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Vanadium(IV) acetylacetonate catalyzed stereoselective synthesis of β-enaminoesters and β-enaminones

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This work is dedicated to Professor Mihir K. Chaudhuri, Vice-chancellor, Tezpur University on the occasion of his 65th birthday.

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$VO(acac)_2$
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ABSTRACT

An efficient and stereoselective procedure has been described for the synthesis of a series of β-enaminoesters and β-enaminones by vanadium(IV) acetylacetonate [$VO(acac)_2$] catalyzed reaction of β-ketoesters and 1,3-diketones with both aliphatic and aromatic amines. X-ray crystallographic studies of some representative compounds corroborate two types of structural geometry formed by inter-molecular as well as intra-molecular hydrogen bonds.

β-Enaminoesters and β-enaminones are the building blocks for an important class of molecules synthesized from the β-dicarbonyl compounds.[1–4] They are the precursors for a variety of versatile biologically active molecules like taxol, peptides, and alkaloids.[1–8] Chiral ligands for diastereoselective synthesis can also be obtained from the optically active enaminones.[9] Moreover, the β-enaminoesters and β-enaminones are significant intermediates for the formation of β-aminoacids and γ-aminoalcohols. The major advantage of these compounds is their stability under simulated physiological pH conditions and low toxicity.[10] Numerous methods for their syntheses are reported in the literature.[1,11–14] The classical among them, is the condensation of amines and 1,3-dicarbonyl compounds where water is removed azeotropically by refluxing in aromatic solvents. Conversion with catalysts like Al_2O_3,[2] SiO_2,[15] montmorillonite K-10,[16] $NaAuCl_4$,[17] $Zn(ClO_4)_2{\cdot}6H_2O$,[18] AcOH under ultrasound,[19] $Zn(OAc)_2{\cdot}2H_2O$,[20] $Bi(OTf)_3$,[21] I_2,[22] $Sc(OTf)_3$,[23a] $HClO_4{\cdot}SiO_2$,[23b] ionic liquid $[EtNH_3]NO_3$[24] and $[Hmin]^+Tfa^-$,[25] $CeCl_3{\cdot}7H_2O$[26] and $ZrOCl_2{\cdot}8H_2O$,[27a] $H_2SO_4{\cdot}SiO_2$,[27b] ceric ammonium nitrate (CAN),[27c] $LiHSO_4/SiO_2$,[27d] and L-proline[27e] have also been reported recently. In spite of their applicability, these methods suffer from drawbacks like prolonged reaction time,[2,15] high temperature,[19] formation of amides as side products, expensive catalysts,[12,17,21] high catalyst loading,[20,22,26] and the use of hazardous solvents for example, benzene. Thus, a search for a new catalyst and simple procedure is of practical importance.

Vanadium acetylacetonate [$VO(acac)_2$] has been proven as a remarkable reagent in various organic syntheses due to its wide spectrum of applicability and profound reactivity. This low cost reagent is convenient to handle due to extremely low toxicity.[28a] Moreover, it is soluble in organic solvents. The catalytic activity of $VO(acac)_2$ in the epoxidation of alkenes and geraniol, oxidation of dialkyl disulfides, and selective aerobic oxidation of activated alcohols into acids or aldehydes is well-known in the literature.[28–30] Recently, the use of $VO(acac)_2$ as catalyst has been reported in the oxidation of β-dicarbonyl compounds,[31] olefination of α,α′-divinyl ketones through catalytic Meyer–Schuster rearrangement,[32a] synthesis of benzimidazoles,[32b] and synthesis of carbon nanospheres.[33] Very recently, we have demonstrated that a combination of $VO(acac)_2$, hydrogen peroxide, and sodium iodide is a good system for cleavage of dithioacetals of sugars into aldehyde sugars[34a] and iodination of various organic substrates.[34b] To

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the best of our knowledge, $VO(acac)_2$ catalyzed synthesis of β-enaminoesters and β-enaminones from β-ketoesters and 1,3-diketones has not yet been reported. Herein, we report an easy and selective procedure for the synthesis of a series of β-enaminoesters and β-enaminones from β-ketoesters and 1,3-diketones respectively using 10 mol % of $VO(acac)_2$ as catalyst as shown in Scheme 1.

For our study, the catalyst $VO(acac)_2$ was prepared by following the literature procedure.[35] For optimization of the reaction conditions, a mixture of methyl acetoacetate (2.4 mmol) and benzyl amine (2.0 mmol) was stirred at room temperature without adding any catalyst. After 3 days of continuous stirring, the desired product **3a** was obtained in 55% yield along with unreacted starting materials. Next, the same mixture was stirred at room temperature in the presence of 1 mol % of vanadyl acetylacetonate and the product **3a** was isolated in 65% yield (Table 1, entry 2). Likewise, similar reactions were examined with 2 mol %, 5 mol %, 10 mol %, and 15 mol % successively and we have noted that 10 mol % catalyst is a sufficient amount for complete conversion as well as to obtain the best yield (Table 1, entries 3–6). However, the same transformation can be achieved using 5 mol % catalyst, but it requires longer duration. The product 3a was characterized by recording ^1H NMR, ^{13}C NMR spectra, and elemental analysis.

After optimizing the reaction conditions,[36] the reaction of a wide variety of β-ketoesters (**1b–j**) was examined with benzyl amine using 10 mol % of $VO(acac)_2$ at room temperature and the desired products **3b–j** were obtained in good yields (Table 2, entries **b–j**). Similarly, various β-ketoesters (**1k–s**) and aromatic amines were scrutinized in the presence of 10 mol % catalyst under identical reaction conditions and the products (**3k–s**) were isolated in moderate to good yields. It is worth-while to mention that electron-rich aromatic amines take a shorter reaction time and provide good yields as compared to aromatic amine having electron-withdrawing substituents. Encouraged by these results, various 1,3-diketones (**1t–x**) were treated with different aromatic amines and benzyl amine using the same amount of catalyst under similar reaction conditions and the results are given in Table 2.

Interestingly, acyclic β-ketoesters and 1,3-diketones result *Z*-β-enaminoesters and *Z*-β-enaminones with 100% stereoselectivity, respectively, whereas cyclic 1,3-diketones give exclusively *E*-β-enaminones as shown in Scheme 1.

From Table 2, it can be seen that the nucleophilic benzylamine reacts faster with a variety of β-ketoesters and 1,3-diketones to give β-enaminoesters and β-enaminones in excellent yields as compared to 2-methoxyaniline (entry **1l**) and 2,6-dimethylaniline (entry **1o**). A plausible mechanistic pathway has been outlined in Scheme 2.

To shed further light on the geometry of the compounds, the molecular structures of **3t** and **3v** were confirmed by a single crystal X-ray analysis (Fig. 1).[37] X-ray crystallographic experiments

Table 1
Optimization of reaction condition using $VO(acac)_2$ catalyst[a]

Entry	Catalyst used	Catalyst amount in (mol %)	Reaction time (min)	Product	Yield[b] (%)
1	No Catalyst	—	3 days	**3a**	55
2	$VO(acac)_2$	1	90	**3a**	65
3	$VO(acac)_2$	2	50	**3a**	74
4	$VO(acac)_2$	5	30	**3a**	90
5	$VO(acac)_2$	10	15	**3a**	93
6	$VO(acac)_2$	15	15	**3a**	92

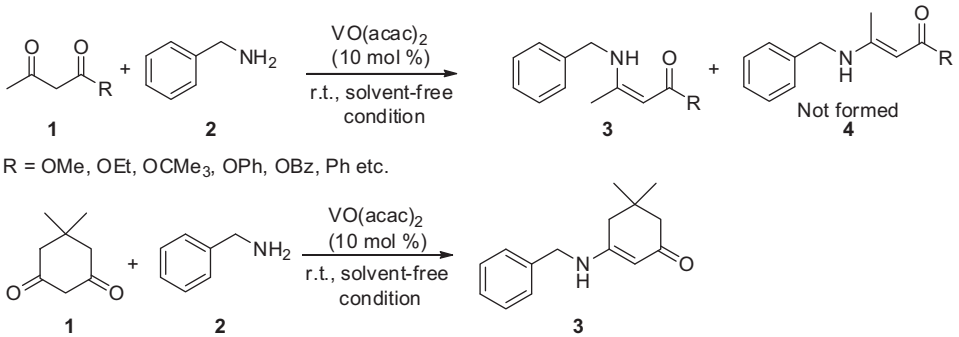
[a] The reactions were carried out with methyl acetoacetate (2.4 mmol) and benzyl amine (2.0 mmol).
[b] Isolated yield.

reveal that **3t** belongs to the triclinic space group $P\bar{1}$ with $Z = 4$ whereas **3v** belongs to the monoclinic space group $P2_1/n$ with $Z = 4$. Crystal structure analysis shows that **3t** forms two independent discrete molecules because of intra-molecular hydrogen bonding interactions (O···H = 1.93 Å, O···N = 2.696 Å and O···H = 1.74 Å, O···N = 2.698 Å) leading to the formation of quasi-aromatic ring. On the other hand, **3v** forms 1D polymer via intermolecular hydrogen bonding interactions through C═O···H–N bonds (O···H = 1.99 Å, O···N = 2.810 Å, ∠O···H–N = 159°). The hydrogen-bonded ring formation could not be possible in the case of **3v** due to the structural constraint as shown in Figure 1a.

The ^1H NMR spectra of the products show two different kinds of chemical shifts of NH protons. Notably, the NH proton of β-enaminone (entry **3v** and **3w**) (derived from dimedone and benzylamine or dimedone and *p*-ethyl aniline) was found at 4.80 ppm and 5.95 ppm which supports the formation of *E*-isomer. In this case the intermolecular hydrogen bond causes the compound to become a 1D-zigzag hydrogen-bonded polymeric form as evident from the X-ray crystallographic structure of Figure 1a. The downfield shift of the NH proton is in the range of δ value 8.9–12.5 ppm which indicates the predominant formation of the *Z*-β-enaminoesters or *Z*-β-enaminones. The intra-molecular hydrogen bonding plays the key role in maintaining the geometry of the molecule intact and responsible for higher δ values because of the formation of quasi-aromatic ring which is evident from Figure 1b.

Again in the case of unsymmetrical diketone, benzoyl acetone (entries **3t–u**), the amine always attacked the keto group positioned α- to the methyl group and in all cases; this is evident from the ^1H NMR spectra. The methyl group exhibited a distinctive singlet at 2.07 ppm, instead of 2.22 ppm which is a characteristic peak of the methyl group of $-COCH_3$.

Stereoselective syntheses of enaminones and enaminoesters using various catalysts have been well-studied.[21,23b,27c] However, it provides further scope to design a particular substrate to obtain stereoselective products unequivocally. The major advantage of our procedure is the stereoselective formation of the products owing to the intermolecular and intramolecular hydrogen-bonding.



Scheme 1.

Table 2
$VO(acac)_2$ catalyzed formation of β-enaminoesters and β-enaminones

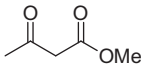
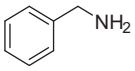
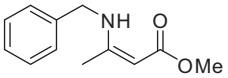
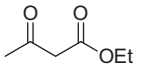
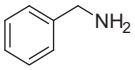
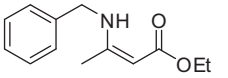
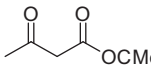
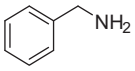
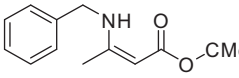
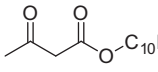
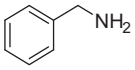
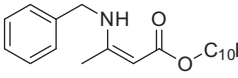
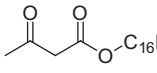
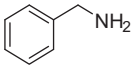
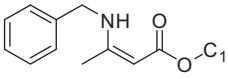
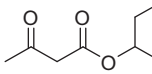
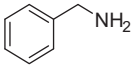
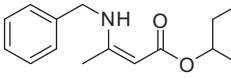
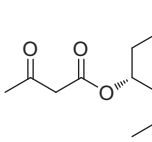
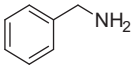
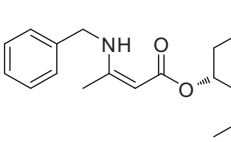
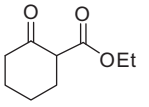
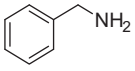
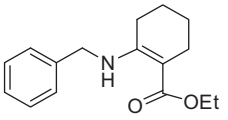
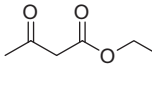
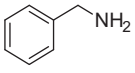
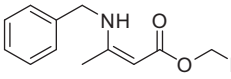
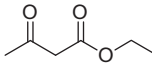
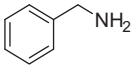
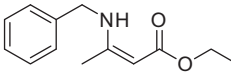
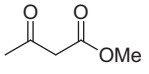
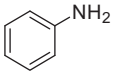
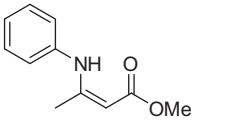
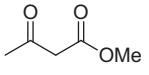
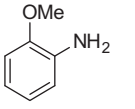
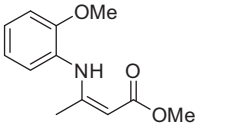
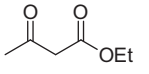
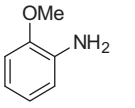
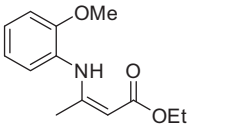
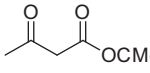
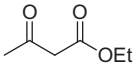
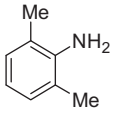
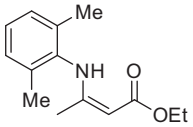
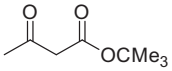
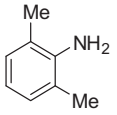
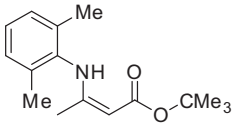
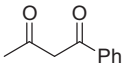
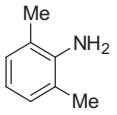
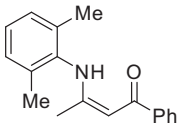
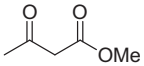
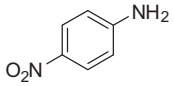
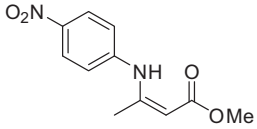
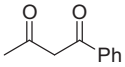
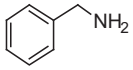
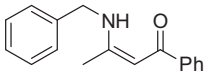
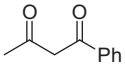
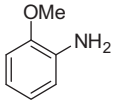
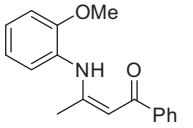
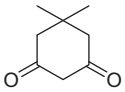
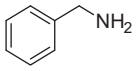
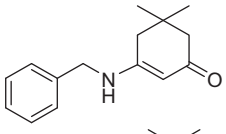
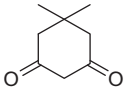
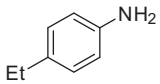
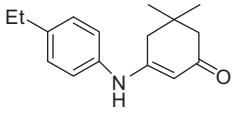
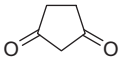
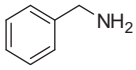
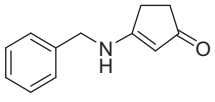
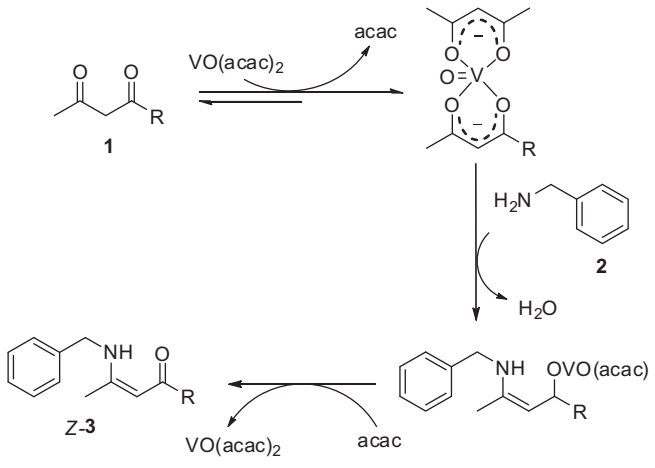
Entry	β-Ketoester or 1,3-diketone (**1**)	Amine (**2**)	Time (min)	Product[a] (**3**)	Yield[b] (%)
a			15		93
b			15		92
c			15		91
d			20		89
e			20		90
f			20		88
g			25		93
h			10		90
i			15		92
j			20		91
k			60		76
l			55		89
m			55		85
n			60		87
o			60		87

Table 2 (*continued*)

Entry	β-Ketoester or 1,3-diketone (**1**)	Amine (**2**)	Time (min)	Product[a] (**3**)	Yield[b] (%)
p			65		89
q			65		88
r			60		92
s			90		62
t			15		86
u			60		88
v			15		89
w			25		81
x			20		83

[a] The reactions were performed using β-ketoester (1.2 mmol) or 1,3-diketone (1.2 mmol), and aromatic amine (1 mmol) or benzylamine (1 mmol).
[b] Isolated yield.



Scheme 2.

This method is applicable for the preparation of the enaminones with a linear long chain and bulky β-keto esters (e.g., entries **1d**–**g**), cyclic β-ketoesters (e.g., entry **1h**), and 1,3-diketones (e.g., entries **1t**–**x**). While both aromatic and benzyl amine reacted to give the products, aromatic amines react comparably slow. The comparison of our protocol with the existing methods of synthesizing β-enaminoesters and β-enaminones in the presence of various catalysts has been shown in Table 3.

In conclusion, we report a simple, efficient, and cost effective protocol for the formation of β-enaminones from β-ketoesters as well as β-diketones by their reaction with both aromatic and aliphatic amines. The reaction occurs in the presence of the catalytic amount of vanadium(IV) acetylacetonate at room temperature under solvent free condition. With the help of X-ray crystallographic data, we have also identified two different types of structural geometries for β-enaminoesters and β-enaminones which explain the upfield and the downfield chemical shifts of NH-proton in the ^{1}H NMR spectra of the corresponding compounds.

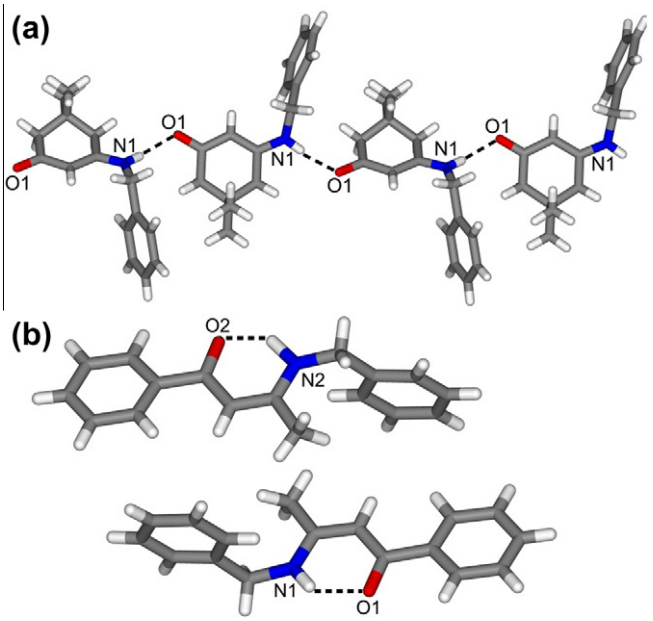


Figure 1. X-ray crystallographic structure of (a) formation of 1D-zigzag polymer in **3v** via inter-molecular hydrogen bonding interactions and (b) **3t** forming quasi-aromatic ring via intra-molecular hydrogen bonding interactions.

Table 3
Synthesis of 5,5-dimethyl-3-(benzylamino)cyclohex-2-enone[a] and ethyl-3-(benzylamino)but-2-enoate[b] in the presence of different catalysts

Catalyst used	Amount used (mol %)	Time (min)	Yield (%)
[a]*p*-Toluenesulfonic acid	10	10 h	87
[a]$H_2SO_4{\cdot}SiO_2$	400 mg/mmol	5	95
[a]$HClO_4{\cdot}SiO_2$	50 mg/mmol	5	96
[a]CAN	20	8	88
[a]$VO(acac)_2$	10	15	89
[b]I_2	20	30	99
[b]$Bi(TFA)_3$	5	5	97
[b]$HClO_4{\cdot}SiO_2$	50 mg/mmol	5	98
[b]$Sc(OTf)_3$	10	2 h	90
[b]$VO(acac)_2$	10	15	92

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.11.051.

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36. *General procedure for the preparation of β-enaminoesters and β-enaminones*: Into a mixture of aromatic amine or benzyl amine (1 mmol) and β-ketoesters or 1,3-diketones (1.2 mmol) in a 25 ml round bottomed flask vanadium(IV) acetylacetonate (0.026 g, 0.10 mmol) was added and it was kept for stirring at room temperature. The completion of the reaction was monitored by TLC. The product was extracted by aqueous MeOH or by CH_2Cl_2 (20 mL). The pure product was obtained either by fractional crystallization using aqueous MeOH (for solid product) or by directly passing through a silica gel (60–120 mesh) column using 1:9 EtOAc/hexane as eluent (for liquid product).
37. *Crystal data*: **3t**: Triclinic space group $P\bar{1}$, $a = 10.1740(5)$, $b = 11.0786(5)$, $c = 14.1398(7)$ Å, $\alpha = 86.629(3)$, $\beta = 84.875(3)$, $\gamma = 63.836(3)°$, $V = 1424.39(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.172$ g cm^{-3}, $\mu = 0.073$ mm^{-1}, $T = 296$ K, R1 = 0.0759, *w*R2 = 0.2380, GOF = 0.979 for $I > 2\sigma(I)$, $Mo_{k\alpha}$-ray ($\lambda = 71{,}073$ pm). **3v**: Monoclinic space group $P2_1/n$, $a = 5.9283(8)$, $b = 19.514(3)$, $c = 11.7648(16)$ Å, $\beta = 102.341(8)°$, $V = 1329.6(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.146$ g cm^{-3}, $\mu = 0.071$ mm^{-1}, $T = 296$ K, R1 = 0.1255, *w*R2 = 0.2968, GOF = 0.942 for $I > 2\sigma(I)$, $Mo_{k\alpha}$-ray ($\lambda = 71{,}073$ pm). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 828349 and 828350. A copy of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK or e-mail: deposit@ccdc.cam.ac.uk.