

One Pot Synthesis of Octahydroxanthene-1, 8-dione Derivatives using Magnesium Vanadium Oxide

Vijay V Dabholkar*, Sandip Gulve, Shrikant Anpat, Karthik Krishnan

Organic Research Laboratory, Department of Chemistry, Guru Nanak College, G.T.B Nagar, Mumbai, Maharashtra, India

ABSTRACT

A simple and efficient one pot synthesis of the 9-aryl substituted octahydroxanthene-1,8-diones. The reaction of aromatic aldehyde and Cyclic 1,3 diketone in ethanol using magnesium vanadium oxide nanocatalyst an efficient heterogeneous solid catalyst which can be easily synthesized and can be recovered from the reaction. This method has many advantages such as catalyst recoverable, recyclable, eco-friendly and simple work up procedure with high yield.

Keywords: Aromatic aldehydes, Cyclic 1,3 diketone, Catalyst.

I. INTRODUCTION

The substance that enhances the reaction rate is called a catalyst. The science and technology of catalysis is of great significance as it affects our daily life. Four major sectors of the world economy is petroleum-energy production, chemicals-polymer production, food industry and pollution control, involve catalytic processes. Now a day's surface active metal oxides are generally used to prepare heterogeneous catalysts material in the field of electronics and nanotechnology. Metal oxides have several applications because of its important and interesting properties such as large expansion coefficient, low magnetic transition temperature, high specific heating and low saturation magnetic moment. These properties are extensively used in catalysis, magnetic properties, sensor etc. [1-2].

In general catalytic property of metal nanoparticle are a function of their size, crystal lattice parameter. The development of new catalyst in nano-range has emerged as a fertile field for innovation and research. Owing to unique and novel properties like reusability, ability to generate clean product, high surface area and non-corrosiveness, recently $Mg_3V_2O_8$ heterogeneous solid nanocatalyst is applied as powerful catalyst for several organic transformation these facts encouraged us to use $Mg_3V_2O_8$ nanocatalyst for the efficient and green synthesis of octahydroxanthene-1,8-diones $Mg_3V_2O_8$ (orthovanadate) have been successfully prepared by the citrate method reported in earlier literature [3]. XRD

spectra of the Mg vanadate phases after calcination at $550^\circ C$ they are in agreement with the standard spectra [4,5,6]. In present work, we demonstrated nanoparticle of magnesium vanadium oxide, a heterogeneous mixed oxides have several applications. Xanthene are of importance as they have various industrial, pharmaceutical and biological applications. Xanthene derivative 1,8-dioxo-octahydroxanthens are of importance as they have various industrial, pharmaceutical and biological applications [7-12]. For example, these compounds have been applied as dyes in laser technology [7], and as pH sensitive fluorescent materials for visualization of biomolecules [8]. Moreover, xanthenes derivatives have been used as antibacterial [9], antiviral [10], antitumor [11] and anti-inflammatory agents [12]. Some solvents and catalysts have been applied silica supported SiO_2 (SPNP), 2,4,6-trichloro-1,3,5-triazine (TCT), p-dodecylbenzenesulfonic acid (DBSA), Tetrabutyl ammonium bromide (TBAB), $BiVO_4$, Tri methylsilyl chloride (TMSCl), Saccharin sulfonic acid (SaSA), $SiO_2-Cu(0)$ for the synthesis of 1,8-dioxo-octahydroxanthenes involves the one-pot multi-component reaction of dimedone (5,5-dimethyl-1,3-cyclohexanedione) (2 mole) with aldehydes (1 mole) [13-22]. But, many of the above methods suffer from limitations such as prolonged reaction time, high temperature and tedious work-up processes, low yield, hazardous reaction conditions are environmentally unacceptable from green chemistry view point

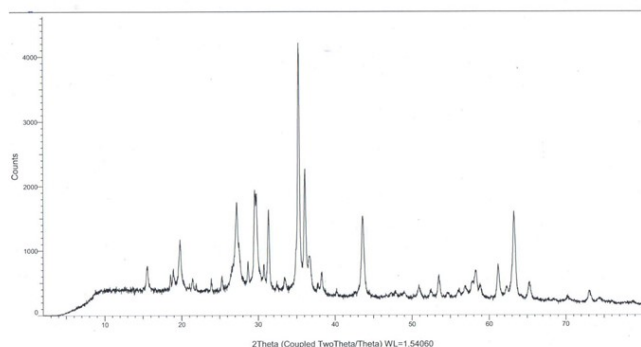
Having the above subjects in mind, we report here a new, highly efficient and simple method for the one-pot synthesis for the formation of 1,8-dioxo-octahydroanthene in low temperature, shortened reaction time, selectivity, recyclability and excellent yields by one-pot Knoevenagel condensation, Michael addition in the presence of magnesium vanadium oxide. The condensation of two equivalent of 1,3-diketones, such as dimedone(5,5-dimethyl-1,3-cyclohexanedione) with various aldehydes.

II. MATERIAL AND METHODS

Melting points of all synthesized compounds were determined in open capillary tubes on an electro thermal apparatus and are uncorrected. The purity of the compounds was monitored by thin layer chromatography on silica gel coated aluminium plates (Merck) as adsorbent and UV light as visualizing agent. ¹H NMR spectra were recorded on BRUKER 400 MHz NMR Spectrophotometer using CDCl₃ as solvent and TMS as an internal standard (chemical shifts in δ ppm).

III. RESULT & DISCUSSION

Mg₃V₂O₈ nanoparticles were synthesized by citrate method. The structural characterization of Mg₃V₂O₈ nanoparticles were done by X-ray Diffraction using CuKα radiation (λ = 1.54059 Å) at 40 kV and 15 mA shown in Figure.



XRD patterns for Mg₃V₂O₈ nanoparticles sintered at 550°C.

Table 1. Synthesis of 9-aryl substituted octahydroanthene-1,8-diones under different solvent systems at 35-40°C.

Entry	Solvent	Temperature°C	Yield of product (%)	Time (min)
1	H ₂ O	35-40	79	60
2	EtOH/H ₂ O	35-40	90	55
3	EtOH	35-40	94	40
4	DMF	35-40	85	55
5	DMSO	35-40	75	90
6	Without Solvent	35-40	35	120

Reaction conditions: Dimedone(1mmol), Benzaldehyde (0.5mmol), Mg₃V₂O₈(0.03g), at 35- 40°C.

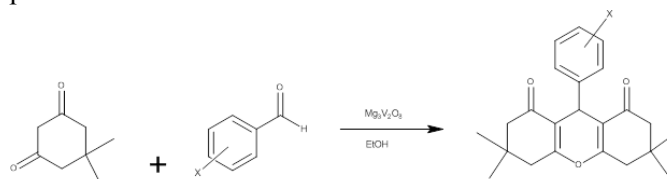
In addition to the above, the effect of catalyst concentration was also studied shown in (Table 2). Which indicated that 0.03g of the Mg₃V₂O₈ nanocatalyst was sufficient to catalyzed the reaction and increase the quantity of catalyst beyond this did not increase the yield.

Table 2. Effect of different quantity of catalyst on reaction.

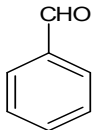
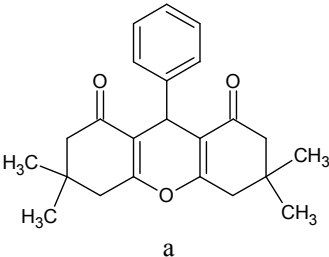
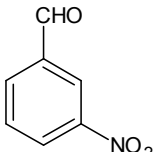
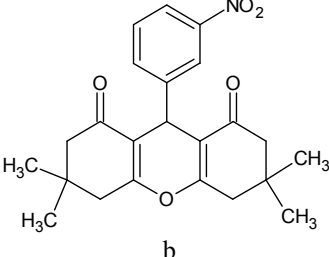
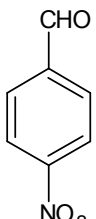
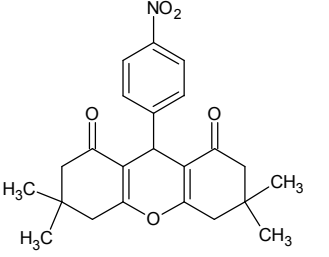
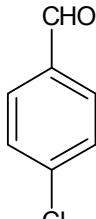
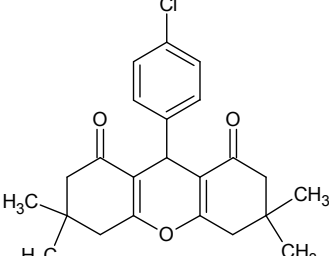
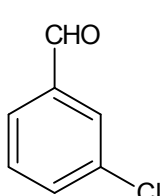
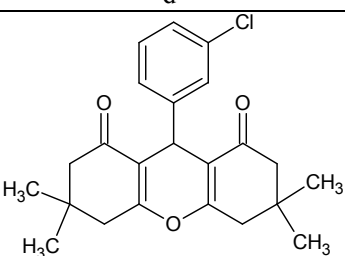
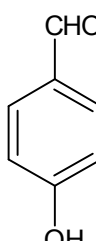
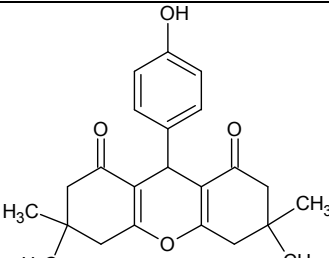
Entry	Catalyst quantity (g)	Yield of product (%)
1	0.01	60
2	0.02	80
3	0.03	94
4	0.04	94
5	0.05	91

Reaction conditions: Dimedone (1mmol), Benzaldehyde (0.5mmol), Ethanol (5ml) at 35- 40°C.

After optimizing the reaction conditions, we applied this catalyst for the synthesis of substituted octahydroanthene-1,8-diones by using substituted aromatic aldehyde. Almost, all the employed aldehyde resulted in good to excellent yield of the corresponding product.



Scheme 1. Synthesis of 9-aryl substituted octahydroanthene-1,8-diones.

Sr.No.	Aldehydes	Product 3	Time/min	%Yield	M.P/°C Found	M.P/°C Reported
1		 a	45	92	199-201	203-205
2		 b	25	94	166-167	165-166
3		 c	30	94	226-229	228-230
4		 d	40	93	230-231	231-233
5		 e	45	91	182-184	183-185
6			50	90	244-247	244-246

		f				
7			45	91	245-248	248-250
8			55	91	239-240	-
9			45	89	187-189	-

IV. EXPERIMENTAL

General procedure for the preparation of 1,8-dioxooctahydroanthene derivatives :

A mixture of 5,5-dimethyl-1,3-cyclohexanedione (0.14 g, 1 mmol), various aldehydes (0.5 mmol), ethanol (5 ml) followed by NPs (0.03 g, 0.1 mmol, 10 mol %) was stirred at 35-40°C for 30-40 min. reaction mixture was monitored by TLC. After completion of the reaction, EtOAc (10 mL) was added to the reaction mixture, stirred for 2 min and filtered. The catalyst was separated by filtration, dried and reused for subsequent reactions. filtrate was evaporated, obtained solid was recrystallized from EtOH to afford the pure product.

3,3,6,6-Tetramethyl-9-(3-chlorophenyl)-1,8-dioxooctahydroanthene.(4d)

IR (KBr, cm^{-1}) ν max 3015, 2960, 1662, 1464, 1375, 1204, 1165, 795; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 1.13 (6H, s, 2 \times CH₃), 1.25 (6H, s, 2 \times CH₃), 2.41 (4H, dd, ,

2 \times CH₂), 2.49 (4H, s, 2 \times CH₂), 5.56(1H, s, CH), 7.11-7.25 (4H, m, ArH).

3,3,6,6-Tetramethyl-9-(2-hydroxyphenyl)-1,8-dioxooctahydroanthene.(8h)

IR (KBr, cm^{-1}) ν max 3250, 2915, 1640, 1454, 1370, 1202, 1166, 799; $^1\text{H NMR}$ (400MHz, CDCl_3) δ 1.04 (6H, s, 2 \times CH₃), 1.16 (6H, s, 2 \times CH₃), 2.30 (4H, dd, , 2 \times CH₂), 2.58 (4H, s, 2 \times CH₂), 4.67(1H, s, CH), 4.80(1H, s, OH), (7.01-7.28 (4H, m, ArH).

V. CONCLUSION

Results revealed that the $\text{Mg}_3\text{V}_2\text{O}_8$ catalyst exhibited excellent catalytic performance in the one-pot condensation of dimedone and aromatic aldehyde, at low temperature. Because of its small particle size and high specific surface area, the catalyst provides a favorable surface for the reactants and the reaction completes successfully in terms of excellent yield with short span

of time, this means that catalyst plays crucial role in this transformation. Finally we concluded that in comparison to existing methods, this method is the best alternative for the synthesis of 9-aryl substituted octahydroxanthene-1,8-diones biologically important compound in presence of $Mg_3V_2O_8$ as a solid base heterogeneous catalyst. Catalyst relatively non-toxic, environmentally safe, easy to recover and reuse.

VI. ACKNOWLEDGEMENT

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VII. REFERENCES

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