Note

Metal Hydrogen Sulfates $M(HSO_4)_n$: As Efficient Catalysts for the Synthesis of Quinoxalines in EtOH at Room Temperature

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A convenient method for the synthesis of quinoxalines catalysed by metal hydrogen sulfates by the reaction of 1,2-diamino compounds and 1,2-dicarbonyl compounds in ethanol as solvent at room temperature is reported.

Keywords: Quinoxalines; Diamino compounds; Dicarbonyl compounds; Metal hydrogen sulfates.

INTRODUCTION

In recent years, the search for environmentally benign chemical processes or methodologies has received much attention from chemists, because they are essential for the conservation of the global ecosystem. The development of heterogeneous catalysts for fine chemical synthesis has become a major area of research, as the potential advantages of these materials (simplified recovery and reusability; the potential for incorporation in continuous reactors and micro reactors) over homogeneous systems can lead to novel environmentally benign chemical procedures for academia and industry.[1] From this viewpoint, catalytic reaction is a valuable process because the use of stoichiometric reagents that are often toxic poses inherent limitations from both economical and environmental viewpoints regarding product purification and waste management.[2]

Application of solid acids in organic transformation have an important role, because solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal. On the other hand, any reduction in the amount of liquid acid needed and/or any simplification in handling procedures is required for risk reduction, economic advantage and environmental protection.[3-8] Among solid acids, silica sulfuric acid[3] and $Al(HSO_4)_3$[6,7] are two nice alternatives for very dangerous concentrated sulfuric acid and there are several reports about using these solid acids in organic transformation.

The preparation of quinoxaline and its derivatives plays an important role in organic synthesis.[9] Quinoxaline and its derivatives are an important class of benzoheterocycles displaying a broad spectrum of biological activities which have made them privileged structures in pharmacologically active compounds.[10-12] They have also found applications as building blocks in the synthesis of organic semiconductors,[13] rigid subunits in macro cyclic receptors or molecular recognition,[14] and chemically controllable switches.[15] In general, these compounds could be achieved via the condensation of aryl 1,2-diamines with 1,2-dicarbonyl compounds in organic solvents for 2-12 h under refluxing conditions with 34-85% yields.[16] However, most of the traditional processes suffer from a variety of disadvantages, such as pollution, high cost, poor chemical yields, requirements for long reaction time, and tedious work-up procedures, which limit their use under the aspect of environmentally benign processes.

Progress has been reported in the literature for the synthesis of quinoxaline derivatives compounds, such as the Bi-catalyzed oxidative coupling reaction,[17] via a tandem oxidation process using $Pd(OAc)_2$ or $RuCl_2$-$(PPh_3)_3$-TEMPO,[18] and MnO_2,[19] heteroannulation of nitroketene N,S-arylaminoacetals with $POCl_3$,[20] a solid-phase synthesis on Synphase TM Lanterns,[21] cyclization of a-arylimino

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oximes compounds under refluxing conditions in acetic anhydride,[22] the condensation of α-phenylene diamines and 1,2-dicarbonyl compounds in MeOH/AcOH under microwave irradiation,[23] and the molecular iodine-catalyzed cyclocondensation reaction in DMSO and CH_3CN,[24] $CuSO_4.5H_2O$ in water and Zn[(L)proline] in HOAc,[25] task-specific ionic liquid,[26] montmorillonite K-10,[27] oxalic acid,[28] and very recently Mozumdar and coworkers reported the synthesis of quinoxaline derivatives catalyzed by Ni-nanoparticles.[29] The search for new readily available and green catalysts is still being actively pursued.

RESULTS AND DISCUSSION

In continuation of our studies on the applications of metal hydrogen sulfates in organic transformations,[6,7] we were interested to find a simple and efficient method for the synthesis of quinoxaline derivatives under mild conditions (Scheme I). To optimize the reaction conditions, for the beginning of this work, the condensation reaction between benzil and *o*-phenylenediamine was employed as the model reaction to screen the suitable solvent (Table 1). As shown in Table 1, condensation reaction in ethanol and methanol gave the best results in the case of time and yield, and we chose ethanol for environmental reasons. Although water is a desirable solvent for chemical reactions for reason of cost, safety and environmental concerns, we found that using water in this reaction gave moderate yields of products at room temperature after long reaction times.

Table 1. The influence of the solvent on the condensation reaction of *o*-phenylenediamine (1 mmol) and benzil (1 mmol) catalyzed by $Al(HSO_4)_3$ (0.05 mmol)

Entry	Solvent	Time (min)	Yield (%)[a]
1	H_2O	120	40
2	C_2H_5OH	20	97
3	CH_3OH	20	95
4	$CHCl_3$	60	63
5	CH_2Cl_2	60	59
6	C_6H_6	60	50

[a] Isolated yield.

Table 2. Influence of the amounts of $M(HSO_4)_n$ on the condensation reaction of *o*-phenylenediamine (1 mmol) and benzil (1 mmol)

Entry	Catalyst	Catalyst (mmol)	Time (min)	Yield (%)[a]
1	None	None	24 h	0
2	$Al(HSO_4)_3$	0.01	12 h	31
3	$Al(HSO_4)_3$	0.03	120	79
4	$Al(HSO_4)_3$	0.05	20	97
5	$NaHSO_4.H_2O$	0.05	15	95
6	$KHSO_4$	0.05	15	88
7	$Mg(HSO_4)_2$	0.05	5	79
8	$Ca(HSO_4)_2$	0.05	5	86

[a] Isolated yield.

The effect of the amounts of metal hydrogen sulfates on the yield of the condensation reaction in EtOH was then explored using the same model reaction (Table 2).

It showed that no product can be detected when a mixture of 10 mmol benzil and 10 mmol *o*-phenylenediamine was stirred for 24 h in the absence of metal hydrogen sulfates (entry 1), which indicated that the catalyst is absolutely necessary for this condensation reaction. When the amount of metal hydrogen sulfate was increased, a ramp in the yields of quinoxaline derivatives was clearly observed. The optimal amount of metal hydrogen sulfates was 0.05 mmol per 1 mmol of 1,2-diketone and also 1 mmol of *o*-phenylenediamine in ethanol (2 mL).

The scope and generality of the present method was then further demonstrated by the condensation of various benzil with *o*-phenylenediamine derivatives using 0.05

Scheme I Synthesis of quinoxaline derivatives catalyzed by metal hydrogen sulfates

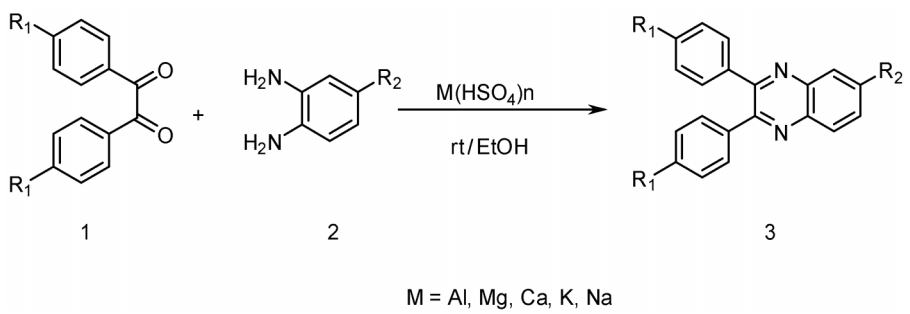
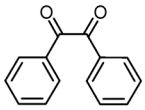
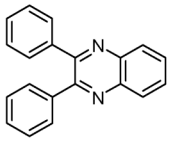
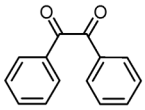
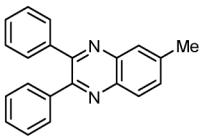
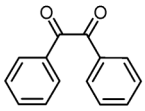
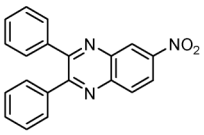
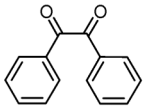
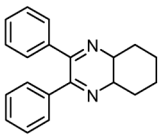
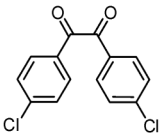
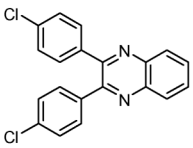
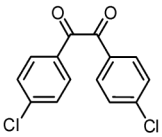
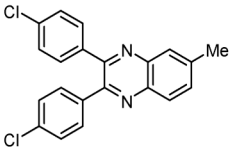
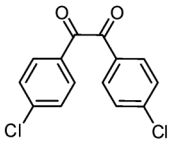
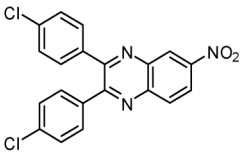
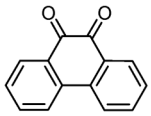
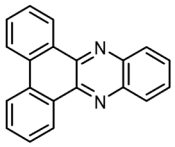
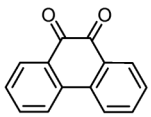
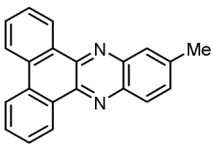
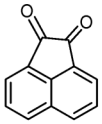
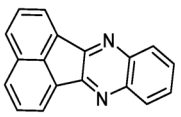
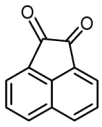
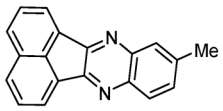
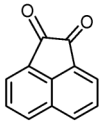
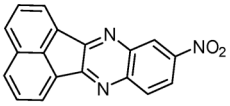
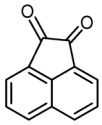
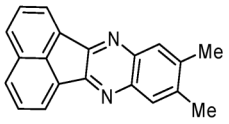
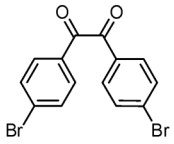
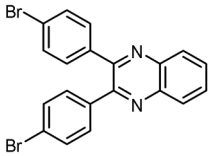


Table 3. Synthesis of quinoxaline derivatives from the corresponding benzil and 1,2-phenylenediamine derivatives catalyzed by metal hydrogen sulfates (Al, **I**; Mg, **II**; Ca, **III**; K, **IV**; Na, **V**) at room temperature

Entry	Dicarbonyl compound	Product	Time (min)					Yeilds (%)[a]				
			I	**II**	**III**	**IV**	**V**	**I**	**II**	**III**	**IV**	**V**
3a			20	5	5	15	15	97	79	86	88	95
3b			40	10	10	15	15	94	97	78	85	87
3c			100	90	90	60	60	69	76	75	76	75
3d			25	25	25	15	15	95	70	80	95	95
3e			15	15	15	7	7	97	98	98	97	96
3f			40	5	7	15	15	95	98	98	95	96
3g			70	60	60	45	45	70	76	75	78	75
3h			3	3	3	3	3	97	98	97	98	96
3i			5	5	5	5	5	97	96	98	96	97
3j			10	5	5	5	5	96	97	96	95	96

3k			15	10	10	10	10	96	95	94	93	94
3l			40	20	20	25	25	96	92	95	95	90
3m			30	15	15	15	15	91	902	95	95	90
3n			20	7	7	15	15	93	97	97	94	95

[a] Isolated yield.

mmol metal hydrogen sulfates in ethanol at room temperature, and the results are presented in Table 3. The reaction proceeds very cleanly at room temperature and was free of side products. After completion of the reaction (monitored by TLC), a precipitate was obtained that a simple filtration affords the products in excellent yields.

It can easily be seen that the condensation reaction proceeded smoothly in ethanol and gave reasonable good to excellent yields ranging from 70% to 97% and no undesirable side reactions were observed. In the case of 1,2-diketones, either electron-withdrawing or electron-donating substituents (R_1) on the aromatic ring gave almost the same yields. But for substituents on *o*-phenylenediamine (R_2), the order of the reactivity for condensation reaction was found to be: $H > CH_3 > NO_2$.

CONCLUSION

In conclusion, the cheapness and availability of the reagents, easy and clean work-up, and high yields make this method practical for quinoxaline synthesis. We believe that the present methodology could be an important addition to the existing methodologies.

EXPERIMENTAL SECTION

General

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The products were characterized by comparison of their spectral and physical data with those reported in the literature.[17-25]

General procedure

To a stirred solution of 1,2-phenylenediamine (1 mmol), and dicarbonyl compound (1 mmol) in EtOH (2 mL) was added $M(HSO_4)_n$ [M = Al, Mg, Ca, K, Na] (0.05 mmol) and stirred at room temperature for the times specified in Table 3. The reaction was followed by TLC. After completion of the reaction, the product that was precipitated was separated by simple filtration. For further purification the products were recrystallized from hot ethanol.

Spectral data

3a: mp 126-127 °C, (Lit.[25b] 128-129 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.40 (m, 6H), 7.58 (m, 4H), 7.83 (m, 2H), 8.23 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 128.70, 129.23, 129.65, 130.28, 130.37, 139.54, 141.68, 153.91.

3b: mp 116-117 °C, (Lit.[25b] 117-118 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.64 (s, 3H), 7.35 (m, 6H), 7.54 (m, 4H), 7.63 (d, 1H, *J* = 8.5 Hz), 8.03 (s, 1H), 8.14 (d, 1H, *J* = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 22.01, 127.69, 128.31, 128.52, 128.88, 128.98, 129.89, 129.94, 132.68, 138.55, 138.68, 139.48, 140.81, 141.02, 152.47, 153.07.

3c: mp 192-193 °C, (Lit.[25b] 193-194 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (m, 6H), 7.58 (m, 4H), 8.32 (d, 1H, *J* = 8.0 Hz), 8.57 (m, 1H), 9.10 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 124.41, 126.74, 129.54, 129.61, 130.80, 130.93, 130.99, 131.07, 131.90, 139.17,

139.23, 141.07, 144.70, 148.96, 156.80, 157.43.

3d: mp 167-169 °C, (Lit.[30] 167 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.46-1.50 (m, 2H), 1.67-1.70 (m, 2H), 1.93-1.96 (m, 2H), 2.54-2.57 (m, 2H), 2.88-2.90 (m, 2H), 7.25-7.29 (m, 4H), 7.31-7.34 (m, 2H), 7.42-7.44 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 25.87, 33.956, 59.95, 128.45, 128.55, 129.88, 138.23, 160.10.

3e: mp 195-196 °C, (Lit.[25b] 195-196 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.39 (dt, 4H, J_1 = 8.5 Hz, J_2 = 2.0 Hz), 7.51 (dt, 4H, J_1 = 8.5 Hz, J_2 = 2.0 Hz), 7.83 (dd, 2H, J_1= 6.3 Hz, J_2= 3.4 Hz), 8.20 (dd, 2H, J_1 = 6.3 Hz, J_2 = 3.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 129.15, 129.63, 130.79, 131.61, 135.78, 137.69, 141.67, 152.34.

3f: mp 178-180 °C, (Lit.[25b] 180 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.66 (s, 3H), 7.38 (d, 4H, J = 8.0 Hz), 7.50 (dd, 4H, J_1 = 8.4 Hz, J_2 = 1.0 Hz), 7.67 (dd, 1H, J_1 = 8.5 Hz, J_2 = 1.8 Hz), 7.97 (s, 1H), 8.08 (d, 1H, J = 8.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 22.36, 128.42, 129.09, 129.11, 131.58, 131.60, 133.16, 135.56, 135.64, 137.85, 140.17, 141.43, 141.75, 151.43, 152.20.

3g: mp 175-176 °C, (Lit.[25b] 176 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.43 (d, 4H, J = 7.6 Hz), 7.54-7.57 (m, 4H), 8.32 (d, 1H, J = 9.1 Hz), 8.58 (dd, 1H, J_1 = 9.1 Hz, J_2 = 2.5 Hz), 9.08 (d, 1H, J = 2.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 124.08, 125.99, 129.37, 131.20, 131.58, 131.66, 136.60, 136.67, 136.72, 136.87, 140.40, 143.91, 148.53, 154.57, 155.18.

3h: mp 223-225 °C, (Lit.[31] 224.8-225.7 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51-7.66 (m, 6H), 8.10-8.13 (m, 2H), 8.33 (d, 2H, J = 8.0 Hz), 9.18 (d, 2H, J = 8.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 124.01, 127.35, 129.01, 130.51, 130.81, 131.41, 133.23, 143.23, 143.51.

3i: mp 208-210 °C, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.46 (s, 3H), 7.46-7.58 (m, 5H), 7.85 (s, 1H), 7.97 (d, 1H, J = 8.0 Hz), 8.32 (d, 2H, J = 8.0 Hz), 9.13-9.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 23.20, 123.95, 127.15, 127.29, 128.92, 129.10, 130.01, 131.07, 131.20, 131.45, 131.49, 132.87, 133.06, 133.45, 141.41, 141.81, 142.72, 143.27, 143.29. Anal. Calc. for $C_{21}H_{14}N_2$: C, 85.69; H, 4.79; N, 9.52; found: C, 85.50; H, 4.61; N, 9.39; IR (KBr): 3055, 2909, 1619, 1497, 1355, 1037, 821, 760, 720 (cm^{-1}).

3j: mp 238-240 °C, (Lit.[31] 239.5-241.3 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55-7.65 (m, 4H), 7.89 (d, 2H, J = 8.4 Hz), 8.00-8.20 (m, 2H), 8.21 (d, 2H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 122.96, 129.78, 130.36, 130.59, 130.74, 131.10, 132.92, 137.60, 142.39, 155.19.

3k: mp > 300 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.60 (s, 3H), 7.55 (d, 1H, J = 8.25 Hz), 7.79 (t, 2H, J = 7.5 Hz), 7.95 (s, 1H), 8.03-8.07 (m, 3H), 8.35 (t, 2H, J = 6.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 22.19, 121.97, 122.12, 129.01, 129.03, 129.21, 129.53, 129.60, 129.75, 130.39, 131.72, 132.44, 136.68, 140.06, 140.10, 141.73, 153.76, 154.48. Anal. Calc. for $C_{19}H_{12}N_2$: C, 85.05; H, 4.51; N, 10.44; found: C, 84.92; H, 4.43; N, 10.30; IR (KBr): 3052, 2910, 1575, 1375, 1332, 1294, 1097, 822, 778 (cm^{-1}).

3l: mp > 300 °C, (Lit.[32] > 300 °C); 1H NMR (500 MHz, DMSO-d_6): δ (ppm) 8.00 (t, 2H, J = 8.0 Hz), 8.37-8.42 (m, 3H), 8.50-8.55 (m, 3H), 8.97 (d, 1H, J = 2.3 Hz).

3m: mp 304-306 °C, (Lit.[28] 304-306 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.51 (s, 6H), 7.78 (m, 2H), 7.89 (s, 2H), 8.03 (m, 2H), 8.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 20.3, 121.5, 127.8, 128.0, 128.6, 128.9, 129.1, 139.5, 140.0, 148.5, 153.3.

3n: mp 192-194 °C, (Lit.[33] 195-197 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.41 (dt, 4H, J_1 = 8.5 Hz, J_2 = 2.0 Hz), 7.51 (dt, 4H, J_1 = 8.5 Hz, J_2 = 2.0 Hz), 7.79 (dd, 2H, J_1 = 6.5 Hz, J_2 = 3.5 Hz), 8.15 (dd, 2H, J_1 = 6.5 Hz, J_2 = 3.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 124.13, 129.64, 130.84, 131.86, 132.12, 138.12, 141.68, 152.34.

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