A mild method for the synthesis of β-enaminones and β-enamino esters using KH_2PO_4 as catalyst

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β-Enaminones and β-enamino esters have been produced by the direct condensation of amines with β-diketones and β-ketoesters using KH_2PO_4 as catalyst under mild, solvent-free conditions.

Keywords: β-enaminones, β-enaminoesters, potassium dihydrogen phosphate, solvent-free condition

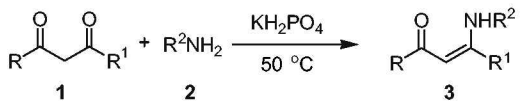
β-Enaminones and β-enamino esters are used as intermediates in organic synthesis and as precursors for the synthesis of a variety of heterocycles[1-3] including pharmaceutical compounds,[4] such as antibacterial, anticonvulsant and antitumor agents.[5,6] Due to the importance of these compounds as intermediates, a simple high yielding one-pot approach for this transformation is highly desirable. Classically, β-enaminones and β-enaminoesters are prepared by the direct condensation of 1,3-dicarbonyl compounds with amines under reflux in an aromatic solvent with the azeotropic removal of water.[7] Several improved methods for the preparation of β-enaminones and β-enamino esters have been reported using protic acids,[8,9] Lewis acids,[10-14] iodine,[15] silica gel,[16] and sulfated zirconia,[15] as catalysts. More recently, $[EtNH_3]NO_3$,[18] $HClO_4$–SiO_2[19] as well as silica chloride[20] also have been used to effect this transformation. Although these methods have improved reaction condition or shorter reaction time, a general procedure is lacking. There is still a need to develop a suitable method for the synthesis of β-enaminones and β-enamino esters conveniently.

Either protic acid or Lewis acid can effect the above transformation. The cheaper protic acid catalyst involve harsh conditions. The more easily handled and environmentally friendly Lewis acid catalysts are associated with a higher cost. We wished to develop a new catalyst which not only possessed the higher effect and inexpensive character of protic acid catalyst, but was also easy to control and environmentally friendly typical of the Lewis acid catalyst. Potassium dihydrogen phosphate, usually used as the buffer in analytical chemistry, possesses the property of protic acid and a Lewis acid, with the advantages of low cost, ease of handling and insensitive to air moisture. The special properties of a metal hydrogen phosphate salt prompted an investigation of the use of potassium dihydrogen phosphate in organic reactions. We wish to report a simple, convenient and efficient method for the chemo-selective enamination of 1,3-dicarbonyl compounds catalysed by KH_2PO_4. This method not only afforded the products in excellent yields but also avoided the problems associated with catalyst cost, and safety. To the best of our knowledge, such efficient and practical method for the synthesis of target compounds has not been reported previously.

Results and discussion

Potassium dihydrogen phosphate catalysed condensation of β-enaminones and β-ketoesters **1** with primary amines **2** affording β-enaminones and β-enamino esters **3** (Scheme 1).

The research began by comparing the catalytic activity of different metal hydrogen phosphate and phosphate salts towards the reaction between acetylacetone and 4-methylaniline under solvent free condition (Table 1). Among the salts that were tested, KH_2PO_4 proved to be the most efficient in giving excellent yields (Table 1, entry 2).



Scheme 1

Table 1 Screening of various phosphate salt catalysts for enamination of acetylacetone and 4-methylaniline

Entry	Catalyst (5 mol%)	Time/min	Yield [a]/%
1	None	40	68
2	KH_2PO_4	40	98
3	$NaH_2PO_4{\cdot}2H_2O$	40	85
4	$Na_2HPO_4{\cdot}12H_2O$	40	60
5	$Na_3(PO4)_3{\cdot}12H_2O$	40	50

[a]Isolated yields after column chromatography.

The effect of the amount of catalyst on the reaction of acetylacetone and 4-methylaniline was also investigated (Table 2). The results show that the yields increased as the amount of catalyst increased from 0% to 5%. A higher catalyst loading (5–10%) did not bring any obvious increase in yield. On the contrary, it caused the yield to slightly decrease. The best catalyst loading for this reaction is 5% based on acetylacetone.

An initial study was performed treating acetylacetone and 4-methylaniline under solvent-free conditions in the presence of a catalytic amount of KH_2PO_4 (5 mol%) at 50 °C. Product **3C** was isolated in 98% yield after 30 minutes. However, the same reaction works carried out in an organic solvent, such as C_2H_5OH, THF, CH_2Cl_2, DMF, gave lower yields of the desired product even over a prolonged reaction time. Various aromatic amines were used in the condensation with β-dicarbonyl compounds to give the corresponding β-enaminones and β-enamino esters in good to nearly quantitative yield under solvent-free condition. The results are summarised in Table 3.

In general, for aromatic primary amines the condensation reactions usually afforded the corresponding β-enaminones and aromatic β-enamino esters in over 80% yields in a short time. However, anilines with electron-donating groups afforded a higher yields than those aniline with an electron-withdrawing substituent. It should be pointed out that in the reaction of β-diketones and β-ketoesters with aromatic amines the corresponding β-enaminones and β-enamino

Table 2 The effect of mol% of KH_2PO_4 on reaction of acetylacetone with 4-methylaniline

Entry	KH_2PO_4 (mol%)	Time/min	Yield [a]/%
1	0	30	68
2	1	30	90
3	3	30	93
4	5	30	98
5	10	30	97

[a]Isolated yields after column chromatography

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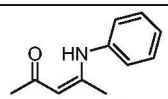
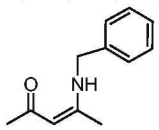
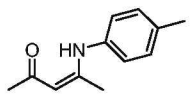
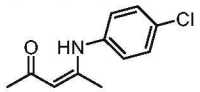
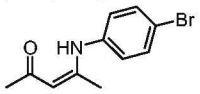
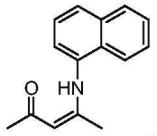
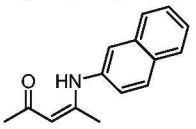
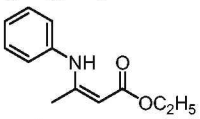
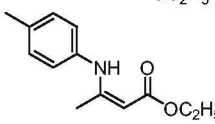
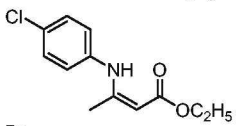
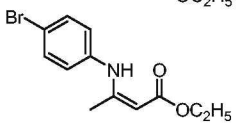
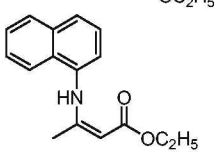
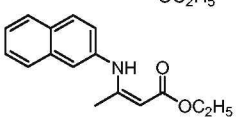
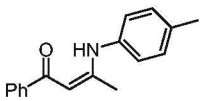
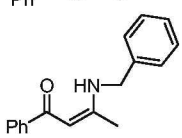
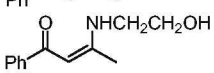
Table 3 Enamination of β-dicarbonyl compounds catalysed by KH_2PO_4 under solvent-free conditions

	3a–p	R	R^1	R^2	Product	Time/h	Yield [b]/%
1	**3a**	CH_3	CH_3	C_6H_5		1.0	88
2	**3b**	CH_3	CH_3	$CH_2C_6H_5$		0.5	95
3	**3c**	CH_3	CH_3	4-$CH_3C_6H_4$		0.5	98
4	**3d**	CH_3	CH_3	4-ClC_6H_3		2	80
5	**3e**[c]	CH_3	CH_3	4-BrC_6H_4		1.0	92
6	**3f**	CH_3	CH_3	1-Naphthyl		1.0	88
7	**3g**[c]	CH_3	CH_3	2-Naphthyl		1.0	91
8	**3h**	OC_2H_5	CH_3	C_6H_5		1.0	87
9	**3i**	OC_2H_5	CH_3	4-$CH_3C_6H_4$		0.5	96
10	**3j**[c]	OC_2H_5	CH_3	4-ClC_6H_3		1.5	79
11	**3k**	OC_2H_5	CH_3	4-BrC_6H_4		1.0	88
12	**3l**	OC_2H_5	CH_3	1-Naphthyl		1.0	90
13	**3m**[c]	OC_2H_5	CH_3	2-Naphthyl		1.0	87
14	**3n**	Ph	CH_3	4-$CH_3C_6H_4$		0.5	97
15	**3o**	Ph	CH_3	$CH_2C_6H_5$		0.5	95
16	**3p**	Ph	CH_3	CH_2CH_2OH		0.5	96

[a]All products were identified by comparison of their physical and spectral data with those of authentic samples.
[b]Isolated yields after column chromatography.
[c]New compound.

esters were always obtained having a (*Z*)-configuration of the carbon–carbon double bond. This is due to the formation of an intramolecular hydrogen bond, as shown by the ^{1}H NMR spectra following the procedure reported by Das *et al.*[19] This reaction is very clean and free from side reactions which are normally observed in other catalyst.

Experimental

Starting materials were obtained from commercial suppliers and used without further purification. Melting points were determined with an X-5 apparatus in open glass capillaries and were uncorrected. IR spectra were recorded on EQUINX 55 FT-IR spectrometer using KBr pellets. NMR spectra were collected on an AVANCE 300 MHz with TMS as an internal standard. Elemental analyses were performed on Vario ELIII instrument. Silica gel (200–300 mesh size) was used as a stationary phase for column chromatography.

Typical procedure for the synthesis of β-enaminone and β-enamino esters catalysed by KH_2PO_4: KH_2PO_4 (0.25 mmol) was added to a mixture of the 1,3-dicarbonyl compound (5 mmol) and amine (5 mmol). The mixture was stirred under solvent-free conditions at 50 °C. After the reaction was complete (monitored by TLC), the reaction mixture was diluted with CH_2Cl_2 (5 ml) and filtered. The filtrate was concentrated and the gummy mass was subjected to column chromatography over silica gel using petroleum ether–EtOAc as eluent to obtain pure β-enaminone and β-enamino esters.

Characterisation data for compounds **3a–p**

(Z)-4-(Phenylamino)-pent-3-en-2-one **(3a)**: White solid: m.p. 50–51 °C; IR (KBr cm^{-1}) 3420, 2926, 1595, 1570, 1510, 1436, 1355, 1316, 1281, 1186, 905, 820, 748; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.99 (s, 3H, CH_3C=C), 2.21 (s, 3H, $COCH_3$), 5.27 (s, 1H, C=CH), 6.67–7.35 (m, 5H, C_6H_5), 12.48 (s, 1H, NH); Anal. Calcd for $C_{11}H_{13}NO$ (175): C, 75.40; H, 7.48; N, 7.99; Found: C, 75.42; H, 7.50; N, 7.90%.

(Z)-4-(benzylamino)-pent-3-en-2-one **(3b):** Yellow oil: IR (KBr cm^{-1}) 3427, 3062, 3029, 2921, 2854, 1610, 1573, 1511, 1439, 1534, 1294, 1236, 1104, 1071, 1025, 984, 736; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.72 (s, 3H, CH_3C=C), 1.84 (s, 3H, $COCH_3$), 4.25 (d, 2H, J = 6.0 Hz, $C_6H_5CH_2$), 4.89 (s,1 H, C=CH), 7.10–7.16 (m, 5H, C_6H_5), 11.04 (s, 1H, NH); Anal. Calcd for $C_{12}H_{15}NO$ (189): C, 76.16; H, 7.99; N, 7.40; Found: C, 76.15; H, 8.00; N, 7.39%.

(Z)-4-(4-Methyl-phenylamino)-pent-3-en-2-one **(3c):** Wine red solid: m.p. 68–69 °C; IR (KBr cm^{-1}) 3437, 3023, 2991,2920, 2854, 1606, 1564, 1518, 1498, 1438, 1354, 1311, 1280, 1215, 1185, 1017, 922, 827, 761; ^{1}H NMR ($CDCl_3$, 300 MHz) 1.91 (s, 3H, CH_3C=C), 2.06 (s, 3H, $COCH_3$), 2.32 (s, 3H, $C_6H_4CH_3$), 5.17 (s, 1H, C=CH), 6.96–7.13 (m, 4H, C_6H_4) 12.41 (s, 1H, NH); Anal. Calcd for $C_{12}H_{15}NO$ (189): C, 76.16; H, 7.99; N, 7.40; Found: C, 76.11; H, 7.85; N, 7.44%.

(Z)-4-(4-chloro-phenylamino)-pent-3-en-2-one **(3d):** Pale white solid: m.p. 60–61 °C; IR (KBr cm^{-1}) 3448, 2991, 2925, 1612, 1565, 1501, 1432, 1403, 1314, 1276, 1212, 1184, 1089, 1010, 839, 796, 754; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.94 (s, 3H, CH_3C=C), 2.17 (s, 3H, $COCH_3$), 5.21 (s, 1H, C=CH), 7.04 (d, 2H, J = 7.8 Hz, C_6H_4), 7.30 (d, 2H, J = 7.8 Hz, C_6H_4,), 12.43 (s, 1H, NH); Anal. Calcd for $C_{11}H_{12}ClNO$ (209): C, 63.01; H, 5.77; N, 6.68; Found: C, 63.03; H, 5.79; N, 6.65%.

(Z)-4-(4-Bromo-phenylamino)-pent-3-en-2-one **(3e):** White solid: m.p. 55–56 °C; IR (KBr cm^{-1}) 3440, 2991, 2926, 1596, 1570, 1509, 1435, 1356, 1315, 1323, 1279, 1185, 1019, 905, 819, 749; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.94 (s, 3H, CH_3C=C), 2.13 (s, 3H, $COCH_3$), 5.21 (s, 1H, C=CH), 6.98 (d, 2H, J = 8.1 Hz, C_6H_4), 7.44 (d, 2H, J = 8.1 Hz, C_6H_4), 12.43 (s, 1H, NH); Anal. Calcd for $C_{11}H_{12}BrNO$ (254): C, 51.99; H, 4.76; N, 5.51; Found: C, 51.98; H, 4.77; N, 5.52%.

(Z)-4-(Naphthalen-1-ylamino)-pent-3-en-2-one **(3f):** Buff solid: m.p. 51–53 °C; IR (KBr cm^{-1}) 3471, 3056, 1599, 1550, 1500, 1429, 1382, 1280, 1156, 1080, 1020, 984, 912, 781, 727; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.82 (s, 3H, CH_3C=C), 2.15 (s, 3H, $COCH_3$), 5.31(s, 1H, C=CH), 7.26–8.04(m, 7H, Ar), 12.75 (s, 1H, NH); Anal. Calcd for $C_{15}H_{15}NO$ (225): C, 79.97; H, 6.71; N, 6.22; Found: C, 79.90; H, 6.80; N, 6.18%.

(Z)-4-(Naphthalen-2-ylamino)-pent-3-en-2-one **(3g):** Pink solid: m.p. 100 °C; IR (KBr cm^{-1}) 3430, 3057, 3014, 2898, 1615, 1586, 1515, 1467,1435, 1380, 1348, 1283, 1175, 1121, 1028, 958, 861, 826, 752; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.02 (s, 3H, CH_3C=C), 2.18 (s, 3H, $COCH_3$), 5.24(s, 1H, C=CH), 7.23–7.82(m, 7H, Ar), 12.65 (s, 1H, NH); Anal. Calcd for $C_{15}H_{15}NO$ (225): C, 79.97; H, 6.71; N, 6.22; Found: C, 79.92; H, 6.75; N, 6.18%.

(Z)-3-(Phenylamino)-but-2-enoic acid ethyl ester **(3h):** Yellow oil: IR (KBr cm^{-1}) 3257, 3184, 2979, 1653, 1620, 1592, 1495, 1440, 1385, 1357, 1271, 1231, 1163, 1094, 1058, 1022, 976, 788, 752, 698; ^{1}H NMR ($CDCl_3$, 300 MHz) δ1.26 (t, 3H, J = 6.9 Hz, OCH_2CH_3), 2.06 (s, 3H, CH_3), 4.13(q, 2H, J = 6.8 Hz, OCH_2CH_3), 4.69(s, 1H, C=CH), 7.04–7.31(m, 5H, C_6H_5), 10.42 (s, 1H, NH); Anal. Calcd for $C_{12}H_{15}NO_2$ (205): C, 70.22; H, 7.37; N, 6.82; Found: C, 70.20; H, 7.42; N, 6.75%.

(Z)-3-(4-Methyl-phenylamino)-but-2-enoic acid ethyl ester **(3i):** Wine red oil: IR (KBr cm^{-1}) 3259, 2979, 2927, 1653, 1608, 1577, 1517, 1488, 1440, 1384, 1357, 1270, 1230, 1162, 1095, 1058, 1019, 807, 787; ^{1}H NMR ($CDCl_3$, 300 MHz) δ1.26 (t, 3H, J = 6.9 Hz, OCH_2CH_3), 1.92 (s, 3H, CH_3), 2.35 (s, 3H, $C_6H_4CH_3$), 4.13 (q, 2H, J = 6.9 Hz, OCH_2CH_3), 4.66 (s, 1H, C=CH), 6.95 (d, 2H, J = 7.7 Hz, C_6H_4), 7.09 (d, 2H, J = 7.7 Hz, C_6H_4), 10.33 (s, 1H, NH) Anal. Calcd for $C_{13}H_{17}NO_2$ (219) C, 71.21; H, 7.81; N, 6.39; Found: C, 71.18; H, 7.90; N, 6.35%.

(Z)-3-(4-chloro-phenylamino)-but-2-enoic acid ethyl ester **(3j):** White solid: m.p. 70–71 °C; IR (KBr cm^{-1}) 3278, 3071, 2979, 2925, 1647, 1610, 1584, 1481, 1439, 1437, 1387, 1351, 1260, 1168, 1062, 1012, 981, 856, 789; ^{1}H NMR ($CDCl_3$, 300 MHz) δ1.29 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 1.95 (s, 3H, CH_3), 4.16 (q, 2H, J = 7.1 Hz, OCH_2CH_3), 4.71 (s, 1H, C=CH), 7.00 (d, 2H, J = 8.3 Hz, C_6H_4), 7.28 (d, 2H, J = 8.6 Hz, C_6H_4), 10.35 (s, 1H, NH); Anal. Calcd for $C_{12}H_{14}ClNO_2$ (239): C, 60.13; H, 5.89; N, 5.84; Found: C, 60.12; H, 5.90 N, 5.83%.

(Z)-3-(4-Bromo-phenylamino)-but-2-enoic acid ethyl ester **(3k):** Buff solid: m.p. 53–54 °C; IR (KBr cm^{-1}) 3275, 3068, 2978, 1646, 1609, 1578, 1479, 1437, 1387, 1352, 1260, 1162, 1005, 853, 790, 719; ^{1}H NMR ($CDCl_3$, 300 MHz) δ1.28 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 2.01 (s, 3H, CH_3), 4.15 (q, 2H, J = 7.0 Hz, OCH_2CH_3), 4.72 (s,1H, C=CH), 6.95(d, 2H, J = 8.1 Hz, C_6H_4), 7.43(d, 2H, J = 8.1 Hz, C_6H_4), 10.35 (s, 1H, NH); Anal. Calcd for $C_{12}H_{14}BrNO_2$ (283): C, 50.72; H, 4.97; N, 4.93; Found: C, 50.75; H, 4.80; N, 4.98%.

(Z)-4-(Naphthalen-1-ylamino)-but-2-enoic acid ethyl ester **(3l):** Red oil: IR (KBr cm^{-1}) 3244, 3047, 2977, 2931, 1651, 1607, 1484, 1435, 1382, 1336, 1272, 1157, 1087, 1058, 1018, 976, 784; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (t, 3H, J = 6.8 Hz, OCH_2CH_3), 2.00 (s, 3H, CH_3), 4.21 (q, 2H, J = 6.7 Hz, OCH_2CH_3), 4.82 (s, 1H, C=CH), 7.19–8.06(m, 7H, Ar), 10.63 (s, 1H, NH); Anal. Calcd for $C_{16}H_{17}NO_2$ (255): C, 75.27; H, 6.71; N, 5.49; Found: C, 75.30; H, 6.77; N, 5.45%.

(Z)-4-(Naphthalen-2-ylamino)-but-2-enoic acid ethyl ester **(3m):** Pink solid: m.p. 67–68 °C; IR (KBr cm^{-1}) 3257, 3057, 2983, 2930, 1646, 1599, 1490, 1436, 1384, 1339, 1257, 1156, 1057, 1019, 974, 901, 865, 830, 784; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (t, 3H, J = 7.0 Hz, OCH_2CH_3), 2.16 (s, 3H, CH_3), 4.18 (q, 2H, J = 7.0 Hz, OCH_2CH_3), 4.75 (s, 1H, C=CH), 7.21–7.80 (m, 7H, Ar), 10.58 (s, 1H, NH); Anal. Calcd for $C_{16}H_{17}NO_2$ (255): C, 75.27; H, 6.71; N, 5.49; Found: C, 75.29; H, 6.78; N, 5.50%.

(Z)-3-(4-Methyl-phenylamino)-1-phenylbut-2-en-1-one **(3n):** Yellow solid: m.p. 88–89 °C; IR (KBr cm^{-1}) 3441, 2918, 2849, 1601, 1569, 1504, 1438, 1380, 1320, 1284, 1195, 1064, 1024, 929, 831, 806, 715; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.11 (s, 3H, CH_3), 2.35 (s, 3H, $C_6H_4CH_3$), 5.87 (s, 1H, C=CH), 7.06 (d, 2H, J = 8.2 Hz, C_6H_4), 7.16 (d, 2H, J = 8.1 Hz, C_6H_4),7.22–7.92 (m, 5H, C_6H_5), 13.03 (s, 1H, NH); Anal. Calcd for $C_{17}H_{17}NO$ (251): C, 81.24; H, 6.82; N, 5.57; Found: C, 81.25; H, 6.83; N, 5.58%.

(Z)-3-(benzylamino)-1-phenylbut-2-en-1-one **(3o):** Beige solid: m.p. 63–64 °C; IR (KBr cm^{-1}) 3055, 3023, 2920, 1602, 1542, 1519, 1445, 1368, 1308, 1062, 1023, 970, 874, 790; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.06 (s, 3H, CH_3), 4.53 (s, 2H, CH_2), 5.74 (s, 1H, C=CH), 7.25–7.35 (m, 5H, $C_6H_5CH_2$),7.38–7.88 (m, 5H, C_6H_5),11.76 (s, 1H, NH); Anal. Calcd for $C_{17}H_{17}NO_2$ (251): C,81.24; H, 6.82; N, 5.57; Found: C, 81.25; H, 6.84; N, 5.56%.

(Z)-3-(2-hydroxyethylamino)-1-phenylbut-2-en-1-one **(3p):** Beige solid: m.p. 80–81 °C; IR (KBr cm^{-1}) 1597, 1546; 1H NMR ($CDCl_3$, 300 MHz) δ:1.99 (s, 3H, CH_3), 3.42 (brs, 1H, OH), 3.45 (q, J = 5.1 Hz, 2H, $NHCH_2$), 3.79 (t, J = 4.4 Hz, 2H CH_2OH,), 5.63 (s, 1H, C=CH), 7.26–7.84 (m, 5H, C_6H_5), 11.46 (s, 1H, NH); Anal. Calcd for $C_{12}H_{15}NO_2$(205): C, 70.24; H, 7.32, N, 6.83; found C,70.19; H, 7.30; N, 6.86%.

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