34, 35].

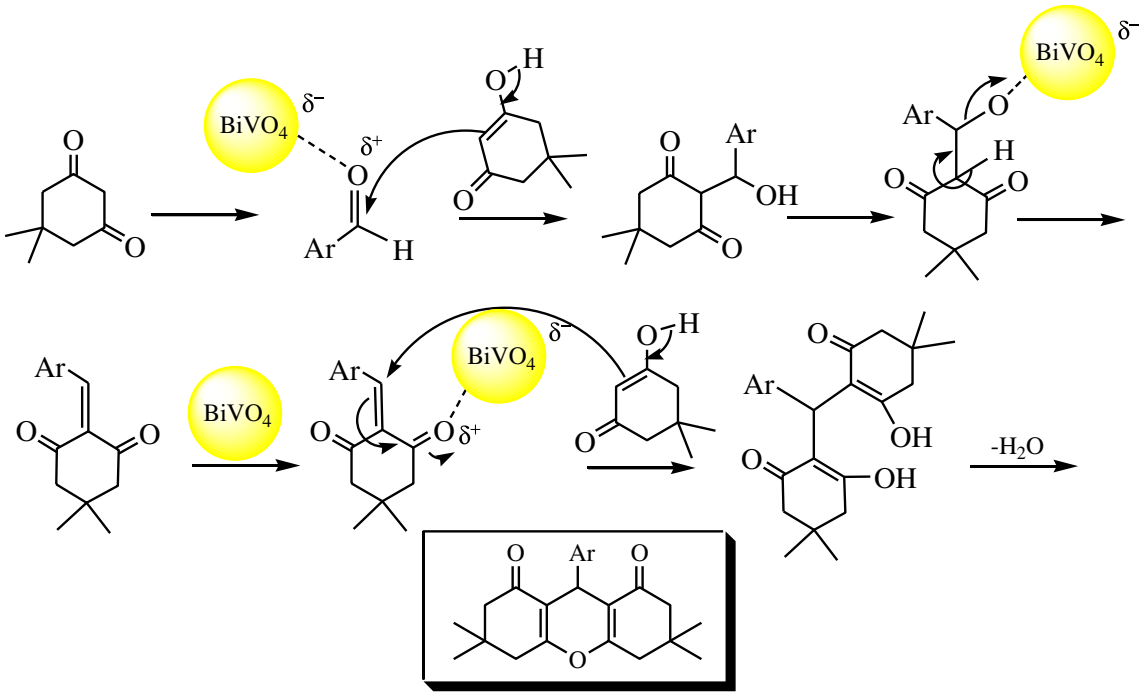
To illustrate the efficiency of the present method, Table 3 compares some of our results obtained from the synthesis of xanthene derivatives with the same results reported by the other groups. This Table clearly shows the applicability and efficiency of the present method. Table 3 also compares the TOF (turnover frequency) of these catalysts in this reaction. As it is clear $BiVO_4$-NPs is superior in terms of TOF to the compared catalysts.

In addition, we decided to study the catalytic activity of the recycled catalyst for the synthesis of xanthenes derivatives. After the separation of the product, the catalyst was

Table 2 Preparation of 1,8-dioxo-octahydro xanthenes in the presence of $BiVO_4$-NPs

Entry	Aldehydes	R	Time (min)	Yield (%)[a]	M.p. (°C)	
					Found	Reported
1	C_6H_5CHO	Me	30 s	99	197–198	199–201 [15]
2	4-ClC_6H_4CHO	Me	30 s	99	227–229	229–231 [15]
3	3-ClC_6H_4CHO	Me	30 s	98	186–187	186–187 [15]
4	2-ClC_6H_4CHO	Me	30 s	98	224–225	225–227 [27]
5	4-BrC_6H_4CHO	Me	30 s	97	239–240	240–242 [28]
6	3-BrC_6H_4CHO	Me	30 s	95	281–282	281–283 [21]
7	4-FC_6H_4CHO	Me	30 s	98	259–260	259–262 [21]
8	4-$NO_2C_6H_4CHO$	Me	4	94	223–224	224–226 [15]
9	3-$NO_2C_6H_4CHO$	Me	30 s	96	164–165	164–166 [15]
10	2-$NO_2C_6H_4CHO$	Me	4	93	251–252	251–252 [27]
11	3-$MeOC_6H_4CHO$	Me	4	95	190–191	192–194 [21]
12	3-MeC_6H_4CHO	Me	5	98	205–206	206–208 [9]
13	Cinnamaldehyde	Me	3	90	170–172	172–174 [15]
14	4-$Me_2NC_6H_4CHO$	Me	3	96	220–221	221–223 [29]
15	C_6H_5CHO	H	30 s	99	203–204	203–205 [27]
16	4-ClC_6H_4CHO	H	30 s	99	228–229	229–232 [27]
17	4-BrC_6H_4CHO	H	30 s	97	227–228	229–231 [27]
18	3-BrC_6H_4CHO	H	30 s	95	280–281	281–283 [21]
19	4-$NO_2C_6H_4CHO$	H	30 s	94	263–264	263–265 [23]
20	3-$NO_2C_6H_4CHO$	H	30 s	96	280–281	281–282 [19]
21	2-$NO_2C_6H_4CHO$	H	30 s	96	238–240	238–240 [19]
22	4-OHC_6H_4CHO	H	30 s	98	245–246	245–247 [30]
23	4-$MeOC_6H_4CHO$	H	6	95	200–201	200–201 [19]

[a] Isolated yields



Scheme 2 Proposed mechanism for the synthesis of 1,8-dioxo-octahydro xanthenes catalyzed by $BiVO_4$-NPs

Table 3 Comparison of the results of the reaction of dimedone with 4-ClC_6H_4CHO using $BiVO_4$-NPs with some of those reported in the literature

Entry	Catalyst (mol%)	Conditions	Time (h)	Yield (%)	TOF (h^{-1})	Refs.
1	$ZrOCl_2 \cdot 8H_2O$ (10)	Solvent-free, 120 °C	0.66	95	14.4	[9]
2	MCM-41-SO_3H (5)	H_2O, 60 °C	1	86	17.2	[12]
3	*N*-Sulfonic acid poly(4-vinyl pyridinium) chloride (4)	Solvent-free, 100 °C	0.05	98	490	[23]
4	1-Butyl-3-methylimidazolium hydrogen sulfate (72)	Solvent-free, 80 °C	3.5	95	0.38	[28]
5	Silica sulfuric acid (7.8)	Solvent-free, 80 °C	0.5	92	23.6	[31]
6	$ZrO(OTf)_2$ (1)	Solvent-free, 90 °C	0.066	94	1,424	[32]
7	Silicabonded *N*-propyl sulfamic acid (1.02)	EtOH, reflux	3	91	29.7	[33]
8	Fe_3O_4 NPs (10)	Solvent-free, 100 °C	0.33	88	26.7	[34]
9	ZnO NPs (10)	Solvent-free, 80 °C	0.25	96	38.4	[35]
10	$BiVO_4$-NPs (6.2)	Solvent-free, 120 °C	30 s	99	956	This work

washed with acetone and derived at 70 °C. As shown in Fig. 1, $BiVO_4$-NPs can be recycled at least six times without significant decrease in its catalytic activity (Table 2, entry 2).

Conclusion

In conclusion, we have introduced an efficient and convenient approach for the synthesis of 1,8-dioxo-octahydro xanthenes using $BiVO_4$-NPs as a novel nano-catalyst.

This method has several advantages such as: ease of preparation and handling of the catalyst, simplicity and easy work-up, high reaction rates, excellent yields and effective reusability of the catalyst for several times without considerable decrease in yields.

Methods

General

All chemicals were purchased from Merck or Fluka Chemical Companies. All yields refer to the isolated products. Products were characterized by their physical constants and comparison with authentic samples. The purity

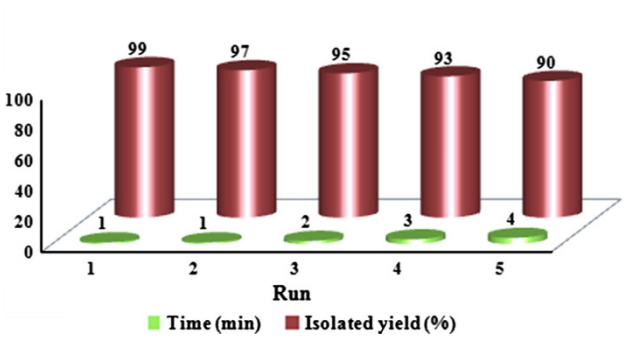


Fig. 1 Reusability of $BiVO_4$-NPs in the reaction of 4-chlorobenzaldehyde with dimedone

determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates. The FT-IR spectra were run on a VERTEX 70 Brucker company (Germany). The ^1H NMR (300, 400 and 500 MHz) and ^{13}C NMR (100 MHz) were run on a Bruker Avance DPX-400 FT-NMR spectrometer (δ in ppm).

General procedure

Synthesis of 1,8-dioxo-octahydro xanthene derivatives

A mixture of dimedone or cyclohexadione (2 mmol), aldehyde (1 mmol) and $BiVO_4$-NPs (20 mg) was stirred at 120 °C under solvent-free conditions for the appropriate time. After completion of the reaction [monitored by TLC: EtOAc: *n*-hexane (2:8)], the reaction was cooled to room temperature, ethanol (5 mL) was added and the mixture was filtered. Evaporation of the solvent, followed by recrystallization of the residue from EtOH:H_2O (95:5) afforded the pure products in good to high yields. The physical and spectral data of the known compounds were in agreement with those reported in the literature.

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