A solvent-free synthesis of β-amino-α,β-unsaturated ketones and esters catalysed by sulfated zirconia

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β-Amino-α,β-unsaturated ketones and esters are synthesised by the condensation of β-dicarbonyl compounds with amines in the presence of a solid superacid sulfated zirconia (SO_4^{2-}/ZrO_2, SZ) under solvent-free conditions.

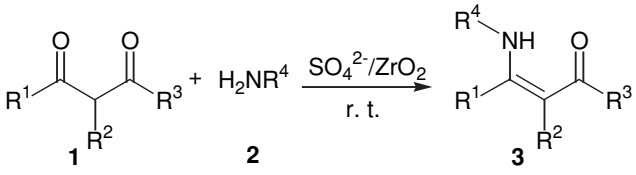
Keywords: β-amino-α,β-unsaturated ketones, β-amino-α,β-unsaturated esters, β-diketone, β-keto ester, amines, sulfated zirconia

β-Amino-α,β-unsaturated ketones and esters are synthetic intermediates in the construction of heterocyclic compounds such as dihydropyridines,[1] pyridines,[2] pyrimidines,[3] indoles,[4] and isothiazoles.[5] They also possess good stability under simulated physiological pH conditions and have a low toxicity.[6] A number of reviews on the chemistry of β-amino-α,β-unsaturated ketones and esters, have been published.[7]

A variety of methods for the synthesis of β-amino-α,β-unsaturated ketones and esters have been developed.[8] The condensation of 1,3-dicarbonyl compounds with amines is the most simple and straightforward synthetic route. However, it usually requires the azeotropic removal of water under reflux using a Dean Stark trap and an aromatic solvent.[9] A variety of catalysts such as HCl,[10] H_2SO_4,[11] *p*-TSA,[12] HAc,[13] trimethylsilyl trifluoromethanesulfonate (TMSTf),[14] montmorillonite K10 under microwave irradiation[15] or ultrasound,[16] I_2,[10b] $BF_3{\cdot}OEt_2$,[17] Al_2O_3,[18] silica gel,[19] $Zn(ClO_4)_2{\cdot}6H_2O$,[20] $CeCl_3{\cdot}7H_2O$,[21] $NaAuCl_4$,[22] $Bi(OTf)_3$[23]and natural clays[24] have been used to effect this transformation. Recently, these compounds have been prepared by direct condensation of β-dicarbonyl compounds and primary amines in water as solvent.[25] The various disadvantages (*e.g.* long reaction[19], high temperature,[10a,12,14,24] use of costly catalysts,[22] high catalyst loading,[21] use of an additional microwave oven[15] and ultrasound,[13b,16] *etc.*) encountered in the reported methodologies necessitate the development of a better method.

Recently attention has been devoted to heterogeneous organic transformations utilising inorganic solid acids.[26] These offer several advantages such as mild reaction conditions, high selectivity, high yields and ease of work-up. Among the various solid acid catalysts investigated, sulfated zirconia has attracted attention because of its superior catalytic activity, nontoxicity and low cost.[27] Many large volume applications based on sulfated zirconia are reported in the literature,[28] especially in the petrochemical industry for light alkane isomerisation and alkylation reactions.[29] As a part of our program aimed at developing selective and environmentally friendly methodologies for the preparation of fine chemicals and in continuation of our interest in solid acid catalysed organic reactions,[30] we report a facile method for the preparation of β-amino-α,β-unsaturated ketones and esters under solvent-free conditions catalysed by a solid superacid catalyst (Scheme 1).

The condensation reaction of 2-bromoaniline (**2h**) was selected as the model system for the enamination reaction with acetylacetone in order to optimise the reaction conditions. The reactions were carried out by taking a 1:1 mole ratio mixture of **2h** and acetylacetone in a round bottom flask with stirring at ambient conditions for 26 h without adding any catalyst under solvent-free condition. The result showed more than 90% of **2h** was recovered. By contrast, in the presence of 30 mg sulfated zirconia β-enaminone **3h** has been



Scheme 1

isolated with an 86% yield under the same reaction. Lower catalyst loading can be used with only a drop in reaction rate. A variety of primary, benzylic and aromatic amines reacted with acetylacetone effectively to afford the corresponding β-enaminone. The results are summarised in Table 1. In general, for primary and benzylic amines, the condensation reactions usually afforded the corresponding β-amino-α,β-unsaturated ketones in over 90% yields in a short time. The presence of an electron-withdrawing group on the benzene ring decreased the reactivity of the substrate (**1g** and **1h**). It should be pointed out that in the reaction of 1-benzoylacetone with amines the regioselective amination of the aliphatic carbonyl group (**1i** and **1j**) was observed.

This method was successfully applied to synthesis of β-amino-α,β-unsaturated esters. Linear (**1k–1t**) and cyclic (**1u–1z**) β-ketoesters were treated with a range of amines under the same conditions. In all cases, the reactions proceeded rapidly and smoothly at room temperature and in comparison to the other methods, the products were obtained in excellent yields and chemoselectivity to afford the *Z*-β-enaminones. This was confirmed by the ^{1}H NMR spectrum of the products (δ = 9.3–12.92 ppm for NH).[21] In the case of 1,3-diaminopropane, 2 equiv of methyl acetoacetate were used giving products with two enamino ester groups (**3m**).

Recycling of catalyst was also investigated. After completion of the reaction, 20 ml of ethyl acetate was added to the reaction mixture and the catalyst was recovered by filtration. The wet catalyst was recycled and no appreciable change in activity was noticed after three cycles.

In summary, the use of SO_4^{2-}/ZrO_2 solid superacid catalyst for the synthesis of β-amino-α,β-unsaturated ketones and esters from β-dicarbonylic compounds and amines is an environmentally benign and atom economic process. The present method has the following advantages compared to those reported in the previous literatures: (1) high catalytic activity and yield of products, (2) simple workup procedure, (3) reusable catalyst and (4) under solvent-free conditions.

Experimental

Melting points were recorded on X-4 apparatus and are uncorrected. IR spectra were recorded on a Bio-Rad FTS 135 spectrophotometer.^{1}H NMR spectra were recorded with a Bruker spectrometer at 300 MHz using TMS as internal standard. Elemental analyses were performed on a Yanaca CDRDER MT-3 analyser.

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Table 1 The preparation of β-amino-α,β-unsaturated ketones and esters catalysed by SO_4^{2-}/ZrO_2

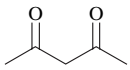
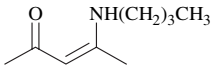
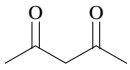
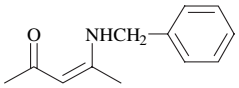
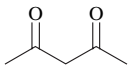
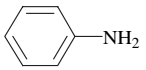
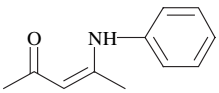
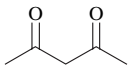
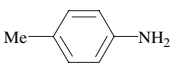
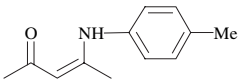
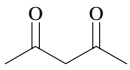
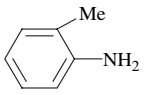
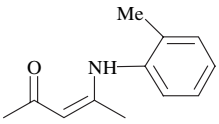
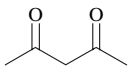
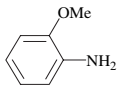
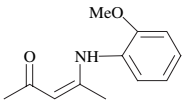
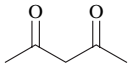
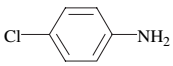
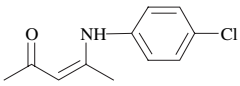
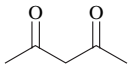
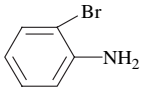
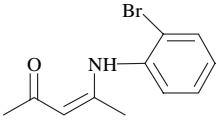
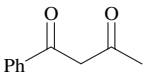
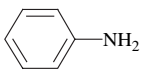
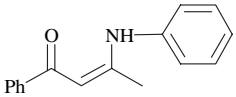
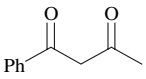
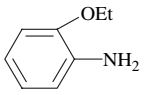
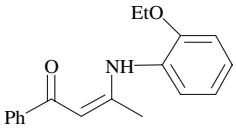
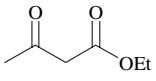
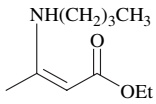
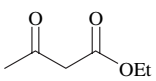
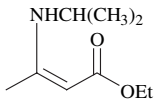
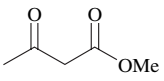
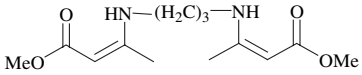
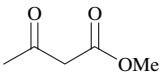
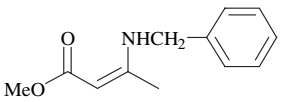
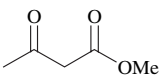
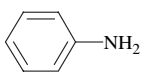
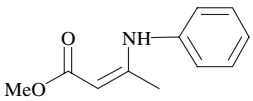
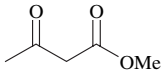
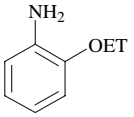
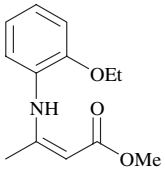
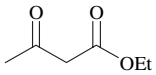
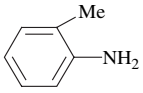
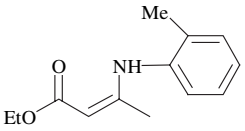
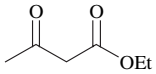
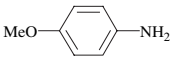
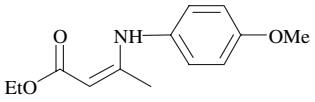
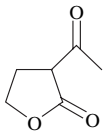
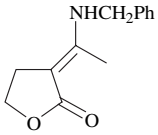
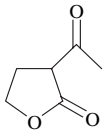
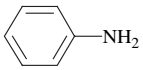
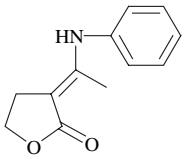
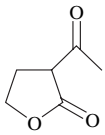
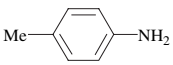
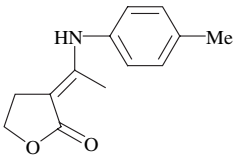
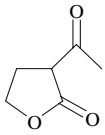
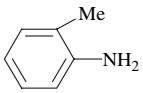
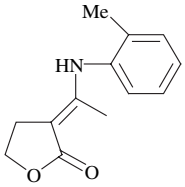
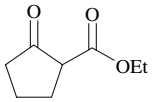
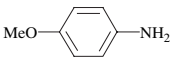
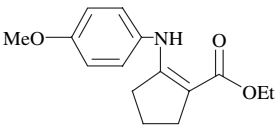
Entry	1,3-Dicarbonyl	Amine	Product	Time/min	Yield/%[a]	M.p.(T/°C) [b.p.(T/°C)/torr	
						Found	Reported
a				20	92	93–95/2	92–94/2[31]
b				18	93	23–24	23–24.5[32]
c				10	95	49–50	48–49[19]
d				10	91	58–59	59–60[23]
e				15	95	38–39	
f				16	94	50–51	51–51.5[33]
g				180	80	60–62	60–61[33]
h				360	86	72–73	72–74[34]
i				50	83	109–110	109–110[11]
j				100	78	104–105	
k				40	94	75–77/2	88/3[31]
l				80	90	73–75/2	75/2[13b]
m				25	92[b]	69–70	
n				25	93	37–38	
o				30	91	46–47	43–45[35]

Table 1 *continued*

Entry	1,3-Dicarbonyl	Amine	Product	Time/min	Yield/%[a]	M.p.(T/°C) [b.p.(T/°C)/torr	
						Found	Reported
p				70	93	45–46	
s				80	92	133–136/2	147/4[36]
t				25	92	43–44	44.5–45[36]
u				30	92	106–107	105–107[21]
w				35	95	90–92	94–95[19]
x				35	93	90–92	92–94[21]
y				120	89	71–73	
z				100	92	52–54	54[13a]

[a]Isolated yield. [b]2 Equiv of methyl acetoacetate (with respect to propane-1,3-diamine) was used.

Preparation of the catalyst: $ZrOCl_2 \cdot 8H_2O$ (25 g) was dissolved in distilled water. To this solution, dilute aqueous ammonia was added drop-wise with vigorous stirring until the pH of the solution reached 8. The precipitate was washed with distilled water several times until it was free from chloride ions and then dried at 393 K for 24 h. The sample thus obtained was ground to a fine powder and immersed in an 0.5 mol/l H_2SO_4 solution (30 ml) for 30 min. Excess water was evaporated on a water bath and the resulting sample was oven dried at 393 K for 12 h and calcined at 873 K for 4 h.[28e]

General procedure for the preparation of β-*amino*-α,β-*unsaturated ketones and esters*

Equimolar amounts of amine (5 mmol) and β-dicarbonylic compounds along with the catalyst (30 mg) were placed in a round bottom flask and stirred with a magnetic stirrer at ambient conditions. After completion of the reaction (monitored by TLC), 20 ml of ethyl acetate was added to the reaction mixture and the catalyst was recovered by filtration. The organic layer was concentrated and the product was purified by silica gel chromatography and eluted by an ethyl acetate and *n*-hexane (2:8 v/v) mixture. The wet catalyst was used for recycling and no appreciable change in the activity was noted after three times cycles.

Spectroscopic and analytical data for new compounds (see Table 1)

4-o-Tolylamino-pent-3-en-2-one (**3e**): IR (KBr): 3448, 2971, 1595, 1560, 1278, 1176, 1027, 823, 755 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 1.87 (s, 3H), 2.11 (s, 3H), 2.28 (s, 3H), 5.20 (s, 1H), 7.09–7.23 (m, 4H), 12.32 (br s, 1H, NH). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.30; H, 7.86; N, 7.62.

3-(2-Ethoxy-phenylamino)-1-phenyl-but-2-en-1-one (**3j**): IR (KBr): 3413, 2978, 1613, 1591, 1577, 1437, 1282, 1121, 1040, 921, 742 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 1.42 (t, *J*=6.9 Hz, 3H), 2.06 (s, 3H),

4.03 (q, *J*=6.9 Hz, 2H), 5.86 (s, 1H), 6.88 (d, *J*=8.7 Hz, 2H), 7.15 (d, *J*=8.7 Hz, 2H), 7.42–7.44 (m, 3H), 7.89–7.92 (m, 2H), 12.92 (br s, 1H, NH). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.95; H, 6.92; N, 4.71.

3-[3-(2-Methoxycarbonyl-1-methyl-vinylamino)-propylamino]-but-2-enoic acid methyl ester (**3m**): IR (KBr): 3443, 2947, 1655, 1602, 1269, 1170, 1053, 786 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 1.83 (t, *J*=6.3 Hz, 2H), 1.92 (s, 6H), 3.30 (t, *J*=6.3 Hz, 4H), 3.62 (s, 6H), 4.47 (s, 2H), 8.55 (br s, 2H, NH). Anal. Calcd for $C_{13}H_{22}N_2O_4$: C, 57.76; H, 8.20; N, 10.36. Found: C, 57.58; H, 8.42; N, 10.20.

3-Benzylamino-but-2-enoic acid methyl ester (**3n**): IR (KBr): 3442, 2947, 1655, 1602, 1506, 1269, 1170, 1053, 786 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 1.92 (s, 3H), 3.63 (s, 3H), 4.43 (d, *J*=6.3 Hz, 2H), 4.53 (s, 1H), 7.24–7.28 (m, 3H), 7.32–7.36 (m, 2H), 8.94 (br s, 1H, NH). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.45; H, 7.18; N, 6.99.

3-(2-Ethoxy-phenylamino)-but-2-enoic acid methyl ester (**3p**): IR (KBr): 3413, 2975, 1658, 1622, 1582, 1514, 1483, 1271, 1165, 1008, 925, 788 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 1.45 (t, *J*=6.9 Hz, 3H), 2.01 (s, 3H), 3.68 (s, 3H), 4.08 (q, *J*=6.9 Hz, 2H), 4.70 (s, 1H), 6.86–6.91 (m, 2H), 7.06–7.11 (m, 2H), 10.27 (br s, 1H, NH). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.50; H, 7.09; N, 6.12.

3-(1-o-Tolylamino-ethylidene)-dihydro-furan-2-one (**3y**): IR (KBr): 3417, 2909, 1682, 1637, 1509, 1287, 1125, 1021, 968, 746 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 1.89 (s, 3H), 2.28 (s, 3H), 2.91 (t, *J*=7.8 Hz, 2H), 4.36 (t, *J*=7.8 Hz, 2H), 7.01–7.23 (m, 4H), 9.77 (br s, 1H, NH). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.69; H, 7.12; N, 6.61.

2-(4-Methoxy-phenylamino)-cyclopent-1-enecarboxylic acid ethyl ester (**3z**): IR (KBr): 3266, 2954, 1623, 1579, 1516, 1148, 1046, 822 cm^{-1}. ^1H NMR ($CDCl_3$) δ ppm: 1.30 (t, *J*=7.2 Hz, 3H), 1.80–1.88 (m, 2H), 2.56 (t, *J*=7.2 Hz, 2H), 2.64 (t, *J*=7.2 Hz, 2H), 3.78 (s, 3H), 4.19 (q, *J*=7.2 Hz, 2H), 6.83 (d, *J*=8.7 Hz, 2H), 6.99 (d, *J*=8.7 Hz, 2H), 9.30 (br s, 1H, NH). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 69.08; H, 7.22; N, 5.58.

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