



Application of SiO₂ nanoparticles as an efficient catalyst to develop syntheses of perimidines and tetraketones

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Abstract. In this paper, we explore the catalytic activity of SiO₂ nanoparticles (NPs) as an eco-friendly, efficient and reusable catalyst in the synthesis of 2,3-dihydro-1*H*-perimidines as well as tetraketones. For tetraketones syntheses, a simple tandem Knoevenagel condensation following Michael addition procedure is performed by the reaction between benzaldehydes and 5,5-dimethyl-1,3-cyclohexanediones under solvent-free condition using SiO₂ NPs as an efficient solid catalyst. In addition, for 2,3-dihydro-1*H*-perimidines syntheses, cyclocondensation of various aldehydes with 1,8-diaminonaphthalene is achieved under solvent-free condition using SiO₂ NPs as a catalyst at room temperature. The results showed catalytic enhancement in both synthetic procedures. In this work, 4-(2,3-dihydro-1*H*-perimidin-2-yl)benzotrile and 2-(pyridin-4-yl)-2,3-dihydro-1*H*-perimidine are synthesized as new compounds. Also, reusability study of SiO₂ NPs was done to ensure its applicability as a recycled catalyst in this work.

Keywords. 2,3-Dihydro-1*H*-perimidines; green synthesis; nano-SiO₂; solid catalyst; solvent-free; tetraketone derivatives.

1. Introduction

Nanoparticles are particles that exist on a nanometre range (i.e., below 100 nm in at least one dimension). They can possess physical properties such as uniformity, conductance or special optical properties that make them desirable in materials science and biology. Inorganic nanoparticles such as SiO₂ nanoparticles (NPs) have attracted considerable attention because of their potential importance in technological applications (e.g., catalysts, filler for polymers, pigments, pharmacy, electronics and thin film substrates, electronic and thermal insulators, and humidity sensors and so on).¹⁻³ Moreover, homogeneous catalysts have many deficiencies in industrial and laboratory processes such as handling, corrosiveness, difficult separation and toxicity of waste. Indeed, most novel solid catalysts are based on silica due to their excellent stability (chemical and thermal), high surface area, and good accessibility of reactive centers.⁴⁻⁹

Perimidine derivatives are attractive either for their biological activities such as antifungal, antimicrobial, antiulcer and antitumor agents¹⁰ or for their application as intermediates in organic synthesis.^{11,12} In addition, tetraketones are also extensively used as important precursors for the synthesis of various acridinediones as laser dyes,^{13,14} DNA intercalator,¹⁵ electron donors and acceptors¹⁶⁻¹⁸ of the photoinitiated polymerization of acrylates and methacrylates,¹⁹ and synthesis of some heterocyclic compounds.²⁰⁻²³

Due to our interest in developing a new synthesis in the field of catalyst applications,²⁴⁻²⁷ herein, we explore the catalytic activity of SiO₂ NPs as an eco-friendly, efficient and reusable catalyst in the synthesis of 2,3-dihydro-1*H*-perimidines as well as tetraketones. In this work 4-(2,3-dihydro-1*H*-perimidin-2-yl)benzotrile and 2-(pyridin-4-yl)-2,3-dihydro-1*H*-perimidine are synthesized as new compounds. Although several approaches for the synthesis of both skeletons have been reported,²⁸⁻³⁵ development of simple and convenient synthetic procedures is attractive for research in synthetic organic chemistry.

*For correspondence

2. Experimental

2.1 General information

All chemicals were used without further purification and purchased from commercial sources as follows: 1,8-diaminonaphthalene (Sigma-Aldrich-99%), dimedone (Sigma-Aldrich-97%), benzaldehyde (Sigma-Aldrich->99%), Tetraethoxysilane (Sigma-Aldrich-98%). Other chemicals and solvents were prepared commercially without further purification. IR spectra were recorded from KBr disk using an FT-IR Bruker Tensor 27 instrument. Melting points were measured by using the capillary tube method with a thermal scientific 1900 apparatus. The progress of reactions was monitored by thin-layer chromatography (TLC) on 0.2 mm silica gel F-252 (Merck) plates using *n*-hexane/ethyl acetate as eluent. The ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) was run on a Bruker DPX using TMS as an internal standard. Scanning Electron Microscopy (SEM) analysis was recorded on an electron microscope model Tescan Vega MV 2300T/40.

2.2 Preparation of silica nanoparticles

Tetraethoxysilane (TEOS) and aqueous ammonia 25% were separately dissolved in ethanol. Then, these two solutions were mixed and stirred for 24 h to obtain white suspension. The particles in the suspension were collected by centrifugation and dried in vacuum for 12 h to produce silica nanoparticles as the literature reported.³⁸

2.3 General procedure for the preparation of 2,3-dihydro-1H-perimidine derivatives (3a–3p)

The mixture of 1,8-diaminonaphthalene (1.0 mmol), carbonyl compound (1.0 mmol) and SiO₂ NPs (0.001 g, 2 mol%) was ground by mortar and pestle at room temperature for an appropriate time. After completion of the reaction as monitored by TLC, the mixture was dissolved in ethyl acetate; then the catalyst was isolated by centrifuging and the solvent was evaporated to yield the crude product (3a–3p).

2.3a 4-(2,3-Dihydro-1H-perimidin-2-yl)benzotrile (3j): Brown powder. M.p.: 177–179 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 5.48 (s, 1H, N-CH-N), 6.49 (s, 2H, NH), 6.94–7.00 (m, 4H, ArH), 7.14 (t, 2H, ArH), 7.75 (d, *J* = 8.0 Hz, 2H, ArH), 7.87 (d, *J* = 8.4 Hz, 2H, ArH). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 60.22, 104.96, 111.40, 112.82, 115.96, 119.23, 127.39, 129.19, 132.70, 134.74, 142.64, 148.27.

2.3b 2-(Thiophen-2-yl)-2,3-dihydro-1H-perimidine (3n): Light yellow powder. M.p.: 115–117 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 5.49 (s, 1H, N-CH-N), 6.48 (s, 2H, NH), 6.78 (m, 2H, ArH), 6.95 (d, *J* = 7.6 Hz, 2H, ArH), 7.12 (m, 2H, ArH), 7.28 (m, 1H, ArH), 7.52 (m, 1H, ArH), 7.54 (m, 1H, ArH). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 62.46, 104.85, 113.04, 115.70, 124.05, 126.68, 127.32, 127.50, 134.82, 143.17, 144.44.

2.3c 2-(Pyridin-4-yl)-2,3-dihydro-1H-perimidine (3o): Light yellow powder. M.p.: 162–163 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 5.42 (s, 1H, N-CH-N), 6.50 (s, 2H, NH), 6.98 (m, 2H, ArH), 7.14 (m, 2H, ArH), 7.54 (m, 2H, ArH), 8.57 (m, 2H, ArH). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 64.84, 105.01, 112.90, 115.96, 123.06, 127.40, 130.08, 134.74, 142.46, 150.10, 151.43.

2.4 General procedure for the preparation of tetraketone derivatives (9a–9p)

A mixture of dimedones (2 mmol), benzaldehydes (1 mmol) and SiO₂ NPs (2 mol%, 0.001 g) was heated at 110 °C under solvent-free condition. After completion of the reaction monitored by TLC, 5 mL THF was added to the reaction mixture. Then after isolating the catalyst by centrifuging, the solvent was evaporated to yield the crude products 2,2'-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1,3-dione) (9a–9p).

2.4a 2,2'-(Phenylmethylene)bis(5,5-dimethylcyclohexane-1,3-dione) (9a): M.p.: 194–195 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.12 (s, 6H, Me), 1.26 (s, 6H, Me), 2.30–2.50 (m, 8H, CH₂), 5.56 (s, 1H, CH), 7.11 (m, 2H, ArH), 7.19 (m, 1H, ArH), 7.21 (m, 1H, ArH), 7.29 (m, 1H, ArH), 11.93 (s, 1H, OH). ¹³C NMR (100 MHz, CDCl₃): δ 27.40, 29.60, 31.42, 32.73, 46.45, 47.06, 115.59, 125.85, 126.77, 128.22, 138.06, 189.41, 190.49.

2.4b 2,2'-((4-Chlorophenyl)methylene)bis(5,5-dimethylcyclohexane-1,3-dione) (9c): M.p.: 136–138 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.12 (s, 6H, Me), 1.23 (s, 6H, Me), 2.19 (m, 4H, CH₂), 2.35 (m, 4H, CH₂), 5.49 (s, 1H, CH), 7.02 (d, *J* = 7.6 Hz, 2H, ArH), 7.23 (m, 2H, ArH), 11.89 (s, 1H, OH). ¹³C NMR (100 MHz, CDCl₃): δ 27.41, 29.68, 31.42, 32.40, 46.42, 47.04, 115.33, 128.19, 128.34, 129.77, 130.01, 131.58, 136.70, 189.43, 190.63.

2.4c 2,2'-((2-Nitrophenyl)methylene)bis(5,5-dimethylcyclohexane-1,3-dione) (9o): M.p.: 204–206 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.02 (s, 6H, Me), 1.12 (s, 6H, Me), 2.26–2.35 (m, 4H, CH₂), 2.43–2.54 (m, 4H, CH₂), 6.05 (s, 1H, CH), 7.26 (s, 1H, ArH), 7.32 (m, 1H, ArH), 7.48 (d, *J* = 7.6 Hz, 1H, ArH), 7.51 (d, *J* = 7.8 Hz, 1H, ArH), 11.60 (s, 1H, OH). ¹³C NMR (100 MHz, CDCl₃): δ 28.14, 28.63, 30.06, 31.90, 46.31, 46.84, 114.64, 124.33, 127.17, 129.57, 131.36, 132.10, 149.73, 189.41, 191.20.

3. Results and Discussion

3.1 SiO₂NPs as an efficient catalyst to improve the synthetic procedure of 2,3-dihydro-1H-perimidines

We wish to report our results in the synthesis of 2,3-dihydro-1H-perimidines (3a–3p) by the reaction

Table 1. Syntheses of 2,3-dihydro-1*H*-perimidine derivatives catalyzed by SiO₂ NPs.

1 + 2 $\xrightarrow[\text{Grinding, 25 } ^\circ\text{C}]{\text{SiO}_2 \text{ NPs (2mol\%)}}$ 3a-3p

R=Ar, Thiophene, Pyridine, Naphthalene

Entry	Reagent 5	Product	Time (min)	Yield (%)	M.p. (°C)
1			30	95	103-104 ²⁸
2			45	90	117-118 ²⁸
3			35	91	144-146 ²⁸
4			60	97	158-160 ³⁶
5			15	95	191-193 ²⁸
6			20	97	200-201 ²⁸
7			20	88	131-133 ²⁸

Table 1. (contd.)


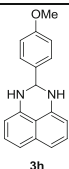
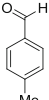
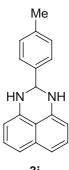
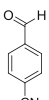
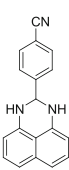
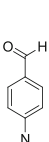
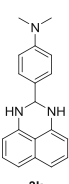
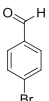
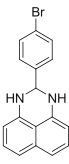
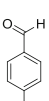
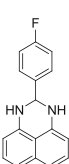
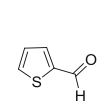
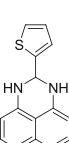

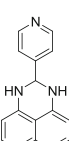

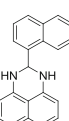
Entry	Reagent 5	Product	Time (min)	Yield (%)	M.p. (°C)
8		 3h	30	92	160-162 ²⁸
9		 3i	20	90	166-167 ²⁸
10		 3j	35	92	new
11		 3k	35	85	49-52 ³⁶
12		 3l	27	90	138-140 ²⁹
13		 3m	10	96	182-183 ²⁸
14		 3n	15	90	115-117 ²³
15		 3o	10	95	new
16		 3p	15	90	165-167 ³⁶

Table 2. Optimization of the reaction condition in the synthesis of compound **3a**.

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	H ₂ O	25	30	trace
2	EtOH	25	30	50
3	CH ₃ CN	25	30	35
4	CH ₂ Cl ₂	25	30	32
5	THF	25	30	44
6	Neat	25	30	95^a
7	Neat	50	15	90
8	Neat	90	15	50

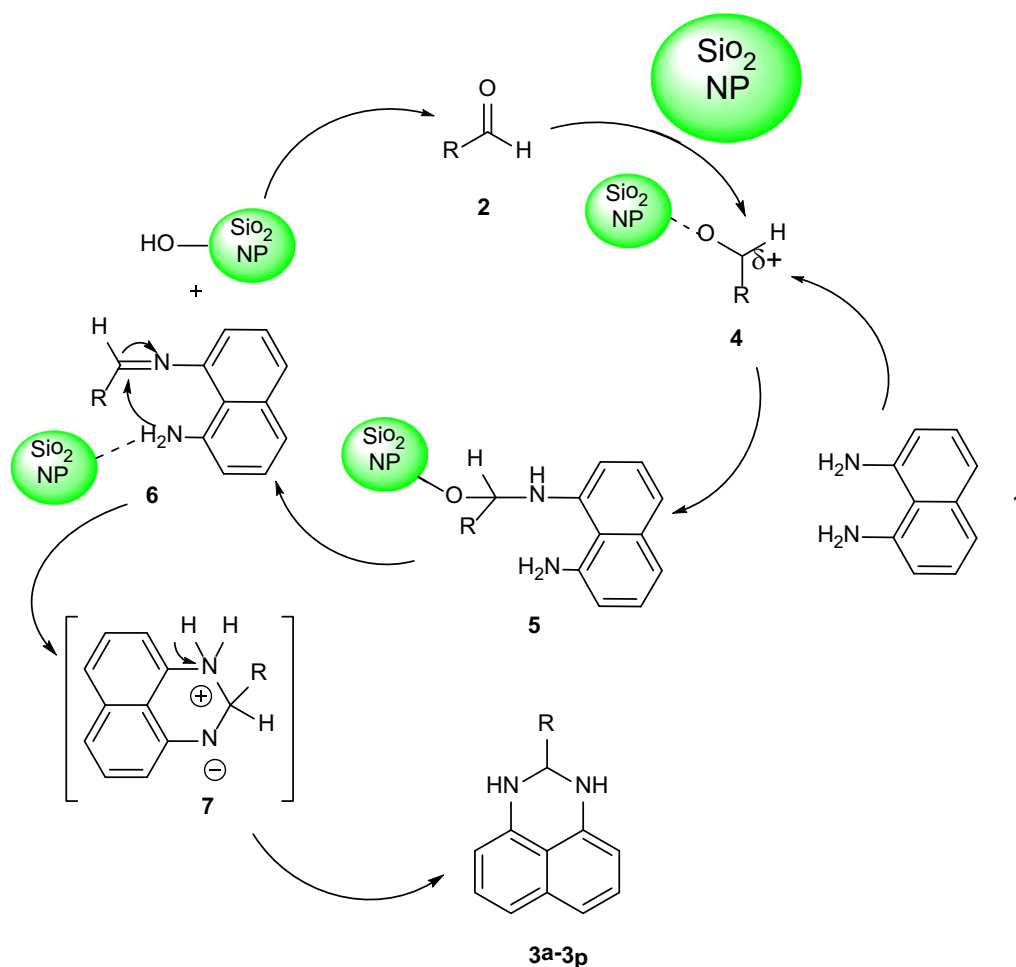
^a The best condition**Table 3.** Optimization of the amount of SiO₂ NPs as a catalyst in the synthesis of compound **3a**.

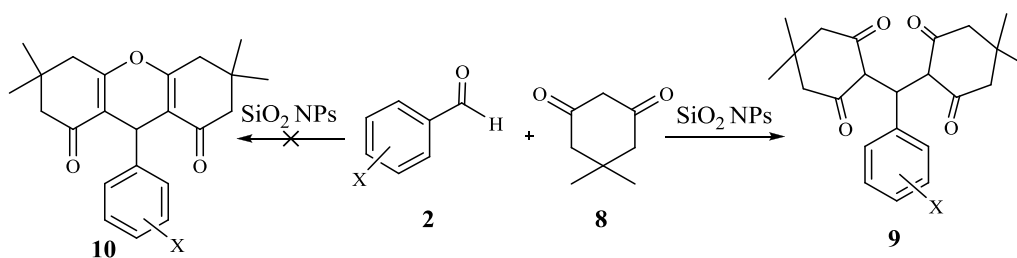
Entry	Catalyst (mol%)	Time (min)	Yield (%)
1	-	60	trace
2	1	60	75
3	2	30	95^a
4	5	25	95
5	10	20	95

^a The best condition

of 1,8-diaminonaphthalene **1** and various aldehydes **2** using SiO₂ as a nano heterogeneous catalyst (Table 1). To study the effect of solvent and temperature in the reaction of benzaldehyde and 1,8-diaminonaphthalene was chosen as a model reaction (Table 2). Among the examined conditions, grinding in a neat condition at 25 °C was found to be the most effective situation to produce excellent yields of products (entry 6). Also, in the optimization procedure, 2 mol% of catalyst was the appropriate amount of the reaction. Lesser amount gave a low yield and bigger amounts could not cause the obvious increase in the production of **3a** (Table 3). Finally, the recovered catalyst could be reused without any noticeable loss in its reactivity. The new structures of products were characterized by spectral data (¹H NMR and ¹³C NMR). Other structures were characterized in comparison to their authentic samples.

A plausible mechanism and the crucial role of SiO₂ NPs in activating the carbonyl group of the aldehyde is shown in Scheme 1. Aldehyde **2** and 1,8-diaminonaphthalene **1** was condensed by releasing one water molecule to form imine intermediate **6**. After

**Scheme 1.** A plausible mechanism for the synthesis of 2,3-dihydro-1H-perimidine derivatives.



Scheme 2. The Crucial role of catalyst in limiting the reaction to yield products **9**.

imine formation **6**, it might be possible to interact with SiO₂ nanoparticle by hydrogen bonding which has an intramolecular react with a second amine group to form intermediate **7**. Finally, 1,3-proton transfer gives the corresponding 2,3-dihydro-1*H*-perimidines (**3a–3p**).

3.2 SiO₂NPs as an efficient catalyst to improve the synthetic procedure of tetraketone derivatives

In continuation of our work, we examined SiO₂ as a nano heterogeneous catalyst in the condensation of benzaldehydes **2** with 5,5-dimethyl-1,3-cyclohexanediones **8**. As illustrated in Scheme 2, the crucial role of catalyst in limiting the reaction to yield products **9** or **10** is evident.³⁷ Surprisingly, only intermediate 2,2'-phenylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1,3-dione) (**9a**) obtained in 92% yield and cyclized product **10** did not form.

Initially, the optimization of reaction condition was studied in a model reaction of benzaldehyde and dione in preparing compound **9a** (Table 4). It was found that solvent-free condition can afford the product in good yield even better than other organic solvents (Entries 1–5). In addition, it was found that increasing the temperature to 110 °C leads to the higher yields (Entries 6 and 7). Entry 7 was the most desired condition among the various reaction conditions used in Table 1. In addition, in the optimization procedure, 2 mol% of catalyst was the appropriate amount for the reaction as shown in Table 5. The fewer amount gave a low yield and the more amounts could not cause the apparent increase in the production of 2,2'-phenylmethylenebis(5,5-dimethyl-2-cyclohexene-1,3-dione) (**9a**). Therefore, a mixture of diones, various benzaldehydes bearing electron-withdrawing and electron-donating substituents and SiO₂ NPs as a catalyst were heated at 110 °C under solvent-free condition to prepare crude products 2,2'-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1,3-diones) (**9a–9p**) in high to excellent yields (Table 6). The resulting solid products were dissolved in hot ethanol to crystallize; then were characterized by ¹H

Table 4. Optimization of the reaction condition in the synthesis of compound **9a**.

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)
1	H ₂ O	70	1	30
2	EtOH	70	1	35
3	Toluene	70	1	50
4	THF	70	1	47
5	Neat	70	1	62
6	Neat	90	30 min	80
7	Neat	110	15 min	92 ^a

^a The best condition

Table 5. Optimization of the amount of nano-SiO₂ as a catalyst in the synthesis of compound **9a**.

Entry	Catalyst (mol%)	Time (min)	Yield (%)
1	-	60	trace
2	1	30	76
3	2	15	92 ^a
4	5	8	95
5	7	5	95

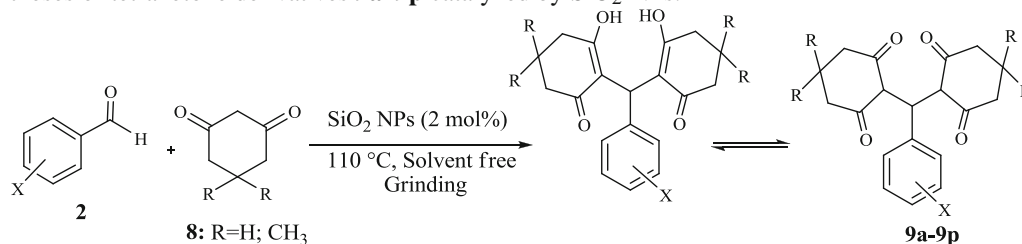
^a The best condition

NMR and ¹³C NMR analysis and by comparison with their authentic samples.

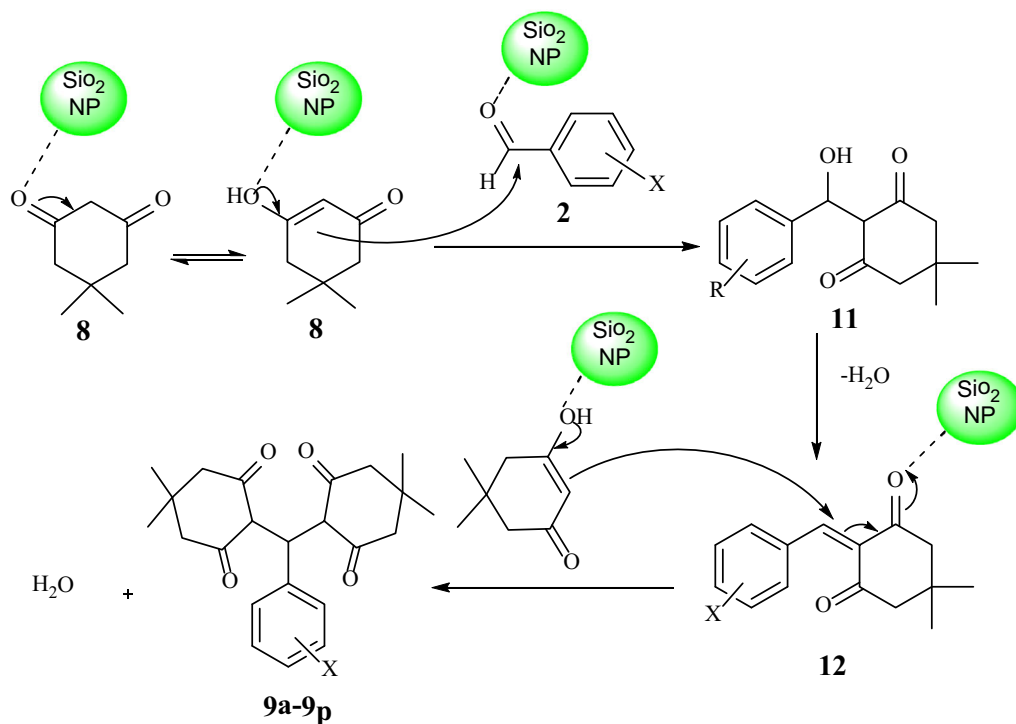
The mechanism seems to proceed *via* sequential Knoevenagel condensation-Michael addition reaction. The crucial role of SiO₂ NPs is shown in Scheme 3 by forming a complex and thus activating the carbonyl group of benzaldehydes for nucleophilic addition. In this protocol, intermediate alcohol **11** is formed by the attack of activated dione **8**. After the Knoevenagel condensation reaction, intermediate **12** which undergoes the nucleophilic attacking of another dione by Michael addition is transformed into the desired products (**9a–9p**).

3.3 Catalyst

Moreover, mesoscopic structure of silica with 50 nm particles is established in the SEM image (Figure 1) of

Table 6. Syntheses of tetraketone derivatives **9a–9p** catalyzed by SiO₂ NPs.

Entry	-X	R	Product	Time (min)	Yield (%)	M.p. (°C)
1	H	Me	9a	15	92	194-195 ³²
2	4-OH	Me	9b	30	74	187-189 ³²
3	4-Cl	Me	9c	15	95	136-138 ³¹
4	4-NO ₂	Me	9d	10	97	177-179 ³¹
5	4-OMe	Me	9e	15	90	136-139 ³¹
6	4-Me	Me	9f	20	92	123-126 ³¹
7	H	H	9g	10	95	208-210 ³¹
8	4-OH	H	9h	30	80	197-199 ³¹
9	4-Cl	H	9i	20	93	202-204 ³¹
10	2-NO ₂	H	9j	8	95	204-206 ³²
11	4-NO ₂	H	9k	5	96	210-212 ³²
12	4-OMe	H	9l	20	90	190-191 ³²
13	3-Br	H	9m	10	96	206-208 ³²
14	4-Me	H	9n	15	92	190-191 ³¹
15	2-NO ₂	Me	9o	10	93	204-206 ³²
16	3-Br	H	9p	7	92	206-208 ³¹

**Scheme 3.** Proposed mechanism for syntheses of tetraketone derivatives.

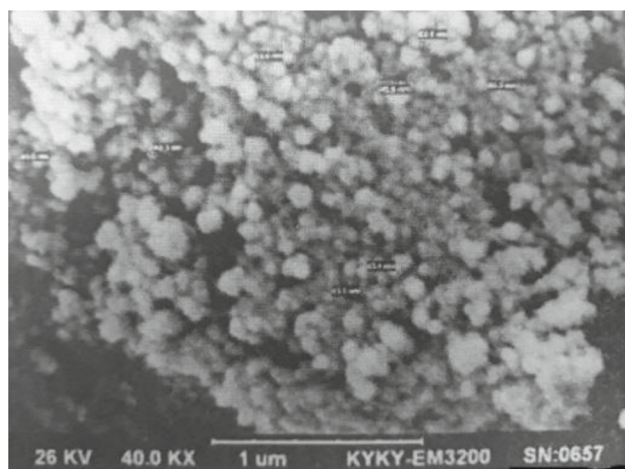


Figure 1. SEM image of SiO₂ NPs.

Table 7. Reusability of SiO₂ NPs as catalyst.

	Run			
	1	2	3	4
Yield of compound 3a	95%	93%	90%	88%
Yield of compound 9a	92%	91%	89%	86%

these nanoparticles which were prepared according to the literature.³⁸

To check the reusability, the recovered catalyst could be washed with diluted aqueous Et₃N solution, water and acetone sequentially. After a period of drying, the catalyst could be reused in the synthesis of compound **9a** and **3a** as a model reaction. The process of recycling

was completed four times without any noticeable loss of reactivity (Table 7).

We have compared the efficiency of SiO₂ NPs with various conditions in the synthesis of 2,3-dihydro-1*H*-perimidines as shown in Table 8. In addition, we have also compared the efficiency of various catalysts in the synthesis of tetraketones (Table 9). The high yield of products and short reaction times demonstrated that SiO₂ NPs acts as an efficient catalyst in these reactions.

4. Conclusions

In conclusion, we have developed a simple strategy for the synthesis of a series of organic compounds using the catalytic amount of SiO₂ nanoparticles under mild condition. The advantages of this method are solvent-free conditions, broad scope, easy handling, and high to excellent yields. Further, some different selectivities of SiO₂ NPs catalytic system is observed which is the formation of 2,2'-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) and not its corresponding cyclized compound.

Supplementary Information (SI)

¹H NMR and ¹³C NMR of some compounds (Figure S2–S21), list of 2,3-dihydro-1*H*-perimidine derivatives, list of 2,3-dihydro-1*H*-perimidine derivatives, some data about catalyst (Tables S1–S9, Scheme S1–S3 and Figures S1) are available at www.ias.ac.in/chemsci.

Table 8. Comparison of various catalysts in the synthesis of 2,3-dihydro-1*H*-perimidines in recent years.

Entry	Catalyst	Solvent	Condition	Time	Yield (%)	Year
1	NaY zeolite	Ethanol	Stir. at rt.	45–50 h	70	2009 ³⁶
2	NSSA	Ethanol	Stir. at rt.	50 min	84	2010 ²⁸
3	CMK-5-SO ₃ H	Ethanol	Stir. at rt.	5 min	91	2013 ³⁹
4	I ₂	Ethanol	Stir. at rt.	40 min	84	2013 ²⁹
5	Comparing the current work with previous works SiO ₂ NPs	Neat	Grinding	10-60 min	85–97	This work

Table 9. Comparison of various conditions in the synthesis of tetraketones in recent years.

Entry	Catalyst	Solvent	Condition	Time	Yield (%)	Ref.
1	-	DMF	Stir. at 80 °C	1 h	65–86	2000 ³⁰
2	Yb(OTf) ₃ -SiO ₂	Neat	Grinding	2–5 min	73–88	2011 ³¹
3	-	H ₂ O	Stir. at rt.	1–4 h	64–99	2010 ³²
4	Comparing the current work with previous works SiO ₂ NPs	Neat	Heating at 110 °C	5–30 min	74–97	This work

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