

Synthesis of 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol/thiol's using Sulfamic Acid, A Green and Recyclable Catalyst

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Abstract: A simple and highly efficient method has been developed for the synthesis of 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ols and 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiols using sulfamic acid (H_2NSO_3H) as a green catalyst in water. The catalyst can be recovered by simple filtration and can be recycled in subsequent reactions. The method is simple, cost-effective and environmentally benign. By employing this method, a series of 14 compounds were synthesized.

Keywords: Sulfamic acid; 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol/thiol's; Recyclable green catalyst

1. Introduction

Hetero cyclic compounds are common structural units in marketed drugs and in medicinal chemistry. Several heterocyclic compounds possess excellent biological activity almost without bearing any substituent's, which means that their heterocyclic core is definitely part of the pharmacophore [1]. Even simple aliphatic heterocycles display astonishing biological activities. For example gem-diethyl-substituted barbituric acid derivative barbital has been widely applied as a sleeping aid [2]. Multi component reactions are important synthetic tools for synthesis of bio active hetero cyclic compounds [3]. The indole moiety is probably the most well-known heterocycle, a common and important feature of a variety of natural products and medicinal agents [4]. In view of this researchers started to explore simple and novel innovative methods to obtain potent bio active heterocyclic compounds [5]. 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ols/thiols and their analogs exhibits varied biological activities such as analgesic [6], blood platelet aggregation inhibitory [7, 8], anti hypersensitive [9, 10], anti viral [9], and antimicrobial activity [11-15] activities. Recently Ivachtchenko et al, and K. Ramesh et al. reported the synthetic methods for 5H- [1, 2, 4] triazino [5, 6-b] indole-3-ole/thioles by using isatin, thio semicarbazide and different catalysts [16, 17]. In view of different biological activities associated with various 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-ols/thiol derivatives we were synthesized by using isatin, semicarbazide and Sulfamic acid as green and reusable catalyst.

In recent years, the use of solid acids as heterogeneous catalysts has received remarkable interest in organic synthesis. Heterogeneous solid acids are more beneficial over conventional homogeneous acid catalysts as they can be easily recovered from the reaction mixture by simple filtration and can be re-used after activation or without

activation, thereby making the process economically more viable. During the last few years, sulfamic acid (NH_2SO_3H SA) has emerged as a substitute for conventional acidic catalysts. Sulfamic acid is a common inorganic acid with mild acidity, is non-volatile and non-corrosive, and is insoluble in common organic solvents. SA has been used as an efficient heterogeneous catalyst for acid catalyzed reactions, viz. acetalization, [18a] esterification, [18b, c] acetylation of alcohols and phenols, [18d] nitrile formation, [18e] tetrahydro pyranulation of alcohols [18f], transesterification of β -ketoesters [18g] Biginelli condensation, [18h] the Beckmann rearrangement, [18i] inter- and intra molecular Diels-Alder reactions [18j] and very recently Pechmann condensations, [18k] have been carried out in the presence of SA. This has encouraged us to investigate further the applications of SA as an acidic catalyst in other carbon-carbon and carbon-heteroatom bond-forming reactions. The use of SA as a recyclable catalyst makes the process convenient, economic and environmentally benign.

2. Material and Methods

Starting materials and reagents were commercially available and purchased from Sisco-Research Laboratory (SRL). Reactions were monitored by TLC, performed on silica gel aluminum plates and visualization on TLC was achieved by UV light or iodine indicator and purification of compounds were achieved by column chromatography by using Ethyl acetate and hexane. The synthesized compounds characterization was done by NMR and HRMS spectroscopy. 1H NMR and ^{13}C NMR in $CDCl_3$ or $DMSO-d_6$ were measured on a Bruker Avance 300 MHz instrument with tetramethylsilane (TMS) as an internal standard, and chemical shifts are reported in δ (ppm). Melting points were determined with an Electro thermal melting point apparatus.

2.1 Experimental Procedure

The synthesis of 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol/thiol derivatives (3a-n):

A mixture of isatin (1 mol), semicarbazide or thiosemicarbazide (1 mol) and SA (15mol %) in H₂O was refluxed at 100°C until the reaction was complete (as monitored by TLC). After completion of the reaction, mixture was cooled to room temperature and ice-cold water was added and stirred for a while. The solid product obtained was filtered and washed with water. This was further purified by crystallisation from ethanol. The catalyst, sulfamic acid, being water soluble, was recovered from the filtrate and was quantitatively recovered by the evaporation of filtrate under reduced pressure. The recovered catalyst could be reused for up to five cycles after washing with diethyl ether and drying.

In this study, a model reaction was conducted by reacting isatin and semicarbazide without any catalyst under various conditions. We found that the reaction did not proceed well even after 12h (Table 1, entry 1-10). Then the same reaction was performed in the presence of different catalysts in methanol and ethanol under refluxing conditions. The catalysts such as HCl, ZnCl₂, CH₃SO₃ and p-TSA can catalyze this reaction with moderate yields (Table 1, entries 11-16). The better result was obtained when SA was used, according to the yield and the reaction time (Table 1, entries 17, 18 & 19). After obtaining the desired product, the amount of catalyst for the completion of reaction were evaluated. The reaction was performed using 10, 15 and 20 mole % of the catalyst and was monitored. It was observed that 15mol% of the catalyst loading provided maximum yield (92%) in one hour (Table 1, entry 21). An additional increase of the catalyst loading to 20% did not improve the yield.

3. Results and Discussions

3.1. Chemistry

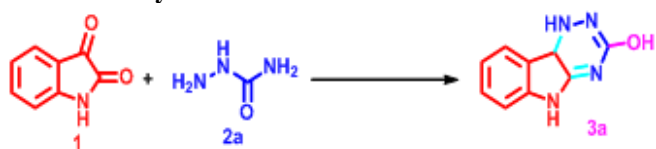
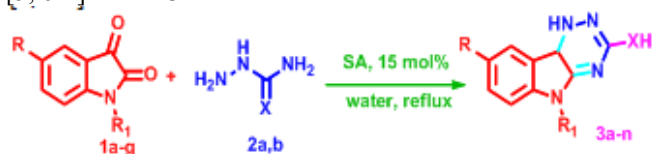


Table 1: Optimization of reaction conditions

Entry	Solvent	Temperature (°C)	Catalyst (mol%)	Time (h)	Yield ^a (%)
1	--	RT	--	12	--
2	CH ₃ CN	RT	--	12	-
3	Methanol	RT	--	12	--
4	Ethanol	RT	--	12	--
5	Water	RT	--	12	--
6	--	100	--	12	--
7	CH ₃ CN	80	--	12	<10
8	Methanol	80	--	12	22
9	Ethanol	80	--	12	28
10	Water	100	--	12	--
11	Ethanol	80	HCl	12	<20
12	Ethanol	80	ZnCl ₂	12	<20
13	Methanol	80	CH ₃ SO ₃ H (10)	6	35
14	Ethanol	80	CH ₃ SO ₃ H (10)	6	36
15	Methanol	80	p-TSA (10)	6	58
16	Ethanol	80	p-TSA (10)	6	65
17	Methanol	80	SA (10)	2	78
18	Ethanol	80	SA (10)	2	80
19	Water	100	SA (10)	2	85
20	Water	100	SA (15)	1	92
21	Water	100	SA (20)	1	92

3.2 Scheme-2

SA catalysed synthesis of 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ols and 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiols



Under these optimized reaction conditions, the scope and generality of the present protocol was examined by employing various substituted isatins possessing both electron-withdrawing as well as electron-donating substituent's and two semicarbazides (Scheme 2) and the results of these observations are summarized in Table 3. The reaction tolerates both electron releasing as well as withdrawing substituent's on the isatin component without any significant deviation in yields N-Protected isatins also afforded the corresponding products in excellent yields.

Table 2: SA catalyzed synthesis of 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ols and 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiols.

Entry	R	R ₁	X	Time(min)	Yield (%)
3a	H	H	O	60	92
3b	Cl	H	O	60	91
3c	Br	H	O	70	88
3d	Me	H	O	80	86
3e	OMe	H	O	80	84
3f	NO ₂	H	O	60	91
3g	H	Benzyl	O	80	88
3h	H	H	S	70	86
3i	Cl	H	S	70	85
3j	Br	H	S	80	85
3k	Me	H	S	100	82
3l	OMe	H	S	100	80
3m	NO ₂	H	S	80	82
3n	H	Benzyl	S	100	84

3.4. Recyclability of the catalyst

We have examined the recyclability of sulfamic acid catalyst for the model reaction. The catalyst used was separated by filtration and was quantitatively recovered by washing with diethyl ether and, after drying, could be reused for at least five cycles without any loss of activity which is evident from Table 3.

Table 3: Yields of the product with various cycles of the catalyst

Entry	Reaction Cycle	Yield (%)
1	1 st cycle (Fresh run)	92
2	2 nd cycle	92
3	3 rd cycle	91
4	4 th cycle	89
5	5 th cycle	88
6	6 th cycle	85

4. Conclusion

In summary, we have developed a simple and convenient, environmentally benign synthetic method for the synthesis of 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ols and 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiols using water as a solvent, with a green and recyclable catalyst in quantitative yields. This method involves the use water and avoids environmentally harmful conventional organic solvents. The simplicity of the method, the ease of product isolation and mild reaction conditions will make this synthetic method useful on an industrial scale. Most importantly of all, the purification procedure is just followed by filtration, washing and drying and the catalyst can be reused for the next cycle, so the waste can be reduced effectively.

4.1. Spectral Data:

3a. 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol.

Yellow solid. M.p. 233-238 °C; ¹H-NMR (300MHz, CDCl₃+DMSO, δ, ppm) 5.9 (s, 2H), 6.25 (d, 1H, J = 7.4 Hz), 6.45 (t, 1H), 6.89 (s, 1H), 7.12 (d, 1H, J = 7.3 Hz), 10.32(m, 1H), 10.41 (s, 1H). ¹³C-NMR (75MHz, DMSO) δ= 110.8,

121.08, 121.3, 122.0, 130.2, 131.0, 141.6, 154.9, 163.7: ESI-MS: m/z = 189 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ C₉H₈N₄O: 189.19; found: 189.23.

3b. 8-chloro-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol.

Yellow solid. M.p. 270-274 °C; ¹H-NMR (300MHz, DMSO, ppm), δ= 6.19 (t, 3H), 6.47 (d, 1H, J = 8.7 Hz), 6.99 (s, 1H), 10.41 (s, 1H), 11.12 (s, 1H). ¹³C-NMR (75MHz, DMSO, δ, ppm) 109.5, 117.9, 120.5, 124.4, 128.0, 128.6, 139.6, 153.7, 161.1. ESI-MS: m/z = 223 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ C₉H₇ClN₄O: 223.63; found: 223.54

3c. 8-bromo-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol.

Light Yellow solid. M.p. 293-294 °C; ¹H-NMR (300MHz, DMSO, ppm), δ= 6.14 (s, 2H), 6.29-6.49 (m, 2H), 7.15-7.19 (m, 1H), 10.32(m, 1H) 10.51 (s, 1H). ¹³C-NMR (75MHz, DMSO, δ) 109.7, 111.2, 120.6, 120.8, 126.6, 130.3, 137.5, 151.9, 159.3. ESI-MS: m/z = 268 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ C₉H₇BrN₄O: 268.08; found: 268.13

3d. 8-methyl-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol.

Yellow solid. M.p. 289-291 °C; ¹H-NMR (300MHz, DMSO, ppm), δ=2.89 (s, 3H), 6.91 (t, 3H), 7.22 (d, 1H, J = 7.6 Hz), 8.0(s, 1H), 10.9 (s, 1H), 10.21(s, 1H). ¹³C-NMR (75MHz, DMSO, δ, ppm) 94.1, 109.6, 117.4, 118.7, 128.2, 129.1, 129.4, 136.4, 153.2, 160.8. ESI-MS: m/z = 203 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ : (C₁₀H₁₀N₄O) 203.09; found: 203.43

3e. 8-methoxy-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol.

Light red solid. M.p. 291-293 °C; ¹H-NMR (300MHz, CDCl₃, ppm), δ= 2.83(s, 3H), 6.89 (t, 2H), 7.1(s, 2H), 7.23 (s, 1H), 10.91 (s, 1H), 11.8 (s, 1H). ¹³C-NMR (75MHz, DMSO, δ) 55.5, 105.5, 112.4, 116.4, 122.1, 132.1, 134.9, 154.6, 155.14, 163.7. ESI-MS: m/z = 219 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ : C₁₀H₁₀N₄O₂; 219.09 found. 219.34

3f. 8-nitro-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol.

Yellow solid. M.p. 291-294 °C; ¹H-NMR (300MHz, CDCl₃, ppm) δ= 6.21(d, 3H, J = 8.1Hz), 7.31-7.35 (m, 1H), 7.61 (s, 1H), 10.73 (s, 1H), 10.94 (s, 1H). ¹³C-NMR (75MHz, DMSO, δ) 111.0, 116.1, 121.2, 126.9, 129.0, 143.1, 146.6, 155.1, and 162.8. ESI-MS: m/z = 234 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ C₉H₇N₅O₃; 234.05; found 234.23

3g. 5-benzyl-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indol-3-ol.

Light Yellow solid. M.p. 220-223 °C; ¹H-NMR (300MHz, CDCl₃, ppm), δ= 4.56 (s, 2H), 8.26-8.78 (m, 12H). ¹³C-NMR (75MHz, DMSO, δ) 43.3, 110.0, 119.9, 119.98, 124.7, 127.4, 127.8, 128.6, 129.8, 130.0, 136.1, 141.8, 155.1, 161.1; ESI-MS: m/z = 279 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ : C₁₆H₁₄N₄O; 279.12: found; 279.34

3h. 5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiol.

Dark yellow solid. M.p. 204-206 °C; ¹H-NMR (300MHz, CDCl₃+DMSO, ppm), δ =6.89 (d, 1H, J = 7.8 Hz), 6.98(t, 1H), 7.24 (s, 1H), 7.61 (d, 1H, J = 7.8 Hz), 8.26 (s, 1H), 8.90 (s, 1H), 11.10 (s, 1H), 12.56 (s, 1H). ¹³C-NMR (75MHz, DMSO, δ) 109.06, 118.05, 119.01, 120.32, 129.10, 129.95, 140.42, 160.70, and 176.85. ESI-MS: m/z = 205 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ : C₉H₈N₄S; 205.05; found 204.99

3i. 8-chloro-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiol.

White solid. M.p. 242-248 °C; ¹H NMR (300MHz, CDCl₃+DMSO, ppm) δ= 3.10 (s, 1H), 6.76 (d, 1H, J = 8.3 Hz), 7.13 (d, 1H, J = 8.1 Hz), 7.55 (s, 1H), 8.01 (s, 1H), 8.65 (s, 1H), 11.00 (s, 1H); ¹³C-NMR (75MHz, DMSO, TMS) δ=110.59, 119.17, 125.38, 128.48, 128.87, 139.19, 160.72, 177.37. 261: ESI-MS: m/z = 239 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ : C₉H₇ClN₄S; 239.01; found 239.31

3j. 8-bromo-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiol.

Light yellow solid. M.p. 257-260 °C; ¹H NMR (300MHz, CDCl₃+DMSO, ppm) δ= 6.67 (d, 1H, J = 7.8 Hz), 7.24 (d, 1H, J = 7.8 Hz), 7.68 (s, 1H), 8.25 (s, 1H), 8.98 (s, 1H), 11.07 (s, 1H), 12.36 (s, 1H); ¹³C-NMR (75MHz, DMSO) δ= 110.9, 119.9, 121.4, 127.4, 129.9, 140.1, 159.9, 177.1. ESI-MS: m/z = 282 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ : C₉H₇BrN₄S; 282.96; found; 282.45

3k. 8-methyl-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiol.

Orange solid. M.p. 253-255 °C; ¹H NMR (300MHz, CDCl₃, ppm) , δ= 2.12 (s, 3H), 6.69 (d, 1H, J = 7.3 Hz), 7.01 (d, 1H, J = 7.3 Hz), 7.29 (s, 1H), 7.67 (s, 1H), 7.83 (s, 1H), 8.63 (s, 1H). 10.63 (s, 1H); ¹³C-NMR (75MHz, DMSO, TMS) δ=107.9, 117.9, 120.1, 130.1, 130.2, 137.9, 159.76, 176.93. ESI-MS: m/z = 219 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ : C₁₀H₁₀N₄S; 219.06; found; 218.98

3l. 8-methoxy-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiol.

Orange solid. M.p. 226-230 °C; ¹H NMR (300MHz, CDCl₃+DMSO, ppm), δ= 3.80 (s, 3H), 6.81 (s, 2H), 7.19 (s, 1H), 8.10 (s, 1H), 8.71 (s, 1H) 10.79 (s, 1H), 12.63 (s, 1H); ¹³C-NMR (75MHz, DMSO) δ=103.5, 109.1, 114.9, 119.6, 131.2, 135.1, 154.3, 161.3, 178.1: ESI-MS: m/z = 235 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ :C₁₀H₁₀N₄OS; 235.06;found; 235.57.

3m. 8-nitro-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiol.

Pale Yellow solid. M.p. 262-264 °C; ¹H NMR (300MHz, CDCl₃, ppm), δ =5.82 (s, 1H), 6.83-7.52 (m, 3H), 8.28 (s, 1H), 10.88 (s, 1H), 11.2(s, 1H); ¹³C-NMR (75MHz, DMSO) δ=98.4, 109.9, 114.3, 119.7, 125.4, 128.4, 142.6, 147.1, 162.4, 178.6: ESI-MS: m/z = 250 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ : C₉H₇N₃O₂S;250.03; found.250.63.

3n. 5-benzyl-5, 9b-dihydro-1H- [1, 2, 4] triazino [5, 6-b] indole-3-thiol.

Yellow solid. M.p. 238-241 °C; ¹H NMR (300MHz, CDCl₃, ppm), δ= 6.87-7.36 (m, 8H), 7.7(m, 1H)8.51 (s, 2H), 8.96 (s, 1H), 10.34(s, 1H) 12.42 (s, 1H); ¹³C-NMR (75MHz, DMSO) δ=98.2, 108.3, 117.3, 118.6, 120.1, 125.3, 125.6, 126.1, 128.70, 133.64, 158.86, 176.95. ESI-MS: m/z = 300 (M+H)⁺; HRMS (ESI) m/z: calc. for [M+H]⁺ : C₁₆H₁₄N₄S; 300.09; found; 300.23.

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