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Succinimidinium *N*-sulfonic acid hydrogen sulfate as an efficient ionic liquid catalyst for the synthesis of 5-arylmethylene-pyrimidine-2,4,6-trione and pyrano[2,3-d]pyrimidinone derivatives

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Abstract Succinimidinium *N*-sulfonic acid hydrogen sulfate ([SuSA-H]HSO_4) as a new ionic liquid is prepared and characterized using a variety of techniques, including infrared spectra (FT-IR), ^{1}H and ^{13}C NMR, scanning electron microscopy, a mass spectra method, as well as by Hammett acidity function. The prepared reagent is efficiently able to catalyze the preparation of 5-arylmethylene-pyrimidine-2,4,6-triones via the condensation of aldehydes and barbituric acid. Further studies showed that the condensation of aldehydes with barbituric acid and malononitrile leading to pyrano[2,3-*d*]pyrimidinone derivatives can also be efficiently promoted in the presence of this reagent. The present methodology offers several advantages, including ease of the preparation and handling of the catalyst, simple and easy work-up, short reaction times, high yields of the products and recyclability of the catalyst.

Keywords Aldehydes · Barbituric acid · 5-Arylmethylene-pyrimidine-2,4,6-trione · Pyrano[2,3-*d*]pyrimidinone · Succinimidinium *N*-sulfonic acid hydrogen sulfate ([SuSA-H]HSO_4)

Introduction

Barbituric acid and its derivatives show a variety of pharmaceutical properties. Among these types of compounds, arylidene barbituric acids and their 2-thio analogues are useful intermediates in the synthesis of heterocyclic compounds, benzyl barbituric derivatives, oxadiazaflavines and unsymmetrical disulphides [1–3].

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5-Arylidenepyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione and pyrano-pyrimidinones, two important derivatives of barbituric acid, have also received significant attention from many pharmaceutical and organic chemists, essentially because of the broad spectrum of their biological and pharmaceutical properties, such as antitumor, antibacterial, vasodilator, bronchiodilator, antimalarial, antifungal, analgesic, sedative-hypnotic, anti parkinsonian and anti-allergic activities [4–8]. In addition, some of these compounds have been studied as non-linear optical materials and dyes [9]. Since most of these compounds are colored, they can be used as synthetic dyes and can gradually replace natural dyes.

There are several reports in the literature for the synthesis of pyrano-pyrimidinones and 5-arylidene barbituric acid derivatives; these include use of PVP-Ni nanoparticles [10], $CoFe_2O_4$ nanoparticles [11], ethyl ammonium nitrate (EAN) [12], copper oxide nanoparticles [13], sodium *p*-toluene sulfonate (NaPTSA) [14], L-Tyrosine [15], $Ce_1Mg_xZr_{1-x}O_2$ (CMZO) [16], basic alumina [17] and $FeCl_3{\cdot}6H_2O$ [18] (for the preparation of 5-arylidene barbituric acid derivatives), $KAl(SO_4)_2{\cdot}12H_2O$ [19], L-proline [20], Zn[(L)proline]$_2$ [21], [BMIm]BF_4 [22], tetrabutylammonium bromide (TBAB) [23], $(NH_4)_2{\cdot}HPO_4$, [24], KBr/Electrolysis [25], DABCO [26] and sulfonic acid nanoporous silica (SBA-Pr-SO_3H) [27]. In addition, microwave irradiation and mechanochemical methods were also used for the synthesis of pyrano-pyrimidinones in the absence of catalyst [28, 29].

Although these procedures provide an improvement, some of these catalysts suffer from disadvantages, such as low yields, long reaction times, harsh reaction conditions, tedious work-up and the requirement of excess amounts of reagents or catalysts.

Therefore, finding simple, efficient, and mild procedures using easily separable and reusable catalysts to overcome these problems is still in demand.

N-Sulfonic acids are important catalysts that could be easily prepared by simple reaction of *N*-substituted organic compounds with chlorosulfonic acid under mild conditions. In recent years, an important part of our research has focused on the preparation, characterization and introduction of different types of these compounds (e.g., saccharin sulfonic acid (SaSA) [30–32], melamine trisulfonic acid (MTSA) [33–35], succinimide-*N*-sulfonic acid (SuSA) [36–38], *N*-sulfonic acid poly(4-vinylpyridinium) chloride (NSPVPC) [39–42] and succinimidinium hydrogen sulfate ([H-Suc]HSO_4) [43]). The use of prepared reagents in organic reactions showed that these compounds can be successfully utilized as catalysts in all the studied reactions.

Herein and in continuation of these studies, we wish to report the preparation, characterization and application of succinimidinium *N*-sulfonic acid hydrogen sulfate ([SuSA-H]HSO_4) as a new efficient ionic liquid catalyst in the promotion of the synthesis of 5-arylmethylene-pyrimidine-2,4,6-trione and pyrano[2,3-*d*]pyrimidinone derivatives.

Experimental

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. All yields refer to the isolated products. Products were characterized by comparison of their physical constants, and also by their infrared (IR) and nuclear magnetic

resonance (NMR) spectra, with authentic samples and those reported in the literature. The purity determination of the substrate and reaction monitoring were accompanied by thin-layer chromatography (TLC) on silicagel polygram SILG/UV 254 plates.

The Fourier transform (FT)-IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer. The ^{1}H NMR spectra were recorded with Bruker Avance 400 instruments. In all cases, the chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. The ^{13}C NMR data were collected on Bruker Avance 100 MHz instrument. Mass spectrometry (MS) studies were performed using 5973 network mass selective detector, Agilent Technology (HP) company (ion source: electroni (EI) 70 eV; ion source temperature: 230 °C; analyzer: quadrupole). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

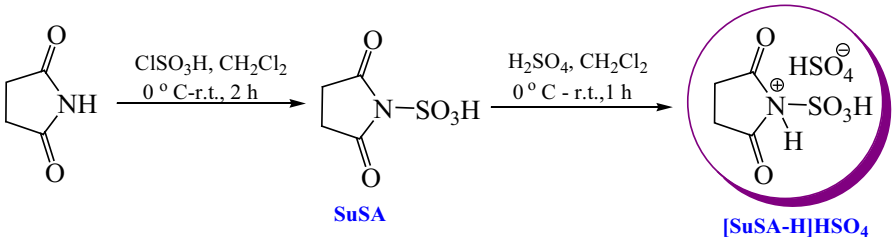
Preparation of [SuSA-H]HSO_4

Succinimide-*N*-sulfonic acid [SuSA] was prepared according to the reported method in the literature [30]. Then, sulfuric acid 98 % (0.5 mL) was added dropwise to a mixture of SuSA (1.68 g) in dry CH_2Cl_2 (10 mL) over a period of 2 min in an ice bath. The resulting mixture was stirred for 1 h and then the solvent was decanted. The obtained compound was washed with dry diethylether (2 × 5 mL) and dried under vacuum to give [SuSA-H]HSO_4 as a white gel in 98 % (Scheme 1). Spectroscopic data for [SuSA-H]HSO_4 are as follow:

FT-IR (KBr, cm^{-1}) υ_{max}: 3418, 1706, 1294, 1182, 855, 581 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 2.49$ (4H, s), 7.39 (2H, s), 10.84 (1H, s, OH) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) $\delta = 29.78$, 180 ppm; MS: 56, 99, 278 m/z.

General procedure for the preparation of 5-arylmethylene-pyrimidine-2,4,6-trione derivatives

A mixture of the aldehyde (1 mmol), barbituric acid (1 mmol) and [SuSA-H]HSO_4 (0.02 mmol) in water (3 mL) was stirred at room temperature. After completion of the reaction, as monitored by TLC, using *n*-hexane:EtOAc (1:3), the crude product was filtered off to separate the catalyst, washed with water and recrystallized from



Scheme 1 The preparation of [SuSA-H]HSO_4

ethanol to afford the pure compound. After separation of the product, the catalyst was recovered by evaporation of water, washed with Et_2O, dried at 50 °C under vacuum for 1 h and reused for the same reaction.

General procedure for the preparation of pyrano[2,3-d]pyrimidinones

A mixture of an aldehyde (1 mmol), malononitrile (1 mmol), barbituric acid (1 mmol) and [SuSA-H]HSO_4 (0.05 mmol) in water (3 mL) was stirred in an oil bath (80 °C) for appropriate time. After completion of the reaction, the solid product was collected by filtration and recrystallized with ethanol to afford the pure compounds.

Results and discussion

Succinimidinium *N*-sulfonic acid hydrogen sulfate ([SuSA-H]HSO_4), as new succinimide-based reagent, was prepared as described in "General procedure for the preparation of pyrano[2,3-d]pyrimidinones" section. This reagent is characterized using different methods, including of techniques including FT-IR, ^{1}H and ^{13}C NMR, scanning electron microscopy (SEM), a mass spectra method, as well as by Hammett acidity function.

Catalyst characterization

IR analysis

The infrared spectra of succinimide, SuSA and [SuSA-H]HSO_4 are shown in Fig. 1. The IR spectrum of the ionic liquid shows a broad peak at 3000–3600 cm^{-1}, which can be related to the OH stretching of the SO_3H groups. Moreover, the strong peaks observed at 581, 882 and 1182 cm^{-1} correspond to the S–O symmetric and asymmetric stretchings, respectively. It should be noted that the two peaks of the carbonyl groups in succinimide, which are observed at 1698 and 17,777 cm^{-1}, converted to one peak (1706 cm^{-1}) in the catalyst [36].

^{1}H NMR analysis

The ^{1}H NMR spectra of succinimidinium hydrogen sulfate [Su-H]HSO_4 and [SuSA-H]HSO_4 are compared in Fig. 2. In the ^{1}H NMR spectrum of [SuSA-H]HSO_4 (Fig. 2a), in addition to the other protons, the acidic hydrogen of HSO_4 appears at 10.84 ppm [43]. This observation clarifies that [SuSA-H]HSO_4 is exactly synthesized (Fig. 2a).

^{13}C NMR analysis

Furthermore, the ^{13}C NMR spectrum of [SuSA-H]HSO_4 is shown in Fig. 3. The peaks corresponding to carbons of the catalyst are shown in 29.78 and 180.14 ppm.

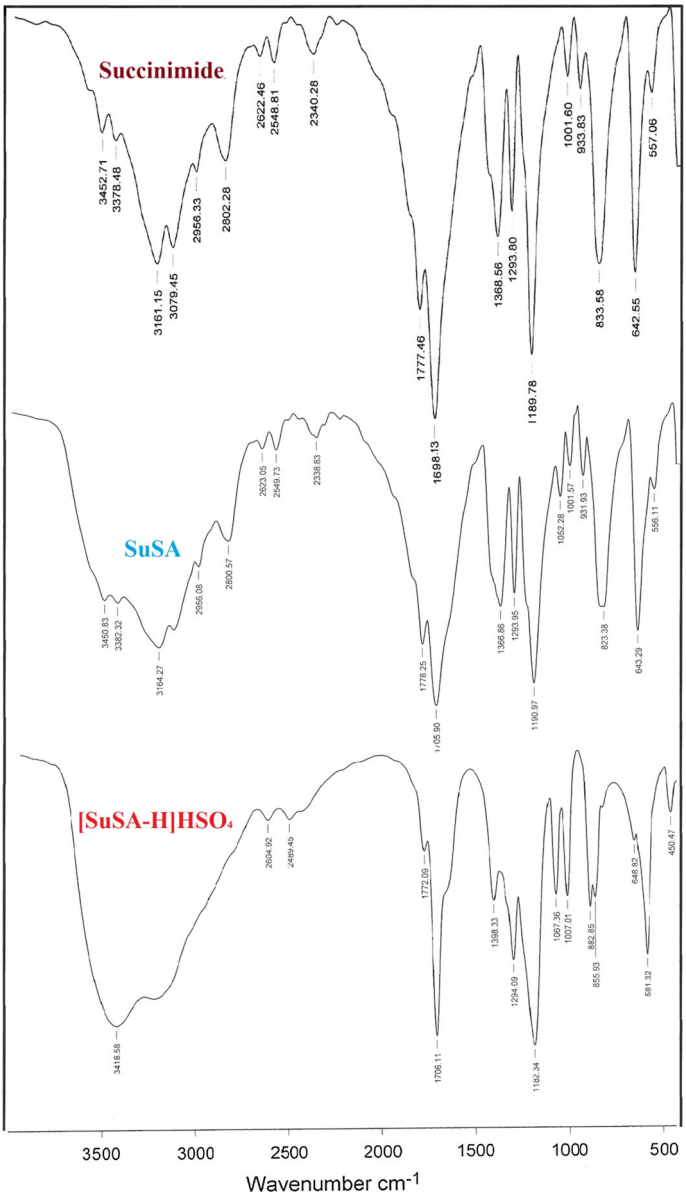


Fig. 1 FT-IR spectra of succinimide, SuSA and [SuSA-H]HSO_4

Mass analysis

The mass spectrum of [SuSA-H]HSO_4 is shown in Fig. 4. In this spectrum, the correct molecular ion peak appears at 278. Another ion peak is observed at 99 (M^+–SO_3H and HSO_4) [43].

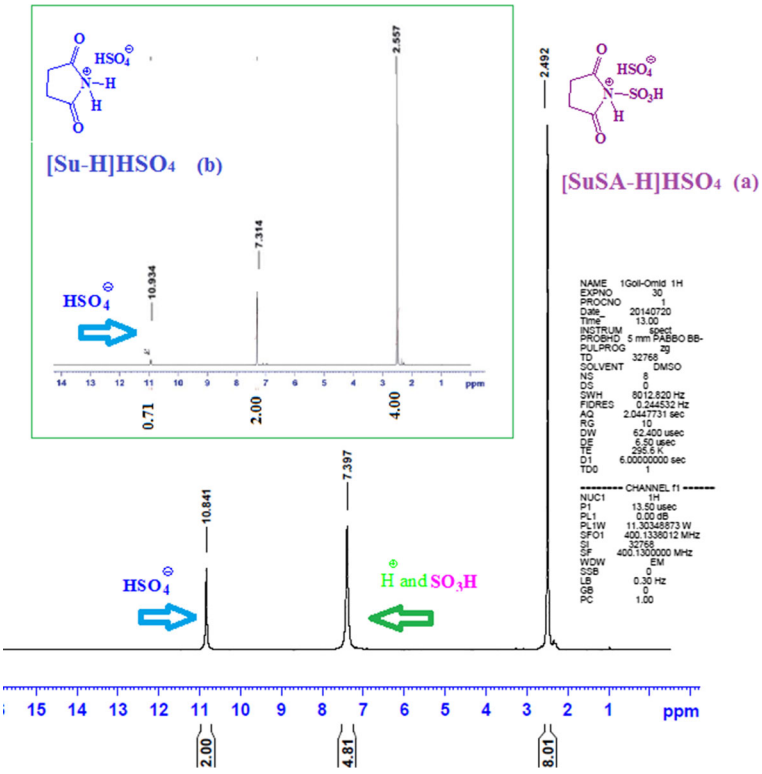


Fig. 2 ^{1}H NMR spectra of [SuSA-H]HSO_4 (**a**) and [Su-H]HSO_4 (**b**)

SEM analysis

The samples of succinimide and [SuSA-H]HSO_4 were also analyzed by SEM with various magnifications for determining the particle shape, size distribution and surface morphology (Fig. 5). These images show that with chemical modification, the primary morphology of succinimide is completely changed and the particles are aggregated in the product. This increases the surface area of the catalyst, and finally its catalytic activity. This aggregation can be caused by hydrogen bonding sites and nearby positive and negative sides [43].

Hammett acidity

The Hammett acidity method is an effective way to assess the acidity strength of an acid in organic solvents, using a UV–Vis technique [44]. The Hammett function is defined as:

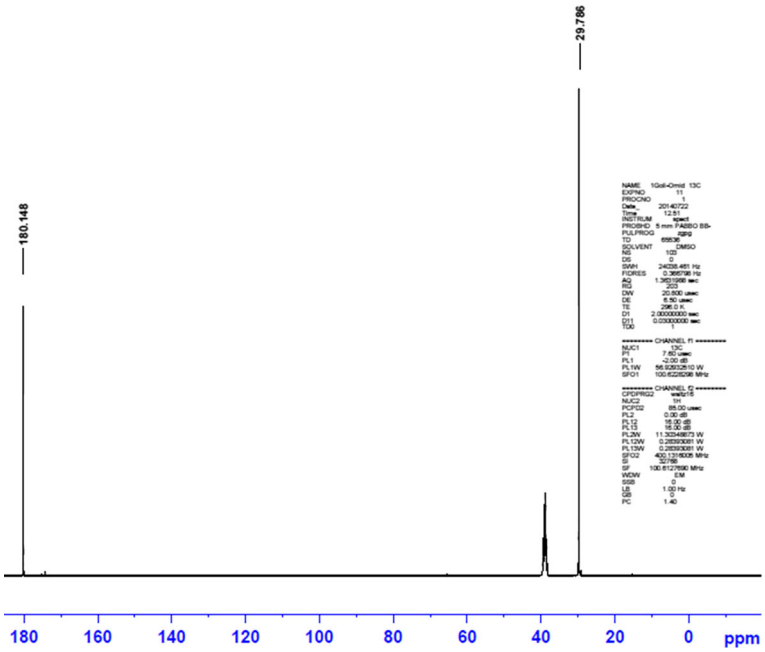


Fig. 3 ^{13}C NMR spectra of [SuSA-H]HSO_4

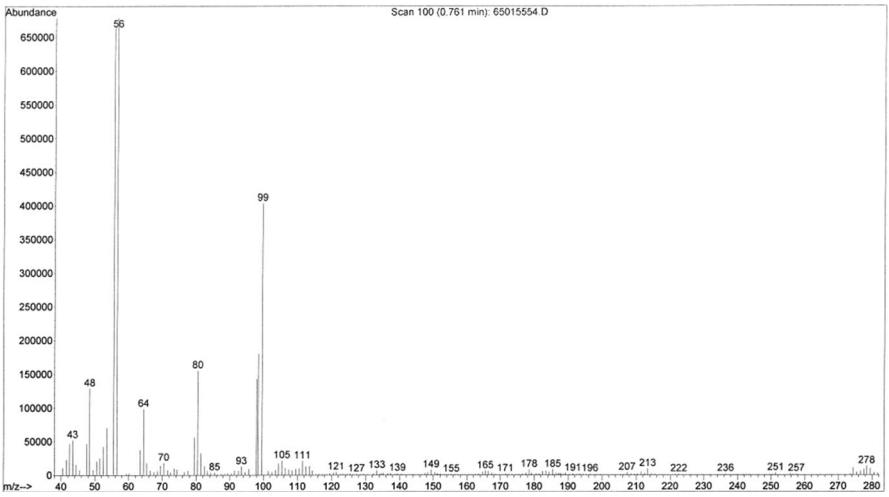


Fig. 4 Mass spectra of [SuSA-H]HSO_4

$$H_0 = pK(I)_{aq} + \log\left([I]_s/[IH^+]_s\right)$$

where the $pK(I)_{aq}$ is the pK_a value of aqueous solution of indicator, $[IH^+]_s$ and $[I]_s$ are the molar concentrations of protonated and unprotonated forms of the indicator

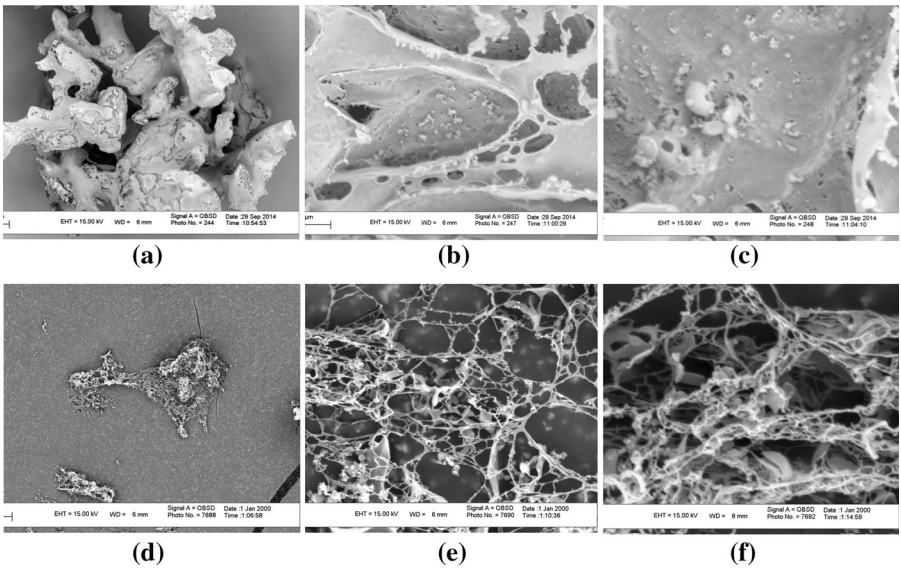


Fig. 5 SEM micrographs of $[SuSA\text{-}H]HSO_4$ (**a**–**c**) and succinimide (**d**–**f**)

in the solvent, respectively. According to Lambert–Beer's Law, the value of $[I]_s/[IH^+]_s$ can be determined and calculated through UV–visible spectrum.

For this purpose, 4-nitroaniline ($pK(I)aq = 0.99$) and CCl_4 were chosen as the basic indicator and the solvent, respectively . As can be seen in Fig. 6, the maximal absorbance of the unprotonated form of the indicator was observed at 330 nm in CCl_4. When $[SuSA\text{-}H]HSO_4$ was added to the indicator solution as the ionic liquid catalyst, the absorbance of the unprotonated form of the indicator decreased, which indicated that the indicator was partially in the form of $[IH^+]$. These results are listed in Table 1, and show the acidity strength of $[SuSA\text{-}H]HSO_4$.

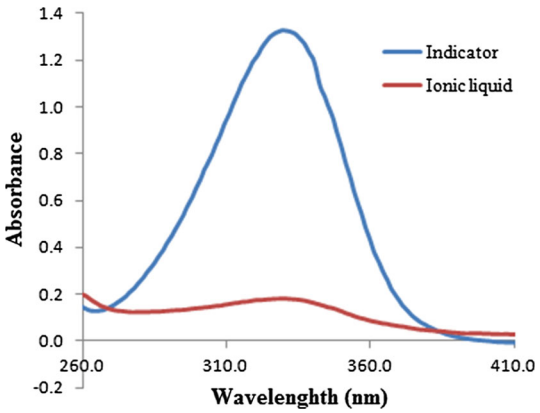


Fig. 6 Absorption spectra of 4-nitroaniline (indicator) and $[SuSA\text{-}H]HSO_4$ (catalyst) in CCl_4

Table 1 Calculation of the Hammett acidity function (H_0) for [SuSA-H]HSO_4

Entry	Catalyst	A_{max}	$[I]_s$ (%)	$[IH^+]_s$ (%)	H_0 [Ref.]
1	–	1.329	100	0	–
2	SuSA	0.412	25.4	74.6	0.52 [36]
3	[SuSA-H]HSO_4	0.182	13.69	86.31	0.191

Condition for UV–visible spectrum measurement: solvent: CCl_4, indicator: 4- nitroaniline ($pK(I)_{aq} = 0.99$), 1.44×10^{-4} mol/L (10 mL); catalyst: [SuSA or [SuSA-H]HSO_4 (10 mg), 25 °C

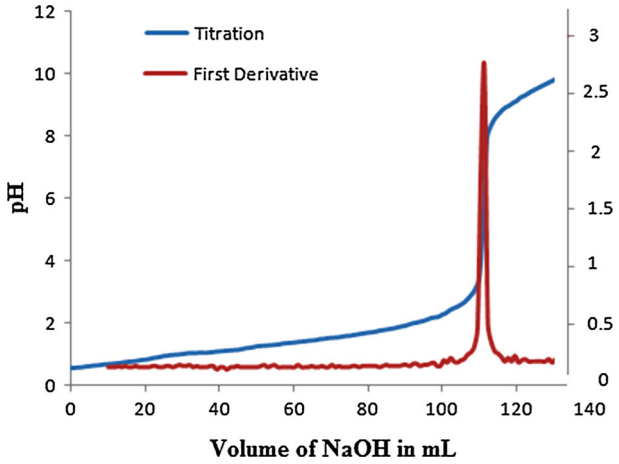


Fig. 7 Titration and the first derivative curves of the ionic liquid with NaOH

Comparison of the Hammett acidity of SuSA (Table 1, entry 2) with [SuSA-H]HSO_4 shows that the prepared ionic liquid is more acidic than SuSA, which may cause it to be a more efficient catalyst for the requested reactions.

A titration method was used to determine the number of protic protons of the prepared catalyst. In this experiment, a solution of the ionic liquid was titrated with NaOH. The titration curve for the reaction of 20.5 mL of 0.09 M ionic liquid with 0.05 M NaOH is given in Fig. 7. This figure clearly shows that, when 110.7 mL of the basic solution is added, all the acidic protons are neutralized. On the other hand, Eq. (1) shows that for the neutralization of each of the acidic protons, 36.9 mL of the basic solution is needed. On the basis of these studies, it can be concluded that this ionic liquid has three protic protons with almost the same acidic power.

$$M(\text{acid}) \times V(\text{acid}) = M(\text{base}) \times V(\text{base})$$

$$0.09\,(\text{molar}) \times 20.5\,(\text{mL}) = 0.05\,(\text{molar}) \times V(\text{base}) \quad (1)$$

$$V(\text{base}) = 36.9\,\text{mL}$$

Catalytic activity

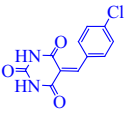
On the basis of the information obtained from the above-mentioned studies, we predicted that [SuSA-H]HSO_4 can be used as an efficient catalyst to promote the reactions, which need an acidic catalyst to speed them up. We were interested in investigating the applicability of this reagent in the promotion of the synthesis the barbituric acid derivatives.

To optimize the amount of the catalyst, kind of solvent and temperature, the reaction of 4-chlorobenzaldehyde (1 mmol) with barbituric acid (1 mmol) was studied in the presence of [SuSA-H]HSO_4 at different conditions, and the results are tabulated in Table 2. On the basis of these results, optimized conditions were selected, as shown in Scheme 2.

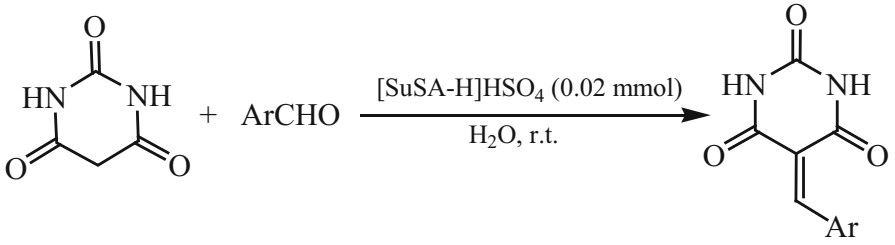
After optimization of the reaction conditions and in order to study the efficiency of [SuSA-H]HSO_4 in this reaction, various aromatic aldehydes were reacted with barbituric acid under the selected conditions to furnish the corresponding products in high yields during short reaction times. The obtained results are summarized in Table 3. It seems that the nature and electronic properties of the substituent had no obvious effect on the rate and reaction yields.

After the successful synthesis of a series of 5-arylmethylene-pyrimidine-2,4,6-trione derivatives, we were interested in extending the applicability of this ionic

Table 2 Optimization of the reaction conditions for the synthesis of 5-arylmethylene-pyrimidine-2,4,6-trione derivative of 4-chlorobenzaldehyde

Entry	[SuSA-H]HSO_4 (mmol)	Solvent	Time (min)	Isolated yield (%)	Product
1	0.1	H_2O	4	98	
2	0.05	H_2O	5	94	
3	0.02	H_2O	6	96	
4	0.1	H_2O[a]	3	95	
5	0.02	EtOH	15	96	
6	0.02	CH_2Cl_2	30	40	
7	0.02	Solvent-free	30	40	

[a] 50 °C



Scheme 2 [SuSA-H]HSO_4 catalyzed the synthesis of 5-arylmethylene-pyrimidine-2,4,6-trione derivatives

Table 3 Preparation of 5-arylmethylene-pyrimidine-2,4,6-trione derivatives using $[SuSA\text{-}H]HSO_4$ as the catalyst

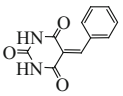
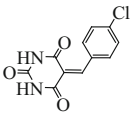
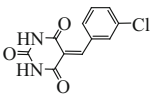
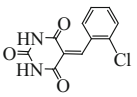
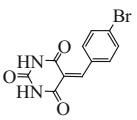
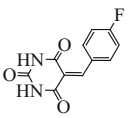
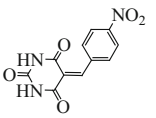
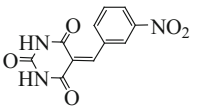
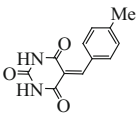
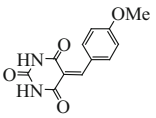
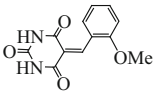
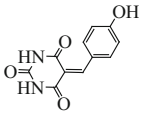
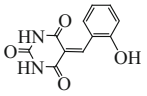
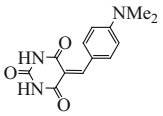
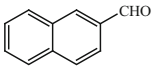
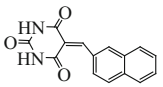
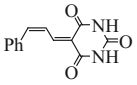
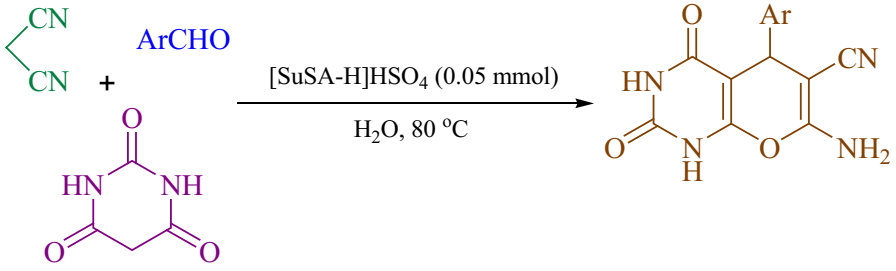
Entry	Aldehyde	Time (min)	Yield (%)[a]	Melting point (°C)		Compound
				Found	Reported [Ref.]	
1	C_6H_5CHO	7	80	263–265	256 [13]	
2	$4\text{-}ClC_6H_4CHO$	6	96	298–299	298 [13]	
3	$3\text{-}ClC_6H_4CHO$	6	93	273–275	274–278 [16]	
4	$2\text{-}ClC_6H_4CHO$	7	95	250–252	252 [13]	
5	$4\text{-}BrC_6H_4CHO$	5	94	290–292	292–293 [13]	
6	$4\text{-}FC_6H_4CHO$	6	85	309–310	309–310 [13]	
7	$4\text{-}NO_2C_6H_4CHO$	6	96	270–272	272–274 [13]	
8	$3\text{-}NO_2C_6H_4CHO$	8	97	231–233	231–232 [13]	
9	$4\text{-}CH_3C_6H_4CHO$	9	98	280–284	282–284 [16]	
10	$4\text{-}CH_3OC_6H_4CHO$	2	85	298–300	306–308 [13]	
11	$2\text{-}CH_3OC_6H_4CHO$	8	98	269–272	268–269 [17]	

Table 3 continued

Entry	Aldehyde	Time (min)	Yield (%)[a]	Melting point (°C)		Compound
				Found	Reported [Ref.]	
12	4-HOC_6H_4CHO	8	90	>300	>300 [13]	
13	2-HOC_6H_4CHO	12	92	249–251	249–251 [15]	
14	4-$(CH_3)_2NC_6H_4CHO$	3	98	281–282	281–282 [16]	
15		10	90	266 (dec)	266 (dec) [10]	
16	Cinnamaldehyde	6	98	266–268	268 [13]	

[a] Isolated yield



Scheme 3 [SuSA-H]HSO_4 catalyzed the synthesis of pyrano-pyrimidinone derivatives

liquid in the promotion of the preparation of pyrano-pyrimidinone derivatives via the reaction of aldehyde and malononitrile with barbituric acid under the previously selected conditions. Our investigations clarified that the synthesis of these types of compounds can be completed with higher amounts of the catalyst (0.05 mmol) at 80 °C (Scheme 3).

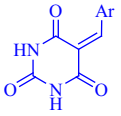
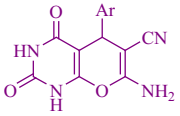
As shown in Table 4, a series of aromatic aldehydes containing either electron-donating or electron-withdrawing substituent successfully reacted and afforded high to excellent yields of the pure products under the selected conditions.

Table 4 Synthesis of pyrano-pyrimidinone derivatives catalyzed by [SuSA-H]HSO_4

Entry	Aldehyde	Time (min)	Yield (%)[a]	Melting point (°C)	
				Found	Reported [Ref.]
1	C_6H_5CHO	30	92	215–217	208–210 [29]
2	4-ClC_6H_4CHO	20	95	245–247	239–240 [29]
3	3-ClC_6H_4CHO	20	90	240–241	240–241 [23]
4	2-ClC_6H_4CHO	10	98	211–212	213–215 [29]
5	4-BrC_6H_4CHO	15	98	231–233	230–231 [29]
6	4-$NO_2C_6H_4CHO$	20	92	236–237	237–238 [29]
7	3-$NO_2C_6H_4CHO$	10	98	267–269	268–270 [21]
8	2-$NO_2C_6H_4CHO$	10	95	253–256	262–263 [29]
9	4-$CH_3C_6H_4CHO$	13	85	224–225	226–227 [27]
10	4-HOC_6H_4CHO	7	98	204–206	206–208 [19]
11	2-HOC_6H_4CHO	14	95	160–162	162–163 [25]
12	4-$CH_3OC_6H_4CHO$	20	98	280–281	280–281 [29]
13	4-$(CH_3)_2NC_6H_4CHO$	15	98	231–233	230 [25]

[a] Isolated yield

Table 5 Comparison of the results obtained from the synthesis of 5-arylmethylene-pyrimidine-2,4,6-trione and pyrano[2,3-*d*]pyrimidinone in the presence of [SuSA-H]$HSO_4$with those obtained using other catalysts

Entry	Catalyst loading (mol%)	Conditions	Time (min)	Yield (%) [Ref.]	Product
1	CuO Nps (100 mg)	Solvent-free, r.t.	7–20	92–98 [13]	
2	50 % Aq. NaPTSA	r.t.	4–15	85–94 [14]	
3	$Ce_1Mg_xZr_{1-x}O_2$ (0.2 gm)	M.W.	3–5	90–94 [16]	
4	$FeCl_3{\cdot}6H_2O$ (15)	H_2O, reflux	20–50	73–96 [18]	
5	EAN (1 mL)	r.t.	3–6 h	84–95 [12]	
6	$CoFe_2O_4$ Nps (1)	H_2O, EtOH, r.t.	2–6	94–80 [11]	
7	[SuSA-H]HSO_4 (2)	H_2O, r.t.	2–12	80–98 This work	
8	SBA-Pr-SO_3H (10 mg)	Solvent-free, 140 °C	5–45	61–90 [27]	
9	TBAB (10)	H_2O, reflux	25–35	80–90 [23]	
10	$(NH_4)_2$ HPO_4 (10)	aq. EtOH, r.t.	2 h	70–90 [24]	
11	L-Proline (5)	aq. EtOH, r.t.	30–150	68–86 [20]	
12	Zn[(L)proline]$_2$ (17)	EtOH, reflux	30–85	80–92 [21]	
13	DABCO (10)	H_2O, EtOH, r.t.	2 h	83–96 [26]	
14	Alum (10)	H_2O, 80 °C	30–45	80–90 [19]	
15	–	M.W., H_2O	3–5	86–94 [28]	
16	[BMIm]BF_4 (30 mg)	Solvent-free, 90 °C	3–5 h	82–95 [22]	
17	[SuSA-H]HSO_4 (5)	H_2O, 80 °C	7–30	85–98 (This work)	

r.t. Room temperature, *M.W.* Microwave

Table 5 compares our results with the results reported in the literature using some of the other catalysts in the synthesis of 5-arylmethylene-pyrimidine-2,4,6-trione and pyrano[2,3-*d*]pyrimidinone derivatives.

This comparison indicates that in some of the other methods, the reactions were completed in the presence of higher amounts of the catalysts and/or during longer times (Table 5, entries 4, 5, 9, 10, 12, 13, 16). In addition, the main drawbacks in the application of some of these catalysts are the difficult and time consuming procedures and/or the use of expensive starting materials (Table 5, entries 1, 6). It is very important to note that the same reactions in the presence of SuSA and succinimidinium hydrogen sulfate are completed in longer reaction times.

Finally, to check the reusability of the catalyst, the synthesis of the requested derivatives of 4-chlorobenzaldehyde (Tables 3, 4, entry 2) under the optimized reaction conditions were selected as model reactions. After the separation of the product, the water was evaporated and the catalyst was washed with Et_2O, dried and reused for the same reactions. These process were carried out over four runs and all reactions led to the desired products with high efficiency (Fig. 8).

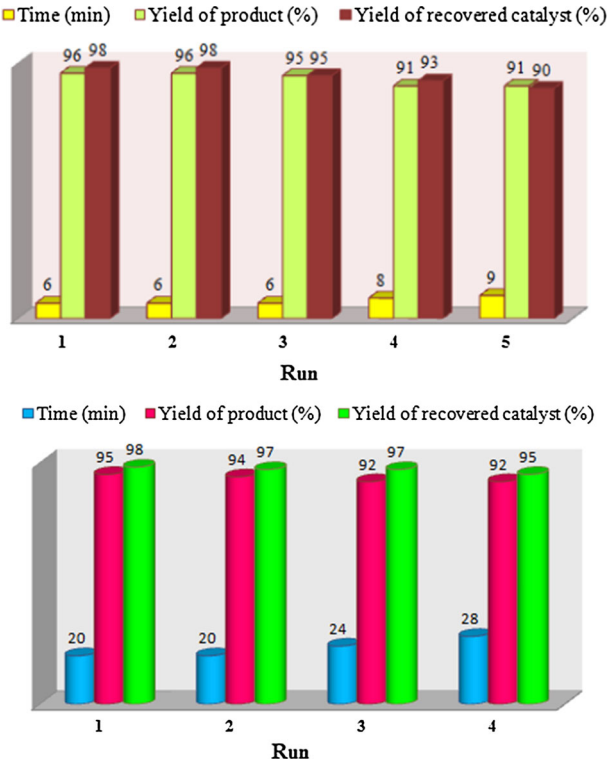


Fig. 8 Recyclability of the [SuSA-H]HSO_4 in the reactions reported in Table 3 (*up*) and Table 4 (*down*), entry 2

Conclusion

In this paper, we have developed an efficient, simple and green method for the synthesis of 5-arylmethylene-pyrimidine-2,4,6-trione and pyrano[2,3-*d*]pyrimidinone derivatives using a new efficient ionic liquid called succinimidinium *N*-sulfonic acid hydrogen sulfate which is simply prepared and characterized with a variety of techniques. Easy preparation of the catalyst, mild and green reaction conditions, easy work-up procedure, short reaction times and high yields of the products are significant advantages of this method. Also, this reagent could be successfully recovered and reused for at least four runs without a significant loss of activity.

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