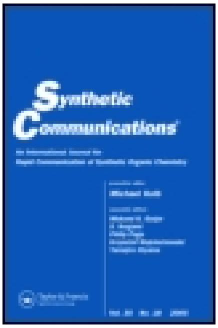

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P_2O_5/SiO_2 as a New, Efficient, and Reusable Catalyst for Preparation of β-Enaminones Under Solvent-Free Conditions

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P_2O_5/SiO_2 as a New, Efficient, and Reusable Catalyst for Preparation of β-Enaminones Under Solvent-Free Conditions

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Abstract: P_2O_5/SiO_2 (30% w/w) was applied as an efficient, heterogeneous, and reusable catalyst for the synthesis of β-enaminones. The reactions were rapidly completed at 80 °C under solvent-free conditions and products were obtained in good to excellent yields.

Keywords: Amines, β-dicarbonyl compounds, β-enaminone, P_2O_5/SiO_2, solvent-free

INTRODUCTION

Enaminones are enamines of β-dicarbonyl compounds, and their chemistry has been widely reviewed.[1,2] They are valuable precursors in organic synthesis,[1–7] in pharmaceutical development,[2–7] and for synthesis of heterocyclic compounds.[4,5] Because of their wide range of activity and importance, a variety of methods for the synthesis of β-enaminones have been developed.[2–7] The most well-known and standard route for synthesis of β-enaminones involves the direct condensation of β-dicarbonyl compounds with amines in refluxing aromatic hydrocarbons with azeotropic removal of water.[8] Several other improved methods for the synthesis of

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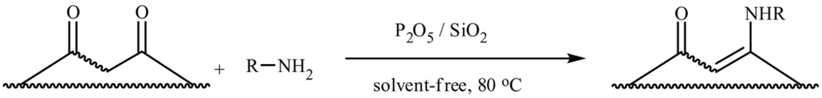


1 2 3

Scheme 1.

β-enaminones have been reported: silica gel under microwave–assisted solvent-free conditions,[9] montmorilonite K–10,[10] $Bi(OTf)_3$,[11] $NaAuCl_4$,[12] $Zn(ClO_4)_2 \cdot 6H_2O$,[13] $Zn(OAc)_2 \cdot 2H_2O$,[14] $InBr_3$,[15] $CoCl_2$,[16] $CeCl_3 \cdot 7H_2O$,[17] I_2,[18] $HClO_4 \cdot SiO_2$,[19] $ZrOCl_2 \cdot 8H_2O$,[20] $Yb(OTF)_3$,[21] $Sc(OTf)_3$,[22] and ionic liquids.[23]

A detailed survey on the methods for the synthesis as well as the chemistry of title compounds has been recently reported.[23,24] Many of these methods suffer from drawbacks such as long reaction times, unsatisfactory yields, low selectivity, use of hazardous solvents, lack of general applicability, higher temperatures, applications of nonavailable and costly reagents, and tedious experimental procedures. So, although different methods are available for the synthesis of β-enaminones, development of other facile, high-yielding, nonpolluting procedures is still of great importance.

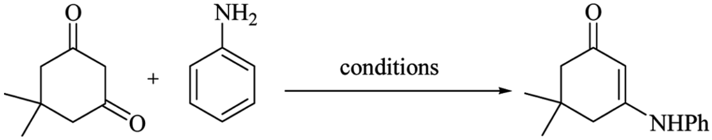
Heterogeneous organic reactions have been recently performed with immobilized reagents on solid supports. These procedures have advantages such as cleaner reactions, easier workup, reduced reaction times, and ecofriendliness.[25] P_2O_5/SiO_2 is an inexpensive, heterogeneous, stable, and commercially available catalytic system with sometimes much more reactivity than unsupported P_2O_5. This catalyst has been used for the Ritter reaction,[26] sulfonylation and nitration of aromatic compounds,[27,28] protection and deprotection of aldehydes[29] or alcohols,[30] Beckmann or Schmidt rearrangements,[31] preparation of bisindolylmethanes,[32] and solvent-free synthesis of N–sulfonyl imines.[33]

In continuation of our previous studies[34] on the synthetic applications of heterogeneous catalysts, we have recently observed that silica-supported phosphorous pentoxide (P_2O_5/SiO_2) is a highly efficient catalyst for the preparation of β-enaminones and β-enamino esters from β-dicarbonyl compounds by treatment with amines (Scheme 1).

RESULTS AND DISCUSSION

To achieve the best results, we examined the efficiency of different reaction media and catalyst amounts for the condensation reactions of dimedone and aniline as a model reaction (Table 1). For each reaction

Table 1. Comparison of the reaction of dimedone with aniline under various conditions



Entry	Solvent[a]	Catalyst amount (g)	Temperature (°C)	Time	Yield (%)[b]
1	Toluene	0.7	80	5 h	20
2	$CHCl_3$	0.7	80	5 h	10
3	THF	0.7	Reflux	5 h	10
4	EtOH	0.7	80	10 h	25
5	CH_3CN	0.7	Reflux	10 h	20
6	EtOAc	0.7	Reflux	10 h	30
7	Solvent-free	0.7	Rt	2.5 h	45
8	Solvent-free	0.7	50	1.5 h	68
9	Solvent-free	0.7	80	3 min	96
10	Solvent-free	0.5	80	4 min	98
11	Solvent-free	0.3	80	11 min	96
12	Solvent-free	0.0	80	5 h	10
13	Solvent-free	SiO_2 (0.5)	80	2 h	28
14	Solvent-free	P_2O_5 (0.3)	80	4 min	75

[a] All reactions were run using dimedone (1 mmol) and aniline (1.1 mmol) in 4 mL solvent.

[b] Yields referred to GC yields.

condition, conversion of dimedone (1 mmol) and aniline (1 mmol) to 5, 5-dimethyl-3-(phenylamino)-2-cyclohexenone was measured by gas–liquid chromatography using a 0.01 M solution of product in toluene as standard. As can be see from Table 1, significant rate enhancement and improved yields were observed using about 0.5 g of P_2O_5/SiO_2 under solvent-free conditions. It is noticeable that P_2O_5 has good efficiency: however, it is not reusable, and its applications suffer from difficulties because of its troublesome handling. SiO_2 has not shown valuable efficiency for this reaction under same conditions.

The experimental procedure for this reaction is remarkably simple and does not require the use of organic solvents or inert atmospheres. About 0.5 g of P_2O_5/SiO_2 and the required amine were added to 1 mmol of the 1,3-dicarbonyl compound, and the mixture was stirred at 80 °C. The reactions took place within only a few minutes to afford the product in excellent yields.

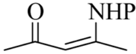
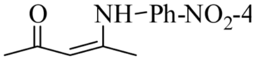
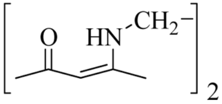
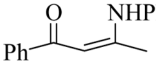
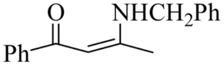
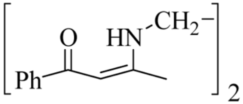
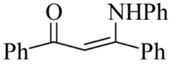
The generality of the method has been shown by the preparation of a series of β-enaminones and β-enamino esters using various β-dicarbonyls and amines (Table 2). The β-dicarbonyl compounds included here are both β-diketones (linear and cyclic) and β-ketoesters. They reacted equally with aromatic as well as aliphatic amines. In the case of 1,2-diaminoethane, 2 equiv of β-dicarbonyl compounds were used giving products with two enaminone groups (entries c and f). In all these cases, the chemoselectivity was very good; that is, only Z-β-enaminones and β-enamino esters were formed predominantly as confirmed by ^{1}H NMR spectra of the crude products. The (Z)-selectivity in the products derived from acyclic diketones and β-ketoesters was secured by intramolecular hydrogen bonding. In the ^{1}H NMR spectra the proton of the –NH– group appeared in the region of δ 8.1–12.5. However, the β-enaminones derived from cyclic diketone, 5,5-dimethyl-1,3-cyclohexadione, displayed the ^{1}H NMR spectra, having the signals for the nonhydrogen bonded proton of the –NH– group in the region of δ 4.5–6.5 and thus indicating the (E)-configuration.

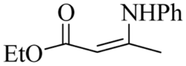
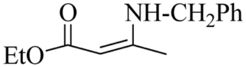
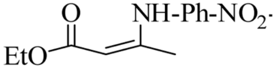
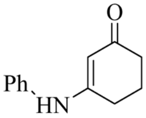
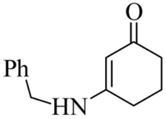
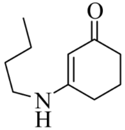
In addition to aniline and weakly activated anilines, this method was successfully applied to aniline with strongly electron-withdrawing groups. For example, 4-nitroaniline reacted with acetylacetone in the presence of P_2O_5/SiO_2 to form the corresponding β-enaminone in 80% yields (entry b). Previously, a similar reaction carried out using other catalytic systems yielded at best less than 30% of product.[17,19] In the cases of β-diketones with two different substituents, such as the commercially available benzoylacetone, we obtained selectively the adduct deriving from a nucleophilic attack of the amine to the carbonyl bearing a methyl group (entries d, e, and f).

The use of P_2O_5/SiO_2 as a heterogeneous catalyst showed rate enhancements, high yields, and short reaction times. However, one of the important points regarding the heterogeneous catalysts is their deactivation and reusability. From every reaction, the P_2O_5/SiO_2 catalytic system has been recovered by filtration of the reaction mixture and washing of the filtrate with acetone. Table 3 shows the results of five consecutive runs of the reaction of dimedone with aniline and shows that the catalyst could be reused several times without noticeable loss of activity. This reusability demonstrates the high stability and turnover of the P_2O_5/SiO_2 catalytic system under operating conditions.

In conclusion, we have developed a simple, fast, and efficient procedure for synthesis of β-enaminones and β-enamino esters catalyzed by P_2O_5/SiO_2 under solvent-free conditions. The mild conditions, simple workup, high yields, and recyclability of the catalyst make our methodology a valid contribution to the existing processes in the field of β-enaminone synthesis. Furthermore, the method was successfully applied for anilines bearing powerful electron-withdrawing substituents, and their corresponding enaminones were obtained in good yields.

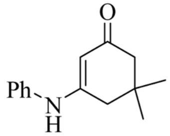
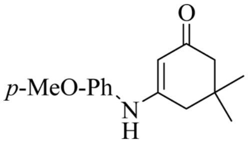
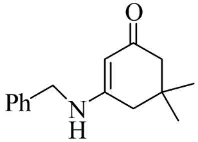
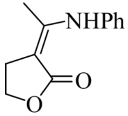
Table 2. Preparation of β-enaminones from β-dicarbonyl compounds and amines[a]

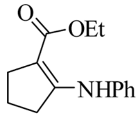
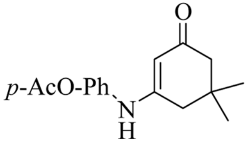
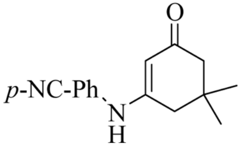
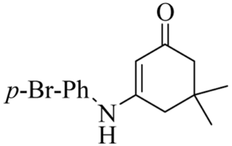
Entry	Substrate	Amine	Product	Time (min)	Isolated yield (%)	Mp (°C)[ref.]
a	Acetylacetone	Aniline		10	85	45–46[15]
b	Acetylacetone	4-Nitroaniline		10	80	144–146[15]
c	Acetylacetone	Ethylenediamine		10	83	109–110[11]
d	Benzoylacetone	Aniline		10	90	108–110[21]
e	Benzoylacetone	Benzylamine		10	91	59–60[35]
f	Benzoylacetone	Ethylenediamine		12	90	178–180[11]
g	Dibenzoylmethane	Aniline		12	86	99–101[15]

h	Ethyl acetoacetae	Aniline		5	90	Viscous oil[10]
i	Ethyl acetoacetae	Benzylamine		4	84	Viscous oil[10]
j	Ethyl acetoacetae	4-Nitroaniline		15	75	111–113[15]
k	1,3-Cyclohexadione	Aniline		4	96	179–180[21]
l	1,3-Cyclohexadione	Benzylamine		4	94	125–127[36]
m	1,3-Cyclohexadione	*n*-Butylamine		6	87	Viscous oil[21]

(*Continued*)

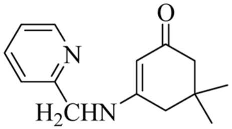
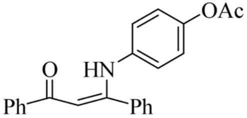
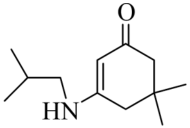
Table 2. Continued

Entry	Substrate	Amine	Product	Time (min)	Isolated yield (%)	Mp (°C)[ref.]
n	Dimedone	Aniline		5	86	184–185[36]
o	Dimedone	*p*-Methoxyaniline		3	97	193–195[36]
p	Dimedone	Benzylamine		5	91	125–126[36]
q	3-Acetyldihydrofuran-2-one	Aniline		5	80	91–93[11]

r	Ethyl 2-oxocyclopentanecarboxylate	Aniline		5	88	Viscous oil[13]
s	Dimedone	4-Aminophenyl acetate		4	95	—
t	Dimedone	*P*-Cyanoaniline		5	91	—
u	Dimedone	*p*-Bromoaniline		5	92	—
v	Dimedone	2-Pyridylmethylamine		8	92	—

(*Continued*)

Table 2. Continued

Entry	Substrate	Amine	Product	Time (min)	Isolated yield (%)	Mp (°C)[ref.]
						
w	Dibenzoylmethane	4-Aminophenyl acetate		15	85	—
x	Dimedone	*iso*-Butylamine		5	86	—

[a]The structures of known enaminones **3a–r** were determined by comparison of their physical properties with those of authentic samples. For new enaminones **3s–x**, the structures of the products were determined from their spectroscopic (^{1}H and ^{13}C NMR) data and CHN analysis.

Table 3. Reusability of the catalyst for a series of five consecutive runs of the reaction of dimedone with aniline

Entry	Time (min)	Conversion (%)	Yield (%)
1	4	100	96
2	4	100	95
3	4	100	96
4	4	100	94
5	4	100	95

EXPERIMENTAL

Preparation of P_2O_5/SiO_2 Catalyst

A mixture of SiO_2 (5 g) and P_2O_5 (1.5 g) at room temperature was ground vigorously for 30 min to give a P_2O_5/SiO_2 catalytic system as a white powder.

General Procedure

To a mixture of a dicarbonyl compound (1 mmol) and an amine (1.1 mmol), P_2O_5/SiO_2 (0.5 g) was added. The mixture was stirred at room temperature. The reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, mixture was diluted with EtOAc (5 ml) and filtered. For the entries **a–e** and **h–j**, the filtrate was concentrated and the gummy mass was subjected to column chromatography over silica gel using *n*-hexane/ethyl acetate (5:1) as eluent to obtain pure β-enaminone. For the entries **f**, **g**, and **k**–x, solvent was evaporated and the pure products were obtained by recrystallization of residue from appropriated solvent. The catalyst was recovered from the residue.

Spectral (^{1}H and ^{13}C NMR) and Analytical Data of New Compounds 3s–x

Compound **3s**

Colorless solid; mp 225–227 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.13 (s, 6H), 2.10 (s, 2H), 2.24 (s, 2H), 2.76 (s, 3H), 5.73 (s, 1H), 7.02 (d, $J = 7.1$ Hz, 2H), 7.12 (s, 1H), 7.84 (d, $J = 7.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 26.4, 28.1, 32.8, 43.6, 50.3, 100.6, 115.8, 121.2, 121.6, 129.8, 133.0, 140.3, 143.2, 158.8, 196.8, 198.4. Anal. calcd. for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.22; H, 7.01; N, 5.00.

Compound **3t**

Colorless solid; mp 213–215 °C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.16 (s, 6H), 2.16 (s, 2H), 2.42 (s, 2H), 5.60 (s, 1H), 7.22 (d, $J = 10$ Hz, 2H), 6.66 (broad pick, 1H), 7.89 (d, $J = 10$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 26.7, 32.8, 43.4, 50.4, 100.8, 106.7, 118.6, 122.1, 133.4, 143.2, 165.1, 198.7. Anal. calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: 75.03; H, 6.64; N, 11.76.

Compound **3u**

Colorless solid; mp 219–220 °C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.02 (s, 6H), 2.14 (s, 2H), 2.36 (s, 2H), 5.13 (s, 1H), 6.66 (broad pick, 1H), 6.96 (d, $J = 8.6$ Hz, 2H), 7.39 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 26.8, 28.5, 31.8, 44.1, 50.4, 100.2, 121.6, 129.8, 132.7, 140.3, 143.2, 198.7. Anal. calcd. for $C_{14}H_{16}BrNO$: C, 57.16; H, 5.48; N, 4.76. Found: C, 57.10; H, 5.55; N, 4.88.

Compound **3v**

Colorless solid; mp 162–163 °C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 1.14 (s, 6H), 1.92 (s, 3H), 2.19 (s, 3H), 4.35 (s, 2H), 5.20 (s, 1H), 6.17 (broad pick, 1H), 7.22 (m, 2H), 7.68 (m, 1H), 8.55 (m, 1H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 28.3, 32.9, 43.4, 46.8, 50.3, 96.3, 122.0, 122.7, 136.9, 148.8, 154.6, 162.2, 196.9. Anal. calcd. for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88; N, 12.16. Found: 73.23; H, 7.96; N, 12.00.

Compound **3w**

Colorless solid; mp 149–150 °C; ^{1}H NMR (CDCl$_3$, 250 MHz) δ 2.49 (s, 3H), 5.28 (s, 1H), 6.77 (d, $J = 7.5$ Hz, 2H), 7.39–7.51 (m, 7H), 7.97 (d, $J = 7.5$ HZ, 2H), 8.10 (d, $J = 7.0$ Hz, 2H), 12.88 (s, 1H); ^{13}C NMR (CDCl$_3$, 63 MHz) δ 26.1, 99.0, 112.3, 113.8, 121.6, 127.4, 128.2, 128.5, 128.9, 129.3, 130.1, 130.8, 131.8, 132.2, 135.5, 139.4, 144.1, 160.0, 163.4, 190.3, 196.8, Anal. calcd. for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.08; H, 5.20; N, 4.06.

Compound **3x**

Colorless solid; mp 162–163 °C, ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.64 (d, $J = 7.5$ Hz, 6H), 1.01(s, 6H), 1.97 (m, 1H), 2.99 (s, 2H), 3.01 (s, 2H), 4.25 (d, $J = 7.5$ Hz, 2H), 5.96 (s, 1H), 8.10 (s, 1H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 20.3, 27.7, 27.9, 32.8, 43.1, 47.2, 51.1, 93.7, 128.0, 192.6, Anal. calcd. for $C_{12}H_{21}NO$: C, 73.80; H, 10.84; N, 7.17. Found: C, 73.69; H, 10.93; N, 7.02.

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