# Phosphotungstic acid catalysed synthesis of β-enamino compounds under solvent-free conditions

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A convenient eco-friendly procedure has been developed for the synthesis of β-enaminones and β-enamino esters by reacting 1,3-dicarbonyl compounds with amines in the presence of catalytic amounts of phosphotungstic acid ($H_3PW_{12}O_{40}$, 1 mol%). The reaction proceeds smoothly at room temperature under solvent-free conditions and gives the corresponding β-enamino compounds in high to excellent yields.

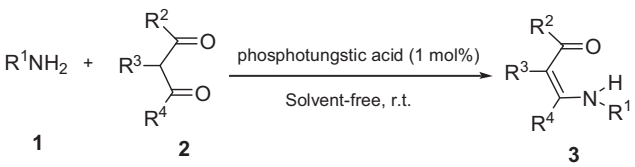
**Keyword:** 1,3-dicarbonyl compounds, amines, enaminones, enamino esters, phosphotungstic acid, solvent-free conditions

Recently, the use of solid acids as heterogeneous catalysts has attracted much attention and has become an area of active studyin chemistry.[1,2] As part of these studies, the use of heteropoly acids (HPAs) which are strong acids, harmless to the environment and highly stable toward humidity and have flexibility in modifying the acid strength has found attention.[3-7] HPAs are green and are efficient bifunctional catalysts. Their acidity is significantly higher than that of traditional mineral acids and inorganic acids. Furthermore, HPAs are capable of protonating and activating some substrate.[8] In particular, the Keggin-type HPAs such as $H_3PW_{12}O_{40}$ (PW), $H_3PMo_{12}O_{40}$ (PMo) or $H_4SiW_{12}O_{40}$ (SiW) are the most efficient catalysts for a variety of catalytic processes for industrial application.[9] PW is considered to be the strongest heteropoly acid in the Keggin series. It has been reported to be an efficient catalyst for many important organic transformations, including the intramolecular rearrangement of benzyl phenyl ether to 2-benzyl phenol,[9] the Beckmann rearrangement,[10] the Fries rearrangement,[11] the synthesis of 1,1-diacetates,[12] β-acetamido ketones,[13] diaryl sulfoxides,[14] diisobornyl ether,[15] 1,3-dioxolane derivatives,[16] 5-alkoxycarbonyl-4-aryl-3,4-dihydropyrimidin-2-ones,[17] quinaldines and lepidines,[18] the diacetal of pentaerythritol,[19] 3,4-dihydropyrimidin-2(1H)-ones[20] and α-amino phosphonates.[21] It also catalyses the *N*-*t*-butoxycarbonylation of amines,[22] the chemoselective oxathioacetalisation of carbonyl compounds,[23] trimethylcyanosilylation reactions of aldehydes and ketones,[24] and the Michael addition reaction of thiols to α,β-unsaturated ketones.[25]

β-Enamino compounds have been extensively used as intermediates in organic synthesis.[26-29] In particular, they have been utilised as synthons for the synthesis of various biologically active heterocyclic compounds having anti-inflammatory, antitumor, antibacterial, and anticonvulsant activities[30-31] and as intermediates for the preparation of β-enaminoacids, γ-enaminoaclohols, and β-enamino esters.[32] Due to its wide range of utility in the pharmaceutical industry, the enamination of β-dicarbonyl compounds with various amines has become an important transformation and consequently several methods have been developed for the synthesis of these compounds. Among them, the most simple and straightforward conventional method is the azeotropic removal of water by refluxing an amine and 1,3-dicarbonyl compounds in an aromatic solvent.[33] Several improved procedures have been subsequently reported using catalyst systems, including the use of protic acids,[34] Lewis acids such as $Zn(ClO_4)_2·6H_2O$,[35] $CeCl_3·7H_2O$,[36] $NaAuCl_4$,[37] $Bi(OTf)_3$,[38] $InBr_3$,[32] $CoCl_2·6H_2O$,[39] CAN,[40-41] $Yb(OTf)_3$,[42,43] $SnCl_4·5H_2O$,[44] $ZrCl_4$,[45] $ZrOCl_2·8H_2O$,[46] $Zn(Ac)_2·2H_2O$[47] and $Sc(OTf)_3$,[48] $I_2$,[49] and solid acids such as montmorillonite K10,[50] silica chloride,[51] silica gel,[52] natural clays,[53] and sulfated zirconia.[54] Recently, $[EtNH_3]NO_3$,[55] and $HClO_4·SiO_2$[56] have also been used to promote this transformation. However, some of these methodologies have not been entirely satisfactory, with disadvantages such as low yields, prolonged reaction time, harsh reaction conditions, use of harmful organic solvents, and a requirement of an excess of the catalysts and of special apparatus. Thus, the development an efficient, practical and environmentally benign synthetic method to overcome the limitations is still an important experimental challenge. Herein, we wish to report a novel and high yielding solvent-free method for the preparation of β-enamino compounds using a catalytic amount of phosphotungstic acid (Scheme 1).

We initially studied the reaction of aniline and ethyl acetoacetate as a benchmark reaction in the presence of 1 mol% of PW at room temperature under solvent-free conditions. To our delight, the reaction occurred to afford ethyl 3-(phenylamino)but-2-enoate (**3f**) in 95% yield when the reaction mixture was allowed to stir for 45 min (Table 1, entry **f**). Further studies established that 1 mol% of catalyst was necessary to promote this reaction. In the absence of catalyst, the model reaction was run and only 30% of the product could be obtained even with stirring for 24 h (Table 1, entry **g**). An increase in the amount of PW to more than 1 mol% showed no substantial improvement in the yield, whereas the yield was reduced by decreasing the amount of PW to 0.1 mol%. Reactions in solvents such as acetonitrile, tetrahydrofuran, ethanol, dichloromethane, ethyl acetoacetate and dimethylformamide gave lower yields of the desired product even at prolonged reaction times. So, we choose the reaction to be proceeded under solvent-free conditions.

Having established the optimised experimental conditions, the scope of the reaction was then explored and several representative results are summarised in Table 1. As shown in Table 1, the present methodology worked efficiently with a wide variety of substrates. In general, primary and benzylic amines reacted with a broad range of structurally diverse 1,3-dicarbonyl compounds to afford the corresponding β-enaminones or β-enamino esters in high yields in short times. However, anilines with an electron-withdrawing group (**1l** and **1y**) retarded the progress of reaction and afforded low yields of the products. It was also found that the substituted groups (**1h** and **1w**) on the *ortho* position in the aniline influenced the reaction rates. Moreover, the optically active (*R*)-( + )-α-methyl benzyl amine (**1d**) was converted into the




**Scheme 1**

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**Table 1** Synthesis of β-enaminones and β-enamino esters catalysed by phosphotungstic acid

| Entry | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Time/min | Yield/%[a] | Ref. |
|---|---|---|---|---|---|---|---|
| **a** | $CH_3(CH_2)_3$ | OMe | H | Me | 15 | 93 | 39 |
| **b** | $C_6H_{11}$ | OEt | H | Me | 15 | 92 | 39 |
| **c** | $H_2C{=}CHCH_2$ | OMe | H | Me | 15 | 91 | 39 |
| **d** | (*R*)-PhCH($CH_3$) | OMe | H | Me | 15 | 90 | 39 |
| **e** | $PhCH_2$ | OEt | H | Me | 18 | 92 | 19 |
| **f** | Ph | OEt | H | Me | 45 | 95 | 39 |
| **g** | Ph | OEt | H | Me | 24 h | 30[b] | 39 |
| **h** | 2-Me–$C_6H_4$ | OMe | H | Me | 60 | 94 | 54 |
| **i** | 4-Me–$C_6H_4$ | OEt | H | Me | 40 | 93 | 40 |
| **j** | 4-OEt–$C_6H_4$ | OEt | H | Me | 40 | 93 | 39 |
| **k** | 4-$^i$Pr–$C_6H_4$ | OEt | H | Me | 40 | 91 | |
| **l** | 4-Br–$C_6H_4$ | OEt | H | Me | 360 | 72 | 45 |
| **m** | $PhCH_2$ | $OCH_2CH_2$ | Me | 30 | 90 | 54 | |
| **n** | Ph | $OCH_2CH_2$ | Me | 75 | 91 | 54 | |
| **o** | 4-OMe–$C_6H_4$ | $OCH_2CH_2$ | Me | 60 | 92 | 39 | |
| **p** | Ph | OEt | $(CH_2)_3$ | 90 | 93 | 39 | |
| **q** | 4-OMe–$C_6H_4$ | OEt | $(CH_2)_3$ | 90 | 92 | 54 | |
| **r** | $CH_3(CH_2)_3$ | Me | H | Me | 15 | 94 | 54 |
| **s** | $H_2C{=}CHCH_2$ | Me | H | Me | 15 | 93 | 39 |
| **t** | $H_2NCH_2CH_2CH_2$ | Me | H | Me | 15 | 95[c] | 39 |
| **u** | $PhCH_2CH_2$ | Me | H | Me | 15 | 92 | 39 |
| **v** | Ph | Me | H | Me | 15 | 95 | 54 |
| **w** | 2-Me–$C_6H_4$ | Me | H | Me | 20 | 92 | 54 |
| **x** | 4-Me–$C_6H_4$ | Me | H | Me | 12 | 95 | 54 |
| **y** | 2-Br–$C_6H_4$ | Me | H | Me | 480 | 80 | 54 |
| **z** | Ph | Ph | H | Me | 120 | 78 | 54 |
| **aa** | 4-OEt–$C_6H_4$ | Ph | H | Me | 120 | 82 | |

[a]Yield refer to isolated products, products were characterised by IR, $^1$H NMR and elemental analysis.
[b]No catalyst.
[c]Two equivalents of acetylacetone were used.

corresponding β-enaminoester (**3d**) without any racemisation or inversion confirmed by measuring **3d**'s optical rotation. When 1,3-diaminopropane (**1t**) was used, two equivalents of acetylacetone were used and the product was formed with two enaminone groups (**3t**). It should be pointed out that when 1,3-diketones with two different substituents, such as 1-benzoylacetone, reacted with amines the regioselective amination of the aliphatic carbonyl group (**2z** and **2aa**) was observed. From linear 1,3-diketones and 1,3-ketoesters we always obtained the corresponding β-enaminones and β-enamino esters having a (*Z*)-configuration of the carbon-carbon double bond due to the formation of intramolecular hydrogen bonding between oxygen atom of carbonyl and NH reside, as determined by $^1$H NMR analysis ($\delta_H > 8.2$ for NH) and comparison with the chemical shifts of vinylic protons of similar *Z*-enaminones.[32]

Recycling of the catalyst was also investigated. After completion of the benchmark reaction, the catalyst was filtered off, washed with diethyl ether and activated at 100°C for 2 h and reused in another reaction with the same substrates. There was no significant change in the activity after two cycles (95, 93 and 90% of product after three runs).

In order to show the merit of phosphotungstic acid in comparison with other recently reported catalysts for the synthesis of **3f** as a model reaction, we have tabulated some of results in Table 2. It is clear from Table 2, that phosphotungstic acid is an equally efficient but a much cheaper and reusable catalyst.

In summary, an environmentally friendly procedure for the synthesis of β-enaminones and β-enamino esters through phosphotungstic acid–catalysed condensation of 1,3-dicarbonyl compounds and amines has been developed. This method has several unique merits, such as simple experimental procedure, solvent-free conditions, short reaction times, high yields of products and chemo- and stereoselectivities. In addition, the catalyst can be easily recovered and reused, providing thereby eco-friendly and economic advantages over previously reported protocols and rendering this methodology highly suitable for industrial applications.

## Experimental

IR spectra were obtained as KBr pellets for samples solid and as thin films for liquid samples with a Thermo Nicolet FT-IR200 spectrometer. NMR spectra were recorded on a Bruker AV 300 spectrometer in $CDCl_3$ using TMS as an internal standard. The melting points are uncorrected and were recorded on a WRR melting point instrument. Elemental analyses were performed on a PE 2400 CHNS/O Analyser.

*General procedure for the synthesis of* β-*enaminones or* β-*enamino esters*: A mixture of ethyl acetoacetate (1.30 g, 10 mmol) with aniline (0.93 g, 10 mmol), and $H_3PW_{12}O_{40}$ (0.29 g, 0.1 mol) was stirred at room temperature. The progress of reaction was followed by TLC. After completion of reaction, as indicated by TLC, the reaction mixture was extracted with diethyl ether (3 × 10 ml) and the catalyst was filtered off. The combined ether extract was treated with saturated sodium bicarbonate and dried over anhydrous $Na_2SO_4$, concentrated under reduced pressure and the resulting product was purified by silica gel column chromatography (20% ethyl acetate in *n*-hexane as eluent) to afford pure ethyl 3-phenylamino-but-2-enoate (1.95 g, 95%). The filtered catalyst was repeatedly washed with diethyl ether and reused.

Selective spectroscopic and analytical data for AA'XX' systems in $^1$H NMR $J^* = J_{23} + J_{25}$.

*Methyl (R)-3-(1-phenyl-ethylamino)but-2-enoate* (**3d**):[39] A colourless liquid, $[\alpha]_D^{20}$: –540 (*c* 1.15, EtOH); IR (neat): 3280, 2973, 2929, 1653, 1608, 1494, 1446, 1378, 1266, 1054, 764, 700 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz) δ ppm: 1.52 (d, $J$ = 6.6 Hz, 3H), 1.78 (s, 3H), 3.67 (s, 3H), 4.49 (s, 1H), 4.65 (q, $J$ = 6.6 Hz, 1H), 7.20–7.38 (m, 5H), 9.00 (br s, NH). $^{13}$C NMR ($CDCl_3$, 75 MHz) δ ppm: 19.7, 25.0, 50.0, 52.9, 82.9, 125.5, 127.2, 128.8, 150.0, 161.6, 180.0. Anal. Calcd. for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.5; H, 7.8; N, 6.5.

*Ethyl 3-(4-isopropylphenylamino)but-2-enoate* (**3k**): A yellow oil; IR (neat): 3262, 2962, 2932, 1655, 1620, 1519, 1362, 1332, 1278, 1162, 1058, 758, 668 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 300 MHz) δ ppm: 1.28 (t, $J$ = 7.2 Hz, 3H), 1.39 (d, $J$ = 7.2 Hz, 6H), 1.98 (s, 3H), 2.94 (m, 1H) 4.22 (q, $J$ = 7.2 Hz, 2H), 5.12 (s, 1H), 7.02 (m, $J^*$ = 8.4 Hz, 2H), 7.18 (m, $J^*$ = 8.4 Hz, 2H), 10.28 (brs, NH). $^{13}$C NMR ($CDCl_3$, 75 MHz) δ ppm: 14.5, 20.0, 23.8, 33.5, 58.5, 85.5, 124.4, 126.8, 137.0, 145.6, 159.0, 170.0. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.7; H, 8.45; N, 5.75.

**Table 2** Synthesis of ethyl 3-(phenylamino)but-2-enoate (**3f**) in the presence of different catalysts

| Catalyst/solvent | Catalyst load | Time | Yield/% | Ref. |
|---|---|---|---|---|
| $InBr_3$/solvent-free | 1 mol% | 10 min | 94 | 32 |
| $Zn(ClO_4)_2{\cdot}6H_2O/CH_2Cl_2$ | 5 mol% | 4 h | 95 | 35 |
| $CeCl_3{\cdot}7H_2O$/solvent-free | 10 mol% | 35 min | 76 | 36 |
| $Bi(OTf)_3/H_2O$ | 5 mol% | 1 h | 64 | 38 |
| $CoCl_2{\cdot}6H_2O$/solvent-free | 5 mol% | 15 min | 95 | 39 |
| CAN/solvent-free | 1 mol% | 60 min | 92 | 40 |
| $Yb(OTf)_3$/solvent-free | 2 mol% | 60 min | 95 | 43 |
| $ZrCl_4$/solvent-free | 1 mol% | 40 | 95 | 45 |
| $ZrOCl_2{\cdot}8H_2O$/solvent-free | 2 mol% | 50 min | 93 | 46 |
| $Zn(OAc)_2{\cdot}2H_2O/CH_2Cl_2$ | 5 mol% | 2 days | 86 | 47 |
| $Sc(OTf)_3$/solvent-free | 5 mol% | 60 min | 95 | 48 |
| $I_2$/solvent-free | 20 mol% | 3 min | 79 | 49 |
| Silica gel/solvent-free | 10 mg | 35 h | 95 | 52 |
| Phosphotungstic acid/solvent-free | 1 mol% | 45 min | 95 | This work |

*Ethyl 3-(4-bromophenylamino)-but-2-enoate* (**3l**):[45] A pale yellow solid; m.p. 52–53°C. IR (KBr) 3276, 2978, 1648, 1610, 1580, 1480, 1385, 1261, 1169, 854, 790 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300 MHz) δ ppm: 1.28 (t, $J$ = 7.2 Hz, 3H), 2.00 (s, 3H), 4.16 (q, $J$ = 7.2 Hz, 2H), 4.72 (s, 1H), 6.96 (m, $J^*$ = 8.4 Hz, 2H), 7.45 (m, $J^*$ = 8.4 Hz, 2H), 10.40 (br s, NH). $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ ppm: 14.6, 20.3, 59.0, 118.0, 125.8, 132.3, 138.6, 162.4, 170.5. Anal. Calcd for $C_{12}H_{14}BrNO_2$: C, 50.72; H, 4.97; N, 4.93; Found: C, 50.85; H, 4.8; N, 5.1.

*3-(4-Ethoxyphenylamino)-1-phenylbut-2-en-1-one* (**3aa**): A yellow solid, m.p. 85–86°C; IR (KBr) 3415, 2980, 1600, 1505, 1475, 1433, 1372, 1322, 820, 745 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300 MHz) δ ppm: 1.44 (t, $J$ = 6.9 Hz, 3H), 2.08 (s, 3H), 4.05 (q, $J$ = 6.9 Hz, 2H), 5.88 (s, 1H), 6.80 (m, $J^*$ = 8.7 Hz, 2H), 7.10 (m, $J^*$ = 8.7 Hz, 2H), 7.43–7.93 (m, 5H), 13.00 (br s, NH). $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ ppm: 14.9, 20.3, 63.8, 93.5, 114.9, 126.6, 127.2, 128.2, 130.8, 131.5, 140.0, 157.2, 163.2, 188.5. Anal. Calcd. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.95; H, 6.8; N, 4.8.

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