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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], $Cu(NO_3)_2$ [12], zeolite NaY [13], $RuCl_3$ [14], CMK-5-SO_3H nanocatalyst [15], $Yb(OTf)_3$ [16], $InCl_3$ [17] and BF_3-H_2O [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 (NH_2SO_3H) 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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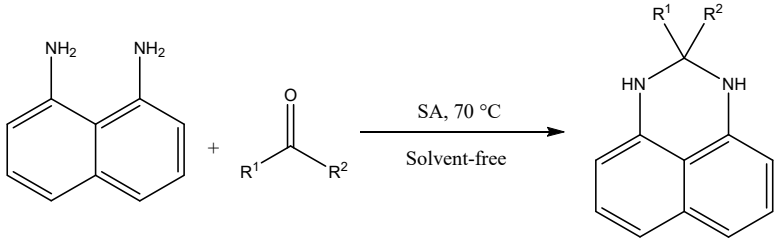

1 **2** **3a-s**

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, ^{1}HNMR and ^{13}CNMR 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 ^{1}HNMR and ^{13}CNMR spectra were recorded on Brucker Avance spectrometer operating at 300 and 75 MHz in 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	H_2O/EtOH(1:1)	70
8	0.01	r.t.	75	H_2O/EtOH(1:1)	70
9	0.01	70	75	H_2O/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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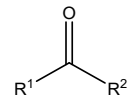
Table 2. Synthesis of dihydroperimidines via condensation of 1,8-diaminonaphthalene and carbonyl compounds using sulfamic acid.[a]

Entry		Product	Time (min)	Yield (%)[b]	m.p. (°C)		Ref.
					Found	Reported	
1	C_6H_5CHO	**3a**	45	90	105-106	101-103	[13]
2	4-Cl C_6H_4CHO	**3b**	40	92	158-159	158-160	[13]
3	4-$N(Me)_2$-C_6H_4CHO	**3c**	70	89	51-53	49-52	[13]
4	4-OH-C_6H_4CHO	**3d**	75	91	164-166	161-163	[13]
5	3,4-$(CH_3O)_2$-C_6H_3CHO	**3e**	65	88	202-205	206-207	[33]
6	4-CH_3O-C_6H_4CHO	**3f**	60	90	154-156	156-158	[34]
7	4-NO_2-C_6H_4CHO	**3g**	75	90	248-250	247-249	[34]
8	3-NO_2-C_6H_4CHO	**3h**	75	90	186-188	188-190	[13]
8	2-Cl-C_6H_4CHO	**3i**	75	88	116-118	116-118	[13]
9	4-F-C_6H_4CHO	**3j**	80	91	182-183	180-182	[13]
10	4-CH_3-C_6H_4CHO	**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]

[a]1,8-naphtalendiamine (1 mmol), carbonyl compound (1 mmol), SA (0.1 mmol), 70 °C, Solvent-free condition.
[b]Isolated 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_2O, r.t.	4	90	[17]
4	$Yb(OTf)_3$	EtOH, r.t.	24	82	[16]
5	BF_3	H_2O, r.t.	2	90	[18]
6	Zeolite NaY	EtOH, r.t.	50	80	[13]
7	NH_2SO_3H	H_2O/EtOH (1:1), 70°C	1.5	89	This work

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