Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Sulfamic Acid as an Effective Catalyst in Solvent-Free Synthesis of β-Enaminoketone Derivatives and X-ray Crystallography of Their Representatives

Min Xia [a], Bin Wu [a] & Guo-Feng Xiang [a]

[a] Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, China

Available online: 17 Apr 2008

To cite this article: Min Xia, Bin Wu & Guo-Feng Xiang (2008): Sulfamic Acid as an Effective Catalyst in Solvent-Free Synthesis of β-Enaminoketone Derivatives and X-ray Crystallography of Their Representatives, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 38:8, 1268-1278

To link to this article: http://dx.doi.org/10.1080/00397910701873250

Synthetic Communications®, 38: 1268–1278, 2008

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910701873250

Sulfamic Acid as an Effective Catalyst in Solvent-Free Synthesis of β-Enaminoketone Derivatives and X-ray Crystallography of Their Representatives

Min Xia, Bin Wu, and Guo-Feng Xiang

Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, China

Abstract: Two types of β-enaminoketone derivatives of 3-(2-oxo-2-arylethylidene)-3,4-dihydro-1H-quinoxalin-2-ones and 3-(2-oxo-2-arylethylidene)-3,4-dihydro-benzo[1,4]oxazin-2- ones were effectively and conveniently prepared in good to excellent yields under solvent-free conditions via the catalysis of sulfamic acid in the corresponding condensations of o-phenylenediamine and o-aminophenol with ethyl 2,4-dioxo-4-arylbutyrate respectively. The compounds were confirmed by IR, ^{1}H NMR, and ^{13}C NMR, and a representative was further determined by X-ray crystallography.

Keywords: Catalysis, β-enaminoketone, solvent free, sulfamic acid, X-ray crystallography

It is well known that β-enolic ketones are O,O-double dentates with powerful capacity to form of various complexes with many metal or nonmetal species. However, their isosteres. β-enaminoketones, are not as familiar as the N,O-double dentates: the complicated and difficult preparations as well as their chemical instability can be attributed to a few reports[1−4] in the literature on their utilizations as ligands. To overcome those drawbacks, β-enaminoketones are designed and arranged into some heterocycles.

Received in Japan October 12, 2007
Address correspondence to Min Xia, Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China. E-mail: xiamin@zstu.edu.cn

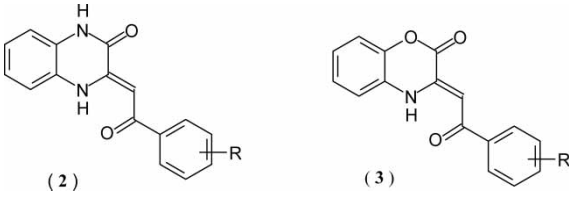
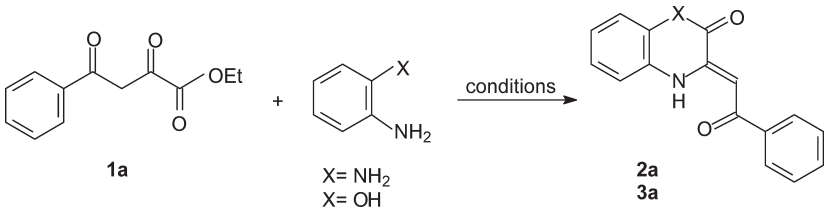


Figure 1. Structures of compound **2** and **3**.

3-(2-Oxo-2-arylethylidene)-3,4-dihydro-1*H*-quinoxalin-2-ones (**2**) and 3-(2-oxo-2-arylethylidene)-3,4-dihydro-benzo[1,4]oxazin-2-ones (**3**) are two types of heterocycles in which β-enaminoketone structures can be skillfully inserted (Fig. 1). To best of our knowledge, there has been no report in the literature on their applications as N,O-double dentates in formation of any complexes.

In the literature, several methods have described the preparations of **2** and **3**, such as 5-aryl-2,3-furandione reacting with a nucleophile and subsequent treatment of *o*-phenylenediamine (*o*-PDA)/*o*-aminophenol (*o*-AP),[5] arylethanones treated with 2-oxo-1,2,3,4-4*H*-quinoxaline in the presence of copper(I) chloride,[6] nucleophilic recyclization of pyrrolo[5,1-*c*][1,4] benzoxazine-1,2,4-triones with *o*-PDA/*o*-AP,[7] α-keto-β-substituted-γ-butyrolactones treated with *o*-PDA/*o*-AP,[8] 4-arylsulfonyl-2-hydroxy-3-aryl-2-cyclobutan-1-ones treated with bisnucleophiles such as *o*-PDA/*o*-AP,[9] thermolysis of 3-bromo-4-aryl-2,4-dioxobutanones with diphenyldiazamethane and *o*-PDA/*o*-AP,[10] recyclization of 3-aroyl-4-methoxycarbonyl-3*H*-1,5-benzodiazepine-2-carboxylates in acidic media,[11] and regioselective synthesis involving 1,3,4,6-tetracarbonyl compounds with *o*-PDA/*o*-AP.[12] However, these methodologies are associated with several drawbacks such as complicated routes, prolonged reaction times, harsh conditions, low product yields, occurrence of some side reactions, very expensive and not easily available substrates, heavy environmental pollution, and so on.

In the past years, owning to its prominent physical and chemical properties such as outstanding stability, nontoxicity, nonvolatility, odorlessness, ready availability, and extremely inexpensive price, sulfamic acid (SA) has increasingly attracted attention as an alternative acidic catalyst in many heterogeneously catalytic reactions.[13–20] Moreover, solid-state reactions have become an intriguing strategy in organic synthesis because of their general merits such as improved yields, shortened time, mild conditions, and avoidance of organic solvents.[21–26] In connection with our research on utilization of SA and development of solvent-free reactions,[27–29] herein we report that 3-(2-oxo-2-arylethylidene)-3,4-dihydro-1*H*-quinoxalin-2-ones (**2**) and 3-(2-oxo-2-arylethylidene)-3,4-dihydro-benzo[1,4]oxazin-2-ones (**3**) can be efficiently and readily generated via the catalysis of SA in the solid-state condensation of aroylpyruvates with *o*-PDA/*o*-AP.

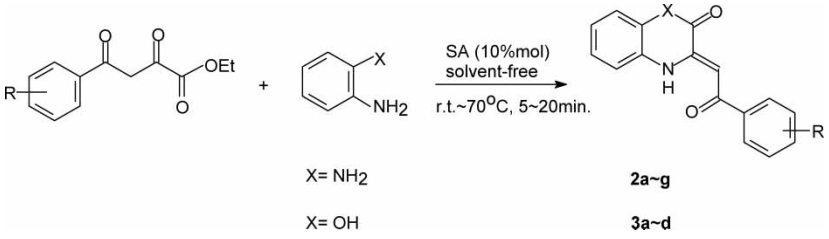


Scheme 1.

First, ethyl benzoylpyruvate was selected as the case to investigate the catalysis of SA (Scheme 1), and the results are indicated in Table 1. In methanol, a yellow solid was precipitated and isolated in 38% yield when ethyl benzoylpyruvate and *o*-phenylenediamine were mixed and stirred at room temperature for 30 min. Instead, when the two substrates were mixed and ground at room temperature, they turned syrupy. The melted mixture was kept for 5 min and gradually solidified. Through washing with methanol, **2a** was collected in 61% yields. The yield of 3-(2-oxo-2-phenylethylidene)-3,4-dihydro-1*H*-quinoxalin-2-one **2a** could be improved dramatically to 82% when 10 mol% SA was added to the mixture under solvent-free conditions. It seemed that 10 mol% SA was sufficient to drive this solid-state condensation, because of more than that amount of catalyst could not significantly increase the yield of **2a**. In the case of the condensation of ethyl benzoylpyruvate with *o*-aminophenol at room temperature, the solution-phase reaction afforded just product **3a** in 31% yield even if the cyclization was carried out in a much prolonged time. Because of the weak nucleophility of *o*-aminophenol, the solid-state reaction involved with it was difficult to execute at room temperature, and **3a** was produced in only 18% yield. It was apparent that increased reaction temperature would be beneficial to

Table 1. Reaction conditions in the generation of compounds **2a** and **3a**

Entry	Compound	Conditions	Temp (°C)	Time (min)	Yield (%)
1	**2a**	MeOH	rt	30	38
2	**2a**	No solvent	rt	5	61
3	**2a**	No solvent/SA (5 mol%)	rt	5	73
4	**2a**	No solvent/SA (10 mol%)	rt	5	81
5	**2a**	No solvent/SA (15 mol%)	rt	5	83
6	**3a**	MeOH	rt	60	31
7	**3a**	No solvent	rt	8	18
8	**3a**	No solvent	70	8	47
9	**3a**	No solvent/SA (5 mol%)	70	8	62
10	**3a**	No solvent/SA (10 mol%)	70	8	73
11	**3a**	No solvent/SA (15 mol%)	70	8	75



Scheme 2.

such solvent-free condensation, because the yield of **3a** was remarkably improved to 47% when the reaction took place at 70 °C. In the presence of 10 mol% SA, the production of **3a** could be further improved to 73% yield. Clearly, the combination of the maximum substrate concentration in the solid-state reactions with the positive catalyst effect resulted in better yields and shorter reaction times than those of the same reactions in solution phase.

According to these facts, the scope of such protocol was tested (Scheme 2), and the results are shown in Table 2. Obviously, SA played the role of an effective catalyst in the solvent-free generations of 3-(2-oxo-2-arylethylidene)-3,4-dihydro-1*H*-quinoxalin-2-ones (**2**) and 3-(2-oxo-2-arylethylidene)-3,4-dihydro-benzo[1,4]oxazin-2-ones (**3**), because all the involved transformations could be carried out within 5–20 min. Besides, ethyl aroylpyruvates were also efficient candidates for the cyclizations with *o*-phenylenediamine or *o*-aminophenol in good to excellent yields. Apparently, an outstanding electronic effect existed in production of compounds **2** and **3**, in which aroylpyruvates containing electron-withdrawing group like NO_2 on aromatic rings afforded only the corresponding products of **2d** and **3d** in 61% and 50% yields respectively, even if their reactions consumed more time, whereas those aroylpyruvates having electron-

Table 2. SA-promoted solid-state synthesis of β-enaminoketone derivatives

Entry	Compound	X	R	Temp (°C)	Time (min)	Yield (%)
1	**2a**	NH_2	H	rt	5	81
2	**2b**	NH_2	4-CH_3O	rt	5	86
3	**2c**	NH_2	4-Cl	rt	10	77
4	**2d**	NH_2	4-NO_2	rt	15	61
5	**2e**	NH_2	4-NH_2	rt	5	81
6	**2f**	NH_2	4-OH	rt	5	88
7	**3a**	OH	H	70	8	73
8	**3b**	OH	4-CH_3O	70	8	76
9	**3c**	OH	4-Cl	70	15	69
10	**3d**	OH	4-NO_2	70	20	50

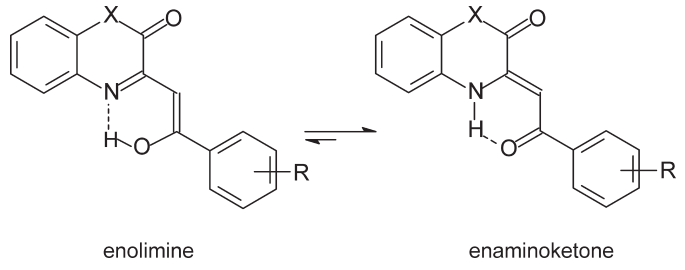


Figure 2. Enaminoketone-enolimine tautomeric equilibrium of compounds **2** and **3**.

donating groups such as methoxyl on their aromatic rings could execute the condensations with improved yields. Because of the weaker nucleophility of hydroxyl than of amino, the yields of products **3** were universally poorer than those of products **2**, but the reaction time was prolonged and it was necessary to raise the reaction temperature for the generation of compounds **3**.

For products **2** and **3**, there are two types of theoretical tautomers (i.e., enolimines and enaminoketones, Fig. 2). In spite of their potential both as N,O-double-dentate ligands, the different structures have distinctively dissimilar behaviors in generation of complexes. Therefore, it is necessary to determine which tautomeric type these important compounds dominantly adopted in their solid and solution states through some more convincing evidence.

Although IR spectra can afford some information about a molecule's structure in its solid state, they are not sufficient and forceful enough, even unidentifiable in many cases. X-ray crystallography can supply more reliable information about the actual structure for a given molecule. Therefore, compound **3b** was screened as an example for X-ray crystallographic measurement. By examining the bond lengths in **3b** (Fig. 3), it was found that C_{10}-O_3 (1.25 Å) and C_8-C_9 (1.36 Å) distances were slightly more stretched than the standard[30] C═O bond (1.20 Å) and C═C bond (1.34 Å), whereas the

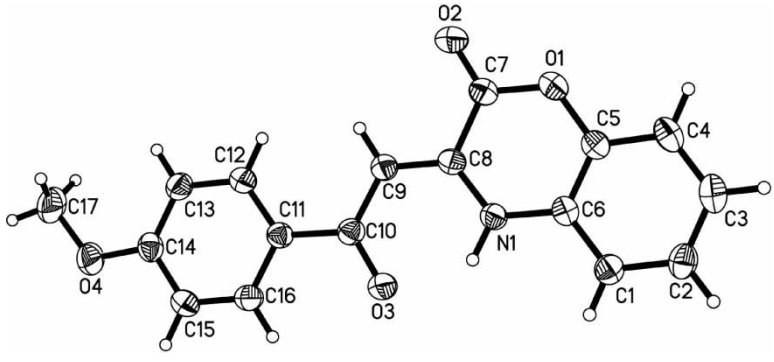


Figure 3. The molecular structure of compound **3b**.

lengths of C_8-N_1 (1.35 Å) and C_9-C_{10} (1.43 Å) were remarkably shorter than those of standard[30] C-N (1.47 Å) and C-C (1.54 Å) bonds, respectively; they were closer to heteroaromatic C═N (1.34 Å) and aromatic C═C (1.40 Å) distances. This indicated that there was obvious delocalization of electrons on the bonds, enolimine structure existed in the tautomeric equilibrium to some degree, but the molecular structure should be dominantly presented as an enaminoketone form in its solid state.

In solution states, it seemed that the ^{13}C NMR spectrum was more favorable than ^{1}H NMR as an effective tool to distinguish unsaturated carbonyl from enolic carbon atoms in such an enolimine- enaminoketone equilibrium. It could be clearly deduced by the ^{13}C NMR spectra of these samples that carbonyls instead of enolic double bonds existed in their molecular structures, because the chemical shifts in the lowest field were located at 185–191 ppm, which corresponded to the approximately standard unsaturated ketones. For enolic carbon atoms attached to hydroxyl, their signals should appear at 150–160 ppm. This phenomenon could account for the fact that the amount of enaminoketone-type structures in solution state was the overwhelming majority in above tautomeric equilibrium. Therefore, such equilibrium between enolimine and enaminoketone was largely shifted to the side of the latter in both solution and solid state.

Herein we describe an effective and convenient approach to 3-(2-oxo-2-arylethylidene)-3,4-dihydroquinoxalin-2(1*H*)-ones and 3-(2-oxo-2-arylethylidene)-3,4-dihydrobenzo[*b*][1,4]oxazin-2-ones via the solid-state condensations of aroylpyruvates with *o*-phenylenediamine or *o*-aminophenol in the catalysis of sulfamic acid. The mild conditions and brief reaction time in addition with good yields and simple operations make our protocol an attractive method for the rapid and efficient preparation of such compounds. The work concerned with their applications as the β-enaminoketone ligands in formation of some novel complexes are in the progress.

EXPERIMENTAL

All the compounds used were analytical reagents, and some chemicals were further purified by recrystallization or distillation. Melting points were determined on an X-4 micromelting instrument, and the thermometer was uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker Avance DMX 400-MHz and 100-MHz instruments respectively using TMS as internal standard in DMSO-d_6. FT-IR spectra were recorded on a Nicolet Avatar 700 spectrophotometer in KBr pellets. X-ray crystallographic data was collected on Rigaku Raxis-Rapid.

General Procedure for the Solvent-Free Synthesis of 2 or 3

At room temperature, aroylpyruvate (1.0 mmol), *o*-phenylenediamine (1.2 mmol) or *o*-aminophenol (1.2 mmol), and SA (10% mol) were mixed

and ground completely. The mixture turned syrupy and was kept at room temperature for *o*-phenylenediamine or at 70 °C for *o*-aminophenol for the appropriate time. The solidified lumps were crushed and washed with water, MeOH, and ether successively two or three times. The obtained solid was pure enough for further spectroscopic analysis.

Data

Compound 2a: Mp 259–260 °C (lit.[31] 266–267 °C); FT-IR (KBr) ν 1685, 1607, 1377, 1262, 1110, 1023, 833, 805, 754 cm^{-1}; ^1H NMR(400 MHz, DMSO-d_6) δ 6.82 (s, 1H, CH═C), 7.15 (s, 3H, Ar-Hs), 7.52–7.61 (m, 4H, Ar-H), 7.99 (d, $J = 7.6$ Hz, 2H, Ar-H), 12.06 (s, 1H, NHCO), 13.65 (s, 1H, *NH*C═CH); ^{13} C NMR (100 MHz, DMSO-d_6) δ 89.55, 115.74, 115.81, 116.90, 117.05, 124.17, 124.43, 127.47, 129.23, 132.41, 139.12, 145.69, 156.10, 188.95.

Compound 2b: Mp 241–243 °C (lit.[31] 245–246 °C); FT-IR(KBr) ν 1683, 1610, 1377, 1266, 1035, 840 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 3.84 (s, 3H, OCH_3), 6.78 (s, 1H, C═CH), 7.05 (d, $J = 8.4$ Hz, 2H, Ar-Hs), 7.11–7.13 (m, 3H, Ar-Hs), 7.45–7.47 (m 1H, Ar-H), 7.97 (d, $J = 8.4$ Hz, 2H, Ar-Hs), 12.00 (s, 1H, NHCO), 13.59 (s, 1H, *NH*C═CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 55.35, 88.83, 113.89, 115.24, 116.18, 123.59, 124.16, 126.34, 129.09, 131.29, 144.53, 144.89, 155.80, 162.26, 187.68.

Compound 2c: Mp 266–267 °C (lit.[31] 270–271 °C); FT-IR (KBr) ν 1688, 1602, 1378, 1114, 1033, 844, 759 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 6.69 (s, 1H, CH═C), 7.15 (s, 3H, Ar-Hs), 7.51–7.53 (m, 1H, Ar-H), 7.58 (d, $J = 8.0$ Hz, 2H, Ar-Hs), 7.99 (d, $J = 8.0$ Hz, 2H, Ar-Hs), 12.06 (s, 1H, NHCO), 13.65 (s, 1H, *NH*C═CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 88.88, 115.28, 115.35, 116.49, 116.63, 123.67, 124.15, 128.77, 128.85, 136.68, 137.27, 145.84, 155.55, 186.92.

Compound 2d: Mp 298–299 °C (lit.[31] 304–305 °C); FT-IR (KBr) ν 1689, 1611, 1379, 1244, 1026, 845 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 6.85 (s, 1H, CH═C), 7.13–7.21 (m, 3H, Ar-Hs), 8.21 (d, $J = 8.8$ Hz, 2H, Ar-Hs), 8.33 (d, $J = 8.8$ Hz, 2H, Ar-Hs), 12.15 (s, 1H, NHCO), 13.79 (s, 1H, *NH*C═CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 89.46, 115.41, 117.12, 123.79, 123.90, 12.69, 127.11, 128.29, 137.44, 143.72, 146.66, 149.08, 155.34, 185.93.

Compound 2e: Mp 301–302 °C; FT-IR (KBr) ν 3230, 1686, 1615, 1344, 1234, 1188, 846, 754, 690 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) 6.79 (s, 1H, CH═C), 7.07 (d, $J = 8.0$ Hz, 2H, Ar-Hs), 7.17–7.23 (m, 4H, Ar-Hs), 7.90 (d, 2H, $J = 8.0$ Hz, Ar-Hs), 8.01 (s, br, 2H, NH_2), 11.97 (s, 1H, NHCO), 13.51 (s, 1H, *NH*C═CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 88.74, 113.34, 115.33, 118.71, 121.22, 124.79, 124.91, 126.77, 130.58, 138.63, 148.11, 150.55, 155.82, 187.01.

Compound 2f: Mp 327–328 °C (lit.[32] 323–324 °C); FT-IR (KBr) ν 3340, 1688, 1608, 1525, 1264, 1182, 833, 750, 699 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) 6.81 (s, 1H, CH═C), 7.01 (d, $J = 8.0$ Hz, 2H, Ar-Hs), 7.11–7.17 (m, 3H, Ar-Hs), 7.43–7.47 (m, m, 1H, Ar-H), 7.93 (d, 2H, $J = 8.0$ Hz, Ar-Hs), 8.88 (s, 1H, OH), 12.01 (s, 1H, NHCO), 13.53 (s, 1H, *NH*C═CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 88.94, 113.97, 115.33, 117.73, 121.23, 124.26, 126.47, 129.13, 131.17, 138.66, 146.35, 156.19, 163.07, 188.13.

Compoudn 3a: Mp 200–201 °C (lit.[33] 203–204 °C); FT-IR (KBr) ν 1761, 1653, 1602, 1562, 1535, 1363, 1049, 753, 692 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.06 (s, 1H, CH═C), 7.09–7.13 (m, 2H, Ar-Hs), 7.18–7.22 (m, 2H, Ar-Hs), 7.47–7.51 (m, 2H, Ar-Hs), 7.54–7.61 (m, 2H, Ar-Hs), 8.01 (d, $J = 7.6$ Hz, 2H, Ar-Hs), 13.07 (s, 1H, NHC═C); ^{13}C NMR (100 MHz, DMSO-d_6) δ 94.58, 115.94, 117.12, 123.72, 123.96, 125.87, 127.64, 128.72, 132.67, 138.19, 139.02, 141.21, 156.24, 191.51.

Compound 3b: Mp 219–220 °C (lit.[34] 215–216 °C); FT-IR (KBr) ν 1757, 1622, 1604, 1595, 1584, 1288, 1256, 1174, 755 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 3.88 (s, 3H, OCH_3), 6.96 (d, $J = 8.8$ Hz, 2H, Ar-Hs), 7.01 (s, 1H, CH═C), 7.03–7.09 (m, 2H, Ar-Hs), 7.16–7.19 (m, 2H, Ar-Hs), 7.99 (d, $J = 8.8$ Hz, 2H, Ar-Hs), 12.98(s, 1H, NHC═C); ^{13}C NMR (100 MHz, DMSO-d_6) δ 55.51, 94.54, 113.93, 115.73, 117.06, 123.59, 123.91, 125.81, 129.87, 131.09, 138.43, 141.04, 156.47, 163.34, 190.33.

Compound 3c: Mp 186–187 °C (lit.[32] 180 °C); FT-IR (KBr) ν 1757, 1624, 1591, 1287, 751 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 6.83 (s, 1H, CH═C), 7.13 (d, $J = 6.8$ Hz, 1H, Ar-H), 7.19 (d, $J = 6.8$ Hz, 1H, Ar-H), 7.24 (d, $J = 7.6$ Hz, 1H, Ar-H), 7.57 (m, 3H, Ar-Hs), 8.00 (d, $J = 7.6$ Hz, 2H, Ar-Hs), 12.78 (s, 1H, NHC═C); ^{13}C NMR (100 MHz, DMSO-d_6) δ 92.29, 116.36, 116.86, 123.80, 123.83, 125.27, 128.90, 129.10, 136.72, 137.30, 140.23, 141.19, 155.85, 188.06.

Compound 3d: Mp 240–241 °C (lit.[34] 236–237 °C); FT-IR (KBr) ν 1750, 1623, 1603, 1565, 1518, 1347, 1272, 759 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 6.88 (s, 1H, CH═C), 7.13–7.26 (m, 3H, Ar-Hs), 7.63 (d, $J = 8.0$ Hz, 1H, Ar-H), 8.21 (d, $J = 8.0$ Hz, 2H, Ar-Hs), 8.31 (d, $J = 8.0$ Hz, 2H, Ar-Hs), 12.88 (s, 1H, NHC═C); ^{13}C NMR (100 MHz, DMSO-d_6) δ 93.02, 116.90, 117.71, 124.18, 124.47, 124.78, 125.79, 129.07, 141.59, 141.98, 146.66, 149.88, 156.36, 187.63.

X-ray Crystallographic Data Collection, Structure Determination, and Refinement

A yellow single crystal (0.62 mm × 0.28 mm × 0.20 mm) was attached to a glass fiber and mounted on a Rigaku Raxis-Rapid equipped with a graphite

monochromated Mo K_α ($\lambda = 0.71073$ Å) radiation source and a IP detector. *Lp* effects and multiscan were applied in data corrections. The structure was solved by direct methods using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. Molecular graphics were produced using ORTEP-3. Nonhydrogen atoms were refined anisotropically; all hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms.

Crystallographic Data for Compound 3a

$C_{17}H_{13}NO_4$, $M = 295.28$, orthorhombic, $a = 11.628(2)$, $b = 7.3761(15)$, $c = 32.679(7)$ Å, $U = 2802.8(10)$ Å^3, $T = 293$ K, P*bca* space group, $Z = 8$, $GOF = 1.096$, $3.05^\circ < \theta < 25.6^\circ$, 21263 reflections measured, 2634 unique [R(*int*) = 0.0338], which were used in all calculation. The final R_1 and wR_2 (all data) were 0.0635 and 0.1227 respectively. CCDC 651042 contains the more supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.uk).

ACKNOWLEDGMENT

We are grateful for the financial support from the Nature Science Foundation of Zhejiang Province (Project No. R405465).

REFERENCES

1. Itoh, K.; Okazaki, K.; Fujimoto, M. The structure of 1,3-enaminoketonatoboron difluorides in solution and in the solid state. *Aust. J. Chem.* **2003**, *56*, 1209.
2. Itoh, K.; Okazaki, K.; Toyotomi, Y. Photodimerization of enaminoketonatoboron difluorides. *New J. Chem.* **2002**, *26*, 1070.
3. Singh, R. V.; Tandon, J. P. Synthesis of some ketimine derivatives of silicon(IV). *J. Prakt. Chem.* **1979**, *321*, 151.
4. Martins, D. F.; Janusonis, G. A.; Martins, B. B. Stabilities of bivalent metal complexes of some β-ketoimines. *J. Am. Chem. Soc.* **1961**, *83*, 73.
5. (a) Milyutin, A. V.; Amirova, L. P.; Kkrylova, I. V.; Nazmetdinov, F. Y.; Novoselova, G. N.; Andreichikov, Y. S.; Kolla, V. E. Synthesis, properties and biological activity of 3-pyridylamides of 4-aryl-2-hydroxy-4- oxo-2-butenioc (aroylpyruvic) acids; *Khim. Farm. Zhur.* **1997**, *31*, 32; (b) Andreichikov, Y. S.; Ionov, Y. V. Chemistry of oxalyl derivatives of methyl ketones. XXVI. Reaction of 5-aryl-2,3-dihydrofuran-2,3-diones with Schiff bases. *Zhur. Org. Khim.* **1982**, *18*, 2430; (c) Andreichikov, Y. S.; Nalimova, Y. A.; Tendryakova, S. P.; Vilenchik, Y. M. *Zhur. Org. Khim.* **1978**, *14*, 160.

6. Rastogi, R. C.; Khan, R. H.; Baruah, K. R.; Sarmah, C. S. A simple one step synthesis of (2-oxo-1,2,3,4-tetrahydroquinoxaline- 3-methylenyl)ketones. *Indian J. Heterocycl. Chem.* **1992**, *1*, 247.
7. (a) Maslivets, A. N.; Mashevskaya, I. V.; Smirnova, L. I.; Andreichikov, Y. S. 2-[(*o*-Ammoniophenyl)amino]-4-oxo-4-pheyl-2-butenoate as intermediate in 3-phenacyl- idene-1,2,3,4-tetrahydro-2-quinoxalinone synthesis. *Khim. Getero. Soed.* **1991**, 1431; (b) Maslivets, A. N.; Mashevskaya, I. V.; Andreichikov, Y. S. Recyclization of methyl 4-hydro-2- (*o*-hydroxylphenylamino)-5-oxo-2,5-dihydropyrrole-2-carboxylate to (2-oxo-3,4-dihydro-2*H*- 1,4-benzoxazine-3-ylidene)-pyruvamide. *Zhur. Org. Khim.* **1993**, *29*, 2056.
8. Adel, A.; Montserrat, V.; Hans, Z. Substituted g-lactones. XXX. Reactions of α-keto-β-substituted-γ-butyrolactones with diamines. *J. Heterocyclic Chem.* **1983**, *20*, 359.
9. Walter, R.; Harald, K. Reaktionen mit cyclobutendionen, XXXIX. Umsetzungen von 4-arylsulfonyl- und 4-phenyl-2-hydroxy-3-phenyl-2-cyclobuten-1-onen mit bisnucleophilen. *Chem. Ber.* **1975**, *108*, 2750.
10. Brigadnova, E. V.; Andreichikov, Y. S. Chemistry of oxalyl derivatives of methyl ketones. XLVI. Reaction of methyl 3-methyl- and 3-bromo-4-aryl-2,4-dioxobutanoates with diphenyldiazomethane. *Zhur. Org. Khim.* **1989**, *25*, 1169.
11. Maslivets, A. N.; Smirnova, L. I.; Andreichikov, Y. S. Ring cleavage of 2-(arylamino)-3-hydroxy-2,5-dihydro-5-(methoxycarbonyl)-2-pyrrolone with hydrazine to give the methyl ester amide of 3,5-pyrazoledicarboxylic acid. *Zhur. Org. Khim.* **1988**, *24*, 2234.
12. Kozminykh, V. O.; Igidov, N. M.; Kozminykh, E. N. Tetracarbonyl synthesis: VII. Reaction of 1,3,4,6-tetracarbonyl compounds with *o*-aminothiophenol in the synthesis of regioisomeric 3(2)-aroylmethylene-1,4-benzothiazin- 2(3)ones. *Russian J. Org. Chem.* **2003**, *39*, 863.
13. Wang, B.; Gu, Y. L.; Song, G. Y.; Yang, T.; Yang, L. M.; Suo, J. S. An efficient procedure for protection of carbonyls catalyzed by sulfamic acid. *J. Molecular Catal. A: Chem.* **2005**, *233*, 121.
14. Singh, P. R.; Singh, D. U.; Samant, S. D. Sulphamic acid: an efficient and cost-effective solid acid catalyst for the Pechmann Reaction. *Synlett* **2004**, 1909.
15. Wang, B.; Gu, Y. L.; Luo, G. Y.; Yang, T.; Yang, L. M.; Suo, J. S. Sulfamic acid as a cost-effective and recyclable catalyst for liquid Beckmann rearrangement, a green process to produce amides from ketoximes without waste. *Tetrahedron Lett.* **2004**, *45*, 3369.
16. Nagarajan, R.; Magesh, C. J.; Perumal, P. T. Inter- and intramolecular imino Diels-Alder reactions catalyzed by sulfamic acid: A mild and efficient catalyst for a one-pot synthesis of tetrahydroquinolines. *Synthesis* **2004**, 69.
17. Yadav, J. S.; Rao, P. P.; Sreenu, D.; Rao, R. S.; Kumar, V. N.; Nagaiah, K.; Prasad, A. R. Sulfamic acid: an efficient, cost-effective and recyclable solid acid catalyst for the Friedlander quinoline synthesis. *Tetrahedron Lett.* **2005**, *46*, 7249.
18. Rajitha, B.; Kumar, B. S.; Reddy, Y. T.; Reddy, P. N.; Sreenivasuhu, N. Sulfamic acid: a novel and efficient catalyst for the synthesis of aryl-14*H*- dibenzo[a.j]-xanthenes under conventional heating and microwave irradiation. *Tetrahedron Lett.* **2005**, *46*, 8691.
19. An, L. T.; Zou, J. P.; Zhang, L. L.; Zhang, Y. Sulfamic acid-catalyzed Michael addition of indoles and pyrrole to electron-deficient nitroolefins under solvent-free condition. *Tetrahedron Lett.* **2007**, *48*, 4297.

20. Heydari, A.; Khaksar, S.; Pourayoubi, M.; Mahjoub, A. R. Sulfamic acid: an efficient, cost-effective and recyclable solid acid catalyst for the three-component synthesis of α-amino nitriles. *Tetrahedron Lett.* **2007**, *48*, 4059.
21. Dabiri, M.; Delbari, A. S.; Bazgir, A. A novel three-component, one-pot synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3] oxazine-3-one merivatives under microwave-assisted and thermal solvent-free conditions. *Synlett* **2007**, 821.
22. Ouyang, Y.; Dong, D. W.; Zheng, C. B.; Yu, H. F.; Liu, Q.; Fu, Z. Q. Chemoselective thioacetalization using 3-(1,3-dithian-2-ylidene)pentane-2,4-dione as an odorless and efficient propane-1,3-dithiol equivalent under solvent-free conditions. *Synthesis* **2006**, 3801.
23. Jagdale, A. R.; Sudalai, A. *p*-Toluenesulfonic acid mediated hydroarylation of cinnamic acids with anisoles and phenols under metal and solvent-free conditions. *Tetrahedron Lett.* **2007**, *48*, 4895.
24. Kumar, A.; Maurya, R. A. Synthesis of 3,4-dihydropyrimidin-2(1H)-ones using Ziegler–Natta catalyst system under solvent free conditions. *J. Mol. Catal. A: Chem.* **2007**, *272*, 53.
25. Xia, M.; Lu, Y. D. Ultrasound-assisted one-pot approach to α-amino phosphonates under solvent-free and catalyst-free conditions. *Ultrason. Sonochem.* **2007**, *14*, 235.
26. Jia, C. S.; Dong, Y. W.; Tu, S. J.; Wang, G. W. Microwave-assisted solvent-free synthesis of substituted 2-quinolones. *Tetrahedron* **2007**, *63*, 892.
27. Xia, M.; Lu, Y. D. Sulfamic acid: an efficient and green catalyst for synthesis of 1,5-benzodiazepines under solvent-free conditions. *Heteroatom Chem.* **2007**, *18*, 354.
28. Xia, M.; Lu, Y. D. A novel direct and one-pot Mannich synthesis of fluorinated β-aminobutanones with sulfamic acid as a green catalyst. *J. Fluorine Chem.* **2006**, *127*, 1119.
29. Xia, M.; Lu, Y. D. Solid-state synthesis of 4-[(indol-3-yl)-arylmethyl]-1-phenyl-3-methyl-5-pyrazolones by catalysis of molecular iodine. *Synth. Commun.* **2006**, *36*, 2389.
30. Allen, F. H.; Kennard, O.; Waston, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. Tables of bond lengths determined by X-ray and neutron diffraction. Part I. Bond lengths in organic compounds. *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.
31. Andreichikov, Y. S.; Pitirimova, S. G.; Saraeva, R. F.; Gein, V. L.; Plakhina, G. D.; Voronova, L. A. 3-Phenacyl-2-quinoxalones and 3-phenacylidene-3,4-dihydro-2-quinoxalones. *Khim. Getero. Soed.* **1978**, 407.
32. Iwanami, Y.; Inagaki, T. 3-Aroylmethyl derivatives of 2(1*H*)-quinoxalinone and *2H*-1,4-benzoxazin-2- ones existing in the enamine form. *J. Heterocycl. Chem.* **1976**, *13*, 681.
33. Andreichikov, Y. S.; Voronova, L. A.; Milyutin, A. V. Chemistry of oxalyl derivatives of methyl ketones. XXI. Reaction of 5-arylfuran-2,3-diones with 1,2-hydroxyamine compounds. *Zhur. Org. Khim.* **1979**, *15*, 847.
34. Andreichikov, Y. S.; Voronova, L. A.; Kozlov, A. P. Chemistry of oxalyl derivatives of methyl ketones. XX. Kinetics of the reaction of benzoyl pyroracemic acids with *o*-aminophenol. *Zhur. Org. Khim.* **1979**, *15*, 520.