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Preparation and application of triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide as new efficient ionic liquid catalyst for synthesis of 5-arylidene barbituric acids and pyrano[2,3-*d*]pyrimidine derivatives

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Abstract

We report synthesis of triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide ([TPPHSP]Br) as a reusable green Brønsted-acidic ionic liquid catalyst and its application for synthesis of 5-arylidene barbituric acids and pyrano[2,3-*d*]pyrimidine derivatives by condensation reaction between aromatic aldehydes and barbituric acid or aromatic aldehydes, malononitrile, and barbituric acid in EtOH–H_2O in reflux condition with good to excellent yield. The [TPPHSP]Br IL catalyst was characterized by Fourier-transform infrared (FT-IR) spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance (NMR), and thermogravimetric (TG) analysis and showed good catalytic activity and reusability.

Keywords Triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide · Brønsted-acidic ionic liquid · Phosphonium ionic liquid · Pyrano[2,3-*d*]pyrimidines · 5-Arylidene barbituric acids

Introduction

In recent years, ionic liquids (ILs) have attracted considerable attention in organic synthesis as solvents, catalysts, or dual-purpose catalyst-solvents due to their special physical and chemical features, such as low volatility, good thermal stability, low melting point, insignificant vapor pressure, and recyclability [1–9]. Ionic liquids are generally

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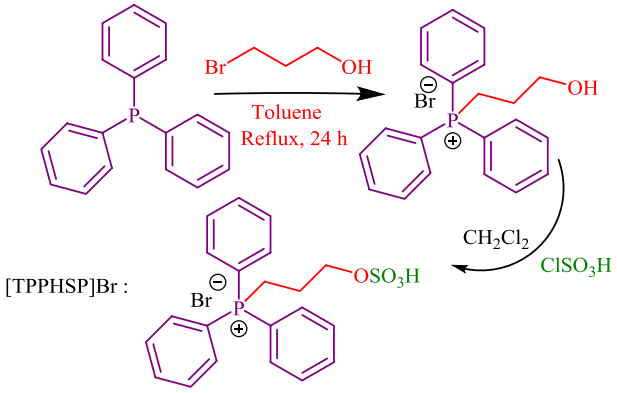
constituted of large asymmetric organic cations of nitrogen or phosphorus and many different inorganic or organic anions [10]. Over the past few years, synthesis of certain ionic liquids known as task-specific ionic liquids (TSILs) with Brønsted-acidic functional groups in their structure has attracted significant interest because of their advantages over traditional mineral liquid and solid acids. Moreover, compared with conventional mineral acids, TSILs present various interesting properties including high catalytic efficiency, high polarity, easy product separation, and environmentally friendly nature [11–16].

Heterocycles are very important in synthesis of active biological compounds. These compounds are also the main structural component of most pharmaceutical molecules [17–19]. Among them, barbituric acid derivatives have attracted much attention in medicinal chemistry. The seductive and hypnotic properties of 5-arylidene barbituric acid derivatives have been known for years [20–23]. Moreover, pyrano[2,3-*d*]pyrimidines show numerous pharmacological activities, including antitumor [24], anticancer [25], antiviral [26], antimicrobial, and antifungal activities [27]. 5-Arylidene barbituric acid derivatives have been synthesized in presence of various catalysts such as 1,4-diazabicyclo[2.2.2]octane (DABCO) [28], L-tyrosine [29] Ni nanoparticles (NPs) [30], silicotungstic acid [31], NH_2SO_3H [32], [bmim]BF_4 [33], ethylammonium nitrate [34], cetyltrimethylammonium bromide [35], and taurine [36]. Several procedures have also been reported for synthesis of pyrano[2,3-*d*]pyrimidines, e.g., using DABCO [37], basic ionic liquid [38], L-proline [39], urea-SO_3H [40], Al-HMS-20 [41], nano-Al_2O_3 [42], alum [43], taurine [36], [H-Suc]HSO_4 [44], CuO/ZnO nanocatalyst [45], $B(OH)_3$ [46], Al-HMS-20 [41], and trichloroisocyanuric acid [47].

Multicomponent reactions (MCRs) are considered to be an important approach in organic synthesis [48], providing a powerful means to synthesize complex compounds in one step without separation of intermediates. Since three or more components react with together in a one-pot process in these reactions, they show high atom economy and high selectivity [49–52]. One type of MCR involves synthesis of pyrano[2,3-*d*] pyrimidines through one-pot, three-component condensation reaction between aldehydes, malononitrile, and barbituric acid. Although several catalysts and different procedures have been reported for synthesis of pyrano[2,3-*d*]pyrimidines, identification of an environmentally compatible approach using a recyclable catalyst is still a great demand in organic synthesis.

In continuation of our research on preparation and application of green catalysts in multicomponent reactions [53–58], we report herein preparation and use of triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide ([TPPHSP]Br) as a green, efficient, and reusable ionic liquid catalyst (Scheme 1) for synthesis of 5-arylidene barbituric acid derivatives and pyrano[2,3-*d*]pyrimidines via one-pot condensation of aromatic aldehydes, malononitrile, and barbituric acid in EtOH–H_2O in reflux condition (Scheme 1).



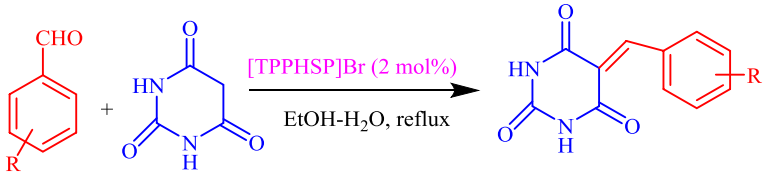
Scheme 1 Synthesis of triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide ([TPPHSP]Br) as green, efficient, and reusable ionic liquid catalyst

Experimental

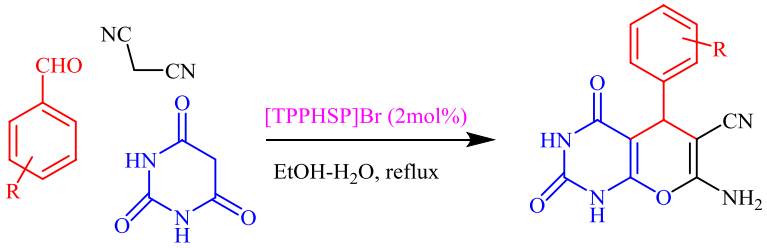
All chemicals were purchased from Merck and Sigma-Aldrich companies. All reagents were applied without any further purification. All known compounds were identified by comparison of their melting points, IR, and NMR data with those reported in literature. Reaction progress was monitored by thin-layer chromatography (TLC) using silica gel SIL G/UV 254 plates. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker Ultrashield spectrometer at 400 MHz and 100 MHz, respectively. Thermogravimetric analysis (TGA) was carried out using a METLLER apparatus. Melting points were measured with an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were recorded with a JASCO 6300 spectrometer from KBr pellets in the range of 400–4000 cm^{-1}.

Preparation of triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide as ionic liquid

Hydroxyl-functionalized phosphonium IL was synthesized using the procedure described in literature with minor modifications [59]. Triphenylphosphine and 3-bromopropanol were combined in equimolar quantities in toluene and heated at reflux condition for 24 h under Ar atmosphere. The reaction mixture was then cooled to room temperature, and the toluene was decanted. The residue was washed several times (3 × 20 mL) with toluene and diethyl ether, then dried under vacuum to give the product as a yellow viscous oil. After this, hydroxyl-functionalized phosphonium IL (2.3 g, 6.0 mmol) in dry CH_2Cl_2 (30 mL) was charged into a 100-mL round-bottomed flask in an ice bath, then chlorosulfonic acid (0.7 g, 6.0 mmol) was added dropwise. After chlorosulfonic acid addition, the reaction mixture was stirred for 30 min, then allowed to stirred for 2 h at room temperature. The solvent was evaporated under reduced pressure to give the desired IL as a yellow viscous liquid. Spectroscopic data for the ionic liquid: IR (KBr, υ, cm^{-1}) = 3302, 1595, 1499, 1474, 1231, 1119, 754, 692, 539. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H, OH),



Scheme 2 Synthesis of 5-arylidene barbituric acid derivatives



Scheme 3 Synthesis of pyrano[2,3-*d*]pyrimidine derivatives

7.32–7.42 (m, 15H), 4.04–4.07 (t, 2H), 3.26–3.33 (m, 2H), 1.86–1.91 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.4, 133.3, 132.1, 132.0, 129.0, 128.9, 118.3, 117.4, 66.0, 21.1, 21.0, 19.4, 18.8 ppm.

General procedure for synthesis of 5-arylidene barbituric acid derivatives

Typically, a mixture of aromatic aldehyde (1.0 mmol), barbituric acid (1.0 mmol), and [TPPHSP]Br (0.01 g, 2 mol%) as catalyst was added to 5 mL EtOH–H_2O (3:1) in a 25-mL round-bottomed flask. The reaction mixture was refluxed with stirring for appropriate time (Table 2). After reaction completion, as monitored by TLC (*n*-hexane:EtOAc), the precipitate was isolated by filtration and washed several times with cold ethanol for purification (Scheme 2). All of the desired product(s) were characterized by comparison of their physical properties and spectral data (IR and NMR) with those of known compounds.

General procedure for synthesis of pyrano[2,3-*d*]pyrimidine derivatives

Aromatic aldehydes (1.0 mmol), malononitrile (1.0 mmol), barbituric acid (1.0 mmol), and 5 mL EtOH–H_2O as solvent were loaded into a 25-mL round-bottomed flask, then [TPPHSP]Br (0.01 g, 2 mol%) was added to the mixture. The resulting reaction mixture was stirred at reflux condition for appropriate time (Table 4). After reaction completion, monitored by TLC (*n*-hexane:EtOAc), the reaction mixture was cooled to room temperature and filtered. After filtration, the solid products were washed with cold water and recrystallized from ethanol to obtain pure products in good to excellent yield (Scheme 3, Table 4). The filtrate of ionic liquid [TPPHSP]Br was then recovered and reused for subsequent reactions.

All desired products were characterized by comparison of their physical properties and spectral data (IR and NMR) with those of known compounds.

Results and discussion

In recent years, synthesis of task-specific ionic liquids with Brønsted-acidic functional groups, particularly SO_3H and SO_4H functional groups, has become increasingly popular [60, 61]. In this research, we synthesized triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide as a new Brønsted-acidic ionic liquid. With the intention of investigating the applicability of [TPPHSP]Br in organic reactions, synthesis of barbiturate derivatives was selected as the model reaction.

Characterization of [TPPHSP]Br as Brønsted-acidic ionic liquid catalyst

The structure of the Brønsted-acidic ionic liquid [TPPHSP]Br was recognized by studying its FT-IR, ^{1}H NMR, ^{13}C NMR, TG, and differential thermogravimetric (DTG) spectra.

In the FT-IR spectrum of [TPPHSP]Br, the characteristic band at 3302 cm^{-1} corresponds to stretching vibration of O–H in SO_4H group. The strong absorptions at 1231.33, 1185.38, 1119.48, and 539.97 cm^{-1} are related to asymmetric stretching and symmetric bending vibrations of S–O of SO_4 group (Fig. 1).

Also, we studied the structure of [TPPHSP]Br by ^{1}H and ^{13}C NMR spectroscopy (Fig. 2). The acidic hydrogen of SO_4H shows a significant peak in the ^{1}H NMR spectrum of the ionic liquid, observed at 8.23 ppm as a broad singlet. Also, there are two multiplet peaks at 1.86–1.91 and 3.26–3.33 ppm and a triplet at 4.05 ppm, related to aliphatic hydrogens, and a multiplet peak at 7.32–7.48 ppm that can be assigned to aromatic ring protons of IL. The signals in the ^{13}C NMR spectrum are in accordance with the structure of [TPPHSP]Br IL. The peaks at $\delta = 117.4$–133.4 are related to aromatic ring carbons of PPh_3. Furthermore, the peaks at 66.0 as a singlet

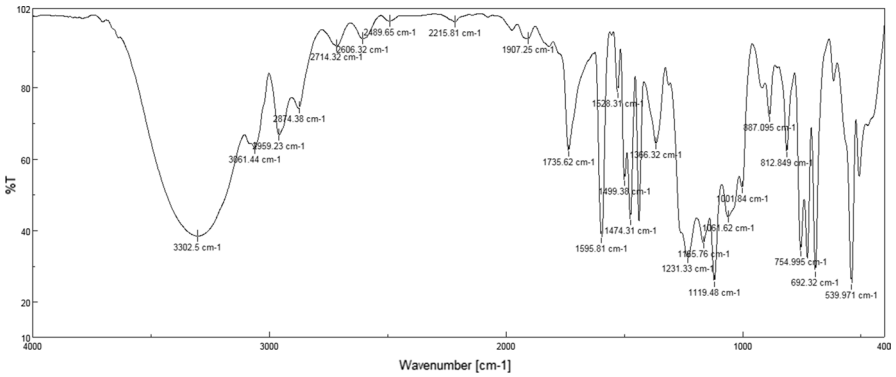


Fig. 1 FT-IR spectrum of triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide as acidic ionic liquid

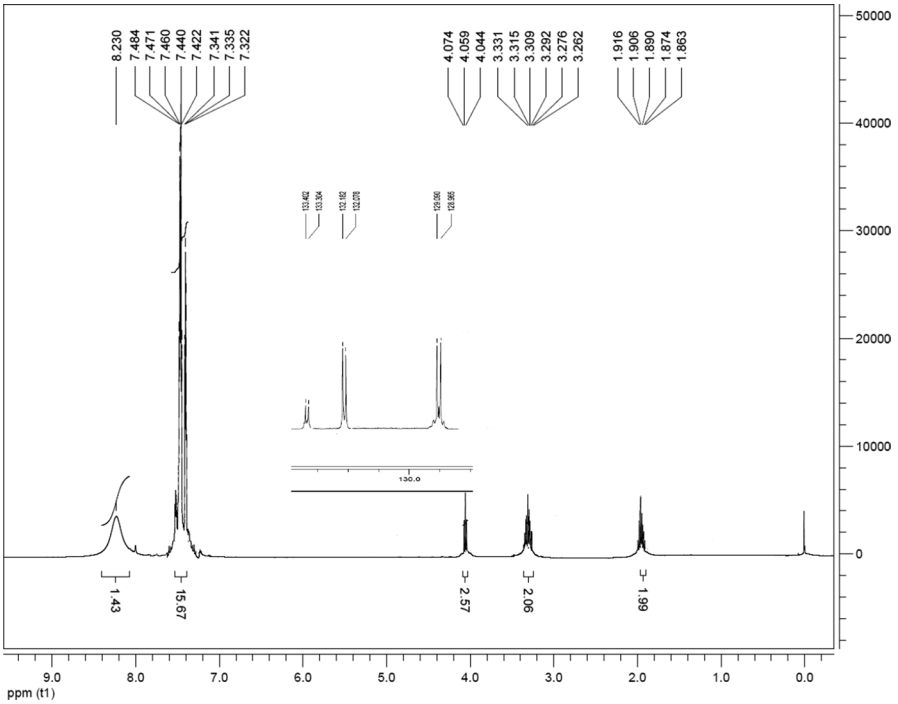


Fig. 2 ^{1}H NMR spectrum of triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide

and the two doublet peaks at 18.8–21.1 ppm are related to aliphatic carbons in the IL coupled with phosphorus atom (Fig. 3).

To investigate the thermal stability of the [TPPHSP]Br catalyst, TG and DTG analyses were performed. As depicted in Fig. 4, a first weight loss step was attributed to loss of adsorbed solvent used during preparation of the catalyst, taking place below 100 °C. The major weight loss and decomposition of the catalyst took place between 250 and 320 °C.

Application of [TPPHSP]Br catalyst in synthesis of barbiturate derivatives

After characterization of the new ionic liquid, we studied its catalytic activity as acidic catalyst in synthesis of 5-arylidene barbituric acids. To define effective reaction conditions, the reaction between 4-nitrobenzaldehyde and barbituric acid was chosen as a model and optimized in terms of various parameters such as solvent, amount of catalyst, and effect of temperature. The results are summarized in Table 1. The effect of different solvents and solvent-free condition was investigated using the model reaction. The results showed that the reaction progressed efficiently in a mixture of EtOH and H_2O as solvent. The progress of the reaction increased considerably on increasing the temperature. Hence, reflux condition was chosen as the best temperature. The amount of catalyst in EtOH–H_2O under reflux condition was

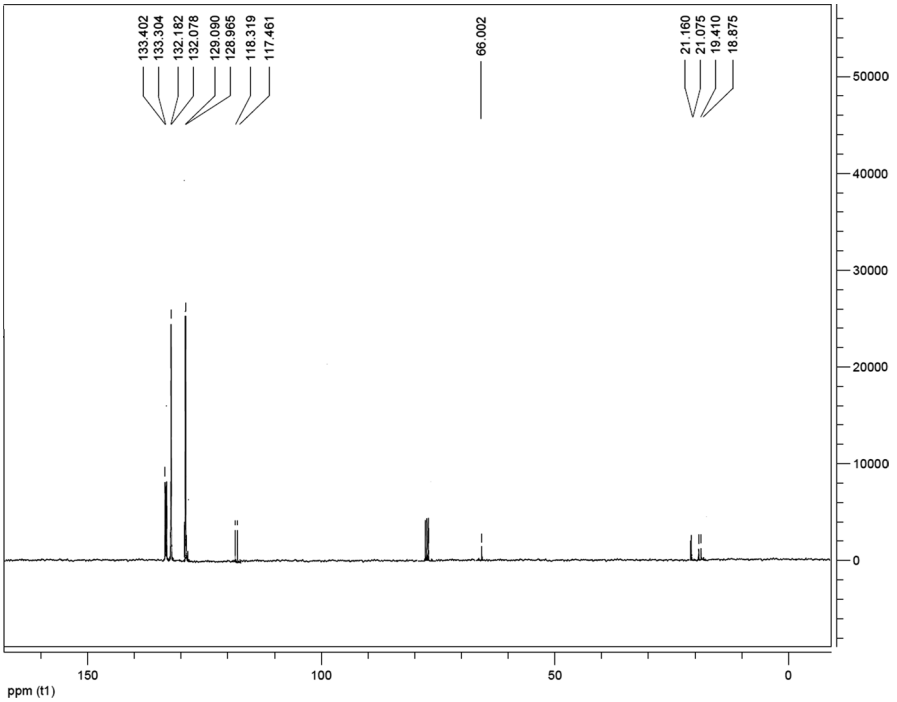


Fig. 3 ^{13}C NMR spectrum of triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide

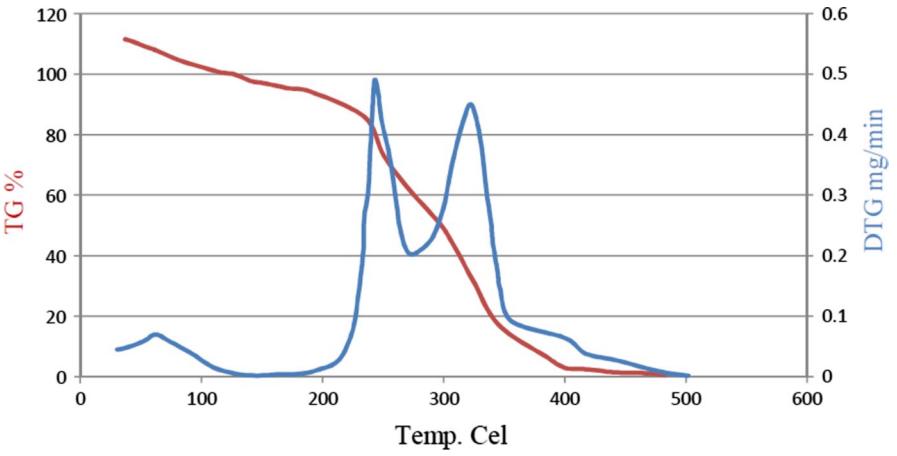


Fig. 4 TGA and DTG analyses of triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide

optimized. As seen from Table 1, 2 mol% [TPPHSP]Br was the optimum amount of catalyst for this reaction (Table 1, entry 9). The results showed that increasing the amount of catalyst had no considerable effect on the product yield (Table 1, entry 10).

Table 1 Optimization of reaction conditions for preparation of 5-arylidene barbituric acid derivatives

Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Time (min)	Yield (%)[a]
1	–	–	100	120	Trace
2	–	H_2O	Reflux	120	Trace
3	–	EtOH	Reflux	120	Trace
4	1	–	100	120	Trace
5	1	$CHCl_3$	Reflux	120	35
6	1	*n*-Hexane	Reflux	120	10
7	1	H_2O	r.t.	180	Trace
8	1	H_2O	Reflux	180	48
9	1	EtOH	r.t.	180	28
10	1	EtOH	Reflux	180	53
11	2	H_2O	r.t	180	10
12	2	H_2O	Reflux	180	55
13	2	EtOH	r.t.	180	30
14	1	EtOH–H_2O[b]	Reflux	60	65
15	0.5	EtOH–H_2O[b]	Reflux	60	43
16	2	EtOH–H_2O[b]	Reflux	20	92
17	3	EtOH–H_2O[b]	Reflux	20	94
18	2	EtOH–H_2O[b]	r.t.	120	70
19	2	EtOH–H_2O[b]	40	90	82
20	2	EtOH–H_2O[b]	60	35	90

Reaction conditions: 4-nitrobenzaldehyde (1.0 mmol), barbituric acid (1.0 mmol), solvent (5 mL), and required amount of catalyst

[a]Yields refer to isolated products

[b]EtOH–H_2O (3:1)

Then, synthesis of 5-arylidene barbituric acids was performed using various aromatic aldehydes and barbituric acid under the optimized conditions, viz. 2 mol% catalyst in EtOH–H_2O under reflux. The results obtained are summarized in Table 2, revealing that all the aromatic aldehydes carrying either electron-donating or electron-withdrawing groups gave the desired products in high yield.

After successful use of [TPPHSP]Br in synthesis of 5-arylidene barbituric acids, we decided to investigate its ability to catalyze synthesis of pyrano[2,3-*d*] pyrimidines.

We used the condensation reaction of malononitrile, 4-nitrobenzaldehyde, and barbituric acid as a model to determined the best conditions. At first, the condensation reaction was investigated under solvent-free condition; as shown in Table 3, no desired product was formed. Therefore, the model reaction was performed in various solvents. The results showed that EtOH–H_2O is a desirable solvent for this reaction. In *n*-hexane as solvent, no condensation product was observed (Table 3, entry 4). Also, the reaction was performed in chloroform as

Table 2 Synthesis of 5-arylidene barbituric acid derivatives catalyzed by [TPPHSP]Br

Entry	R	Time (min)	Yield (%)[a]	Melting point (°C)	
				Found	Lit. [Refs.]
1	H	15	86	260–262	255–256 [28]
2	4-OH	15	94	> 300	> 300 [28]
3	4-Cl	10	93	298–300	292–293 [34]
4	3-NO_2	12	98	229–230	230–232 [37]
5	2-Cl	8	93	252–254	245–247 [37]
6	4-CH_3O	13	89	297–299	299–300 [28]
7	4-NO_2	15	92	268–270	265–268 [37]
8	4-Br	18	92	289–290	229–231 [28]
9	4-CH_3	15	96	292–294	287–289 [34]
10	4-F	12	90	254–255	256–260 [28]
11	3-CH_3O	15	90	218–220	223–224 [37]

Reaction conditions: arylaldehyde (1.0 mmol), barbituric acid (1.0 mmol), solvent (5 mL), and catalyst (2 mol%)

[a]Isolated yields

Table 3 Optimization of reaction conditions for preparation of pyrano[2,3-*d*]pyrimidine derivatives

Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Time (min)	Yield (%)[a]
1	–	–	100	180	–
2	–	H_2O	Reflux	180	–
3	–	EtOH	Reflux	180	–
4	1	–	100	180	–
5	1	$CHCl_3$	Reflux	180	–
6	1	*n*-Hexane	Reflux	180	–
7	1	H_2O	r.t.	180	Trace
8	1	H_2O	Reflux	180	40
9	1	EtOH	r.t.	180	10
10	1	EtOH	Reflux	90	65
11	2	H_2O	Reflux	180	45
12	2	EtOH	Reflux	90	75
13	1	EtOH–H_2O[b]	Reflux	90	75
14	0.5	EtOH–H_2O[b]	Reflux	90	49
15	2	EtOH–H_2O[b]	Reflux	50	90
16	3	EtOH–H_2O[b]	Reflux	50	90
17	2	EtOH–H_2O[b]	r.t.	150	40
18	2	EtOH–H_2O[b]	40	120	55
19	2	EtOH–H_2O[b]	60	90	62

Reaction conditions: 4-nitrobenzaldehyde (1.0 mmol), barbituric acid (1.0 mmol), malononitrile (1.0 mmol), solvent (5 mL), and required amount of catalyst

[a]Yields refer to isolated products

[b]EtOH–H_2O (3:1)

Table 4 Synthesis of pyrano[2,3-*d*]pyrimidine derivatives using [TPPHSP]Br as catalyst

Entry	R	Time (min)	Yield (%)[a]	Melting point (°C)	
				Found	Lit. [Refs.]
1	H	70	80	210–212	219–222 [28]
2	4-OH	85	90	> 300	> 300 [42]
3	4-Cl	45	92	238–240	238–240 [38]
4	3-NO_2	60	95	212–214	212 [41]
5	2-Cl	40	90	210–212	209–214 [38]
6	4-CH_3O	55	83	278–280	276–279 [38]
7	4-NO_2	60	93	236–238	238–240 [46]
8	4-Br	75	88	230–232	227–230 [38]
9	4-CH_3	80	91	227–228	229–230 [41]
10	4-F	90	90	265–266	268–270 [46]
11	3-OH	45	92	162–164	161–162 [46]
12	3-CH_3O	50	90	200–202	200–202 [46]
13	3-CH_3	70	92	220–222	224–226 [46]
14	4-CHO	65	76	> 300	> 300 [38]
15	4-$C_6H_5CH_2O$	35	92	158–160	151–152 [46]

Reaction conditions: arylaldehyde (1.0 mmol), barbituric acid (1.0 mmol), malononitrile (1.0 mmol), solvent (5 mL), and catalyst (2 mol%)

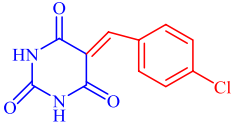
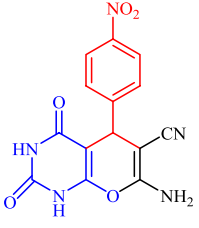
[a]Isolated yields

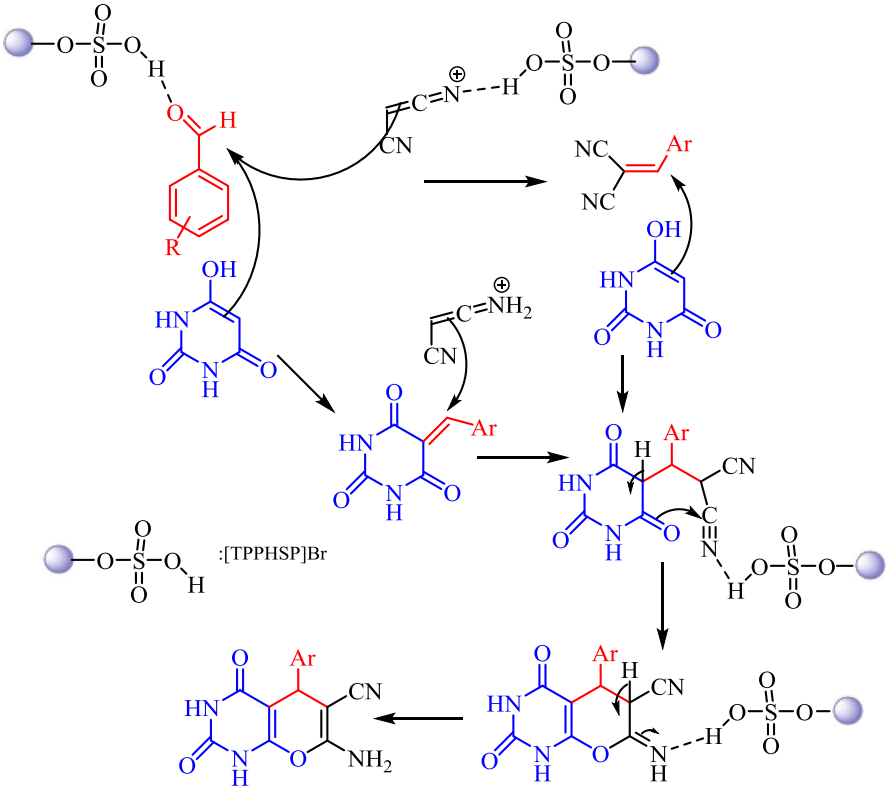
solvent, and the desired product was achieved in 50 % yield but the reaction did not reach completion (Table 3, entry 3).

The amount of catalyst was also investigated. When the reaction was performed without any catalyst, no desired product was formed. The amount of catalyst in the model reaction was then changed from 0.5 to 3 mol%. The results showed that 2 mol [TPPHSP]Br is the optimal amount of catalyst in terms of reaction time and yield, while increasing the amount of catalyst had no significant effect on the progress of the reaction (Table 3, entries 9, 10). To investigate the effect of temperature in improving the reaction, the model reaction was carried out at different temperatures. It was observed that the progress of the reaction was very slow at room temperature (Table 3, entry 11). Increasing the temperature from room temperature to reflux condition led to an increase in product yield from 40 to 90 % while the reaction time decreased from 150 to 50 min. Therefore, reflux was chosen as the best temperature. According to these results, the optimum condition for synthesis of pyrano[2,3-*d*]pyrimidines is 2 mol% [TPPHSP]Br as catalyst in EtOH–H_2O under reflux condition.

After optimization of the reaction conditions (Table 3), the generality of the reaction was investigated in synthesis of pyrano[2,3-*d*]pyrimidines using different substituted aromatic aldehydes (Table 4). All reactions proceeded efficiently within 35–90 min to give the corresponding pyrano[2,3-*d*]pyrimidine derivatives in good to excellent yield (76–95 %). These results indicate that all the aromatic

Table 5 Comparison of [TPPHSP]Br catalyst with other recently reported catalysts

	Catalyst	Catalyst amount	Reaction conditions	Time (min)	Yield (%)	Refs.
	L-Tyrosine	2 mmol	H_2O, r.t.	10	96	[29]
	Ni-NPs	1.5 mol%	Ethylene glycol, 50 °C	10	82	[30]
	NH_2SO_3H	100 mmol	Grinding	180	93	[32]
	Taurine	20 mol%	H_2O, 90 °C	18	91	[36]
	DABCO	0.02 mmol	H_2O, r.t.	7	90	[28]
	[TPPHSP]Br	2 mol%	EtOH–H_2O, reflux	10	93	This work
	DABCO	0.016 mmol	H_2O, 75 °C	22	85	[37]
	Urea-SO_3H	0.01 g	Solvent-free	30	95	[40]
	Taurine	20 mol%	H_2O, reflux	60	88	[36]
	ZnO–CuO	0.03 g	H_2O, reflux	10	92	[45]
	$B(OH)_3$	10 mol%	THF–H_2O, reflux	100	89	[46]
	Al-HMS-20	0.03 g	EtOH, reflux	12 h	95	[41]
	Trichloroisocyanuric acid	10 mol%	H_2O, reflux	180	95	[47]
	[TPPHSP]Br	2 mol%	EtOH–H_2O, reflux	60	93	This work



Scheme 4 Plausible mechanism for synthesis of 5-arylidene barbituric acids and pyrano[2,3-*d*]pyrimidine derivatives catalyzed by [TPPHSP]Br

aldehydes with various substituents on the aromatic ring reacted efficiently with barbituric acid and malononitrile to afford the desired products in high yield.

To confirm the validity of the present approach versus literature, the results obtained in this work using triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide are compared with those obtained using other reported catalysts for synthesis of 5-arylidene barbituric acid and pyrano[2,3-*d*]pyrimidine derivatives in Table 5, revealing that the performance of the ionic liquid is comparable to the others in terms of reaction time and product yield.

Scheme 4 illustrates a possible mechanism for preparation of above-mentioned barbiturate derivatives catalyzed by [TPPHSP]Br. Initially, arylaldehyde is activated by hydrogen bonding with IL catalyst. Then, malononitrile or barbituric acid intermediate adds to the activated aldehyde. Finally, through nucleophilic attack followed by cyclocondensation then tautomerization, the final product is formed.

The reusability of the catalyst was also studied using the condensation reaction of 4-nitrobenzaldehyde, malononitrile, and barbituric acid. After reaction completion, the solid product was washed with water, then evaporated under reduced pressure to recover the catalyst, which was washed with acetone, dried, and reused for the same

Table 6 Reusability of [TPPHSP]Br in model reaction

Run	Fresh	1	2	3	4
Isolated yield (%)	93	92	92	90	88

Reaction conditions: 4-nitrobenzaldehyde (1.0 mmol), malononitrile (1.0 mmol), barbituric acid (1.0 mmol), solvent 5 mL, and IL catalyst (2 mol%) at reflux condition

reaction. The recovered catalyst was reused five times with minimal change in activity (Table 6).

Conclusions

An efficient Brønsted-acidic ionic liquid catalyst triphenyl(propyl-3-hydrogen sulfate)phosphonium bromide was synthesized and characterized. Its catalytic activity was studied in synthesis of 5-arylidene barbituric acids and pyrano[2,3-*d*]pyrimidine derivatives via three-component, one-pot condensation reaction between several aromatic aldehydes, malononitrile, and barbituric acid. Short reaction time, high yield, and easy workup are some advantages of this catalyst. The [TPPHSP]Br catalyst is recyclable and can be reused in five consecutive cycles without significant loss of activity.

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