

Sulfamic acid: A green and efficient catalyst for synthesis of mono-, bis-, and spiro- perimidines

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ABSTRACT

Mild and applicable synthesis of mono-, bis-, and spiro- perimidines is demonstrated in high yields via the condensation of 1,8-diaminonaphthalene and aldehydes or ketones in the presence of sulfamic acid as a green and highly efficient catalyst. This environmentally benign and clean synthetic pathway offers several advantages, such as high yields, short reaction times and easy work-up procedure.

Keywords: Sulfamic acid, Perimidine, Spiroperimidine, Catalyst, Green synthesis.

1. Introduction

The heteroaromatic perimidine (peri-naphtho-fused pyrimidine ring systems) structure exhibits simultaneously the distinct properties of compounds with an excess and a deficiency of π electrons, together with a wide variety of practical applications [1,2]. Perimidines have attracted great interest due to the fact that they constitute an important class of natural and synthetic products, many of which exhibit useful biological activities [1,2]. These compounds have properties such as antifungal, antimicrobial, antiulcer and antitumor agents [1-6]. 2,3-Dihydroperimidine derivatives have been used as dyes [7], antioxidant stabilizers [8], photochromic compounds [9] and catalysts [10].

There are different methods for the synthesis of perimidine derivatives. The simple and general method for the synthesis of perimidines involves the reaction of 1,8-diaminonaphthalene with carbonyl compounds in the presence of a Lewis or mineral acid. These compounds have been synthesized in the presence of various catalysts, such as BiCl_3 [11], $\text{Cu}(\text{NO}_3)_2$ [12], zeolite NaY [13], RuCl_3 [14], CMK-5- SO_3H nanocatalyst [15], $\text{Yb}(\text{OTf})_3$ [16], InCl_3 [17] and $\text{BF}_3\text{-H}_2\text{O}$ [18]. Despite the efficiency of these methods, some of them suffer from disadvantages such as longer

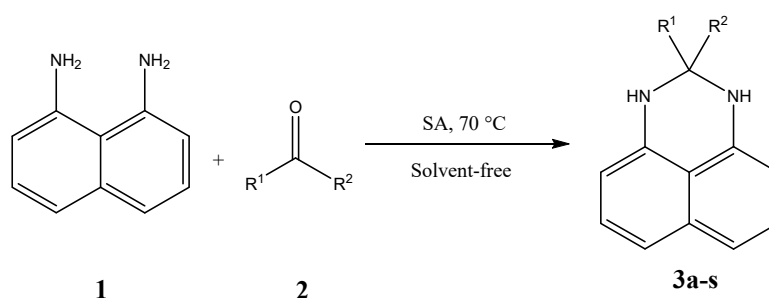
reaction time, use of non-reusable and expensive catalysts, harsh conditions, side reactions and limitation in the use of ketone as a substrate. Therefore, there is an ongoing interest to develop environmentally benign and efficient protocols for this organic transformation.

Sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$) has emerged as a promising substance for conventional bronsted and Lewis acid catalysts. It is relatively stable, non-volatile, non-hygroscopic and non-corrosive. It possesses distinctive catalytic features related to its Zwitter ionic nature and displays an excellent activity over a vast array of acid catalyzed organic transformations, as witnessed by numerous reports published in the past years [19-31]. For unique catalyst features of the SA and in continuation of our efforts to the development of green and mild methodologies for synthesis of heterocycles [27, 32], herein we wish to report a mild and green procedure for the synthesis of biologically interesting mono-, bis- and spiro- perimidine derivatives by the reaction of 1,8-diaminonaphthalene and aldehydes or ketones in the presence of sulfamic acid under solvent-free condition (Scheme 1).

2. Experimental

All chemicals for this research were purchased from Merck or Acros chemical companies and were used without further purification. Melting points were measured by electro-thermal digital apparatus and were not corrected.

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Scheme 1. Efficient synthesis of perimidines in the presence of sulfamic acid (SA).

The reaction progress was followed by TLC on UV active aluminum-backed plates of silica gel (TLC silica gel 60 F254). The products were identified by spectral data using elemental analysis, FT-IR, ^1H NMR and ^{13}C NMR spectroscopy. FT-IR spectra were recorded on Unicom Galaxy Series FT-IR 5030 spectrophotometer using pressed KBr disks. The vibrations are in wave number (cm^{-1}) unit. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance spectrometer operating at 300 and 75 MHz in $\text{DMSO}-d_6$ with TMS as an internal standard. NMR splittings have been marked as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). The elemental analyses were measured by Vario El III apparatus.

2.1. General procedure for synthesis of perimidines and spiroperimidines:

A mixture of 1,8-diaminonaphthalene (1 mmol), aldehyde or ketone (1 mmol) and sulfamic acid (0.1 mmol) was heated at 70°C under solvent free conditions. After reaction completion (monitored by TLC), the reaction mixture was cooled to room temperature and washed with cool water and then recrystallized with hot ethanol.

2.2. General procedure for synthesis of bis-perimidines:

A mixture of an 1,8-diaminonaphthalene (2 mmol), aldehyde or ketone (1 mmol) and sulfamic acid (0.1 mmol) was heated at 70°C under solvent free conditions. After the reaction was completed (as it was monitored by TLC), the reaction mixture was cooled to room temperature and washed with cool water and then recrystallized with hot ethanol.

3. Results and Discussion

At the beginning, a systematic study was carried out for the catalytic evaluation of SA toward the synthesis of perimidine derivatives. Initially, a blank reaction was conducted using 4-chlorobenzaldehyde and naphthalene-1,8-diamine under solvent-free medium at room temperature in the absence of SA which resulted in no formation of desired perimidine after 12 h (Table 1, entry 1). The reaction with the same substrates using a catalytic amount of SA (0.1 mmol) at room temperature under solvent-free medium, afforded the product **3b** in 18% yield after 6 h (Table 1, entry 2).

Table 1. Optimization of reaction condition for efficient synthesis of perimidines.

Entry	Catalyst (g)	Temperature	Time (min)	Solvent	Yield%
1	-	r.t.	720	Solvent-free	-
2	-	70	360	Solvent-free	18
3	0.01	70	40	Solvent-free	92
4	0.01	50	60	Solvent-free	81
5	0.02	70	50	Solvent-free	90
6	0.01	r.t.	80	H_2O	76
7	0.01	r.t.	75	$\text{H}_2\text{O}/\text{EtOH}(1:1)$	70
8	0.01	r.t.	75	$\text{H}_2\text{O}/\text{EtOH}(1:1)$	70
9	0.01	70	75	$\text{H}_2\text{O}/\text{EtOH}(1:1)$	91
10	0.01	Reflux	120	CHCl_3	30
11	0.01	Reflux	120	CH_3CN	49
12	0.01	Reflux	120	Toluene	20

Next, we screened the effect of different solvents and temperatures on the model reaction. The best result was obtained under solvent-free conditions at 70°C using 0.10 mol of the catalyst (Table 1, entry 3). The separation and work-up procedure were very easy and the crude product was recrystallized with hot ethanol.

To explore the majority of the reaction, we extended our study using different aldehydes and ketones to prepare the perimidine and spiroperimidine derivatives. A variety of aromatic aldehydes and ketones were subjected in this condensation reaction to afford the desired perimidines (**3a-o**) and spiroperimidines (**3p-s**) in good to excellent yields (Table 2).

This method is equally effective for aldehydes bearing electron withdrawing or donating substituents in the aromatic ring. Moreover, acid sensitive aldehydes worked well without any decomposition or polymerization under these reaction conditions (Table 2, entry 13). Furthermore, reactions of ketones with naphthalene-1,8-diamine were satisfactorily performed by the current pathway in high yields.

Table 3 compares efficiency of sulfamic acid (time, yield, reaction conditions) with the efficiency of other catalysts in the synthesis of perimidine derivatives. It is clear that catalytic activity of sulfamic acid is comparable to the catalysts used previously for the synthesis of perimidines. Moreover, the sulfamic acid is an inexpensive solid with intrinsic safety.

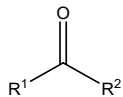
4. Conclusions

We have demonstrated an impressive, green and simple method for synthesis of mono-, bis-, and spiroperimidines using sulfamic acid as an efficient, inexpensive and environmentally friendly catalyst. The use of solvent-free conditions, simple work-up procedure, high yields, nice revenue and short reaction times are some profits of this method.

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Table 2. Synthesis of dihydroperimidines via condensation of 1,8-diaminonaphthalene and carbonyl compounds using sulfamic acid.^a

Entry		Product	Time (min)	Yield (%) ^b	m.p. (°C)		Ref.
					Found	Reported	
1	C ₆ H ₅ CHO	3a	45	90	105-106	101-103	[13]
2	4-Cl C ₆ H ₄ CHO	3b	40	92	158-159	158-160	[13]
3	4-N(Me) ₂ -C ₆ H ₄ CHO	3c	70	89	51-53	49-52	[13]
4	4-OH-C ₆ H ₄ CHO	3d	75	91	164-166	161-163	[13]
5	3,4-(CH ₃ O) ₂ -C ₆ H ₃ CHO	3e	65	88	202-205	206-207	[33]
6	4-CH ₃ O-C ₆ H ₄ CHO	3f	60	90	154-156	156-158	[34]
7	4-NO ₂ -C ₆ H ₄ CHO	3g	75	90	248-250	247-249	[34]
8	3-NO ₂ -C ₆ H ₄ CHO	3h	75	90	186-188	188-190	[13]
8	2-Cl-C ₆ H ₄ CHO	3i	75	88	116-118	116-118	[13]
9	4-F-C ₆ H ₄ CHO	3j	80	91	182-183	180-182	[13]
10	4-CH ₃ -C ₆ H ₄ CHO	3k	55	92	165-167	161-163	[13]
11	Naphthyl-2-CHO	3l	65	88	168-170	165-167	[13]
13	Thiophene-2-CHO	3m	95	82	135-137	138	[35]
12	Terphthaldehyde	3n	80	92	217-219	222-224	[36]
13	Isophthaldehyde	3o	80	94	210-212	-	-
14	Cyclohexanone	3p	75	81	113-116	110-111	[14]
15	Cyclopentanone	3q	80	84	83-86	85-86	[14]
16	Indoline-2,3-dione	3r	90	89	238-241	244-246	[17]
17	1-Methylindoline-2,3-dione	3s	80	92	275-278	281	[17]

^a1,8-naphthalendiamine (1 mmol), carbonyl compound (1 mmol), SA (0.1 mmol), 70 °C, Solvent-free condition.

^bIsolated yields.

Table 3. Comparison of the efficiency of various catalysts in synthesis of spiroperimidines.

Entry	Reagent	Condition	Time (h)	Yield (%)	Ref.
1	BiCl ₃	EtOH, r.t.	6	82	[11]
2	RuCl ₃	EtOH, 40°C	24	91	[14]
3	InCl ₃	H ₂ O, r.t.	4	90	[17]
4	Yb(OTf) ₃	EtOH, r.t.	24	82	[16]
5	BF ₃	H ₂ O, r.t.	2	90	[18]
6	Zeolite NaY	EtOH, r.t.	50	80	[13]
7	NH ₂ SO ₃ H	H ₂ O/EtOH (1:1), 70°C	1.5	89	This work

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