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Short Communication

Solvent-free sonochemical preparation of α-aminophosphonates catalyzed by 1-hexanesulphonic acid sodium salt

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ABSTRACT

1-Hexanesulphonic acid sodium salt was found to be an efficient catalyst for the green synthesis of α-aminophosphonates by the coupling of aldehydes/ketone, an amine and triethyl phosphite under ultrasound irradiation at ambient temperature for appropriate time to furnish the desired product in good to excellent yield under solvent-free condition. This catalyst provides clean conversion; greater selectivity and easy workup make this protocol practical and economically attractive.

1. Introduction

Phosphonic acids and their phosphonate derivatives are of immense interest in synthetic organic chemistry due to their biological activities [1]. They are employed in synthetic operations leading to carbon–carbon bond formation [2] and as transition state analogues in production of antibody catalysts for a wide variety of reactions [3]. In recent years, considerable interest has been focused on the synthesis of α-aminophosphonates, because they are considered to be structural analogues of the corresponding α-amino acids and transition state mimics of peptide hydrolysis. In these connections, the utilities of α-aminophosphonates as peptide mimics [4], enzymes inhibitors [5], haptens of catalytic antibodies [6], antibiotics and pharmacologic agents [7] are well documented.

A number of synthetic methods for the preparation of α-aminophosphonates have been carried out under solvent-free conditions in the presence of TFA [8], TsCl [9], $LiClO_4$ [10], $Mg(ClO_4)_2$ [11], metal triflate [12]. The α-aminophosphonates also been synthesized in organic solvents using $In(OTf)_3/MgSO_4$ [13], GaI_3 [14], $BiCl_3$ [15], $Cu(OTf)_2$ [16], $SbCl_3/Al_2O_3$ [17]. The synthesis of α-aminophosphonates have also been carried out in presence of ionic liquids [18], Lewis acid–surfactant-combined catalyst [19] and even in absence of solvent and catalyst [20]. However, most of these procedures are sluggish, requires long reaction time, use of strong acidic condition, unsatisfactory yield, which also suffer from the formation of many side products. Consequently, there is still needs to develop a more efficient, simple, milder and high yield protocol for the synthesis of α-aminophosphonates.

Ultrasonication has increasingly been used in organic synthesis in the last three decades. It has been demonstrated as an alternative energy source for organic reactions ordinarily accomplished by heating. A great number of organic reactions can be carried out in short reaction time, high yields and mild reaction condition under ultrasonication [21]. The use of ultrasound-irradiation technique for activating various reactions is well documented in the literature such as Reformatsky reaction [22], Pinacol–pinacolone reaction [23], Ullmann condensation [24] and Suzuki cross-coupling [21a].

A search of the literature revealed that the 1-hexanesulphonic acid sodium salt [25] liberates corresponding acid with extreme wide applications such as sulphonation of alkanes [26]. However, there are very few reports using hexanesulphonic acid sodium salt as a catalyst in the organic transformation [27]. For the first time we herein report the use of 1-hexanesulphonic acid sodium salt for the synthesis of α-aminophosphonates under ultrasound irradiation and solvent-free condition.

2. Experimental

Melting points were determined in open capillaries in a paraffin bath and are uncorrected. IR spectra were recorded on a Bruker spectrophotometer using KBr discs, and the absorption bands are expressed in cm^{-1}. ^1H NMR spectra were recorded on a Varian

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AS 400 MHz spectrometer in $CDCl_3$/DMSO-d_6, chemical shifts (δ) are in ppm relative to TMS, and coupling constants (J) are expressed in Hertz (Hz). Mass spectra were taken on a Macro mass spectrometer (Waters) by electro-spray method (ES). Bandelin Sonorex (with a frequency of 35 kHz and a nominal power 200 W) ultrasonic bath was used for ultrasonic irradiation. Built-in heating, 30–80 °C thermostatically adjustable. The reaction vessel placed in side the ultrasonic bath containing water.

3. General procedure

A mixture of substituted aldehydes/ketone (1 mmol), amine (1 mmol), and triethyl phosphite (1.2 mmol) were placed in a round bottom flask. Further 1-hexanesulphonic acid (10 mol%) was added, this mixture was irradiated under ultrasonic irradiation at ambient temperature for the precised time. After the completion of reaction as monitored by TLC; 20 mL ice cold water was added to the reaction mixture and product was extracted by chloroform (2×25 mL). The organic layer washed by brine (2×20 mL) and dried over anhydrous sodium sulphate. The solvent was distilled out on rota-evaporator under reduced pressure to afford the pure products. The products 4(a–n) were confirmed by their spectral data after comparisons with authentic samples [31], IR, ^{1}H NMR, mass spectra and melting point.

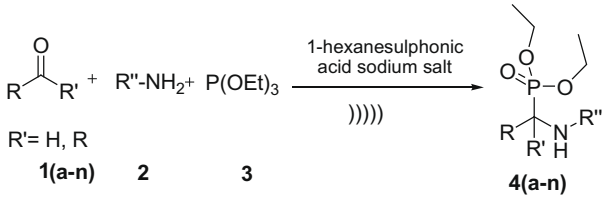
4. Results and discussion

In the continuation of our research work of developing methods in various organic transformations [28–30]. Herein, we have developed methodology for the synthesis of α-aminophosphonates using 1-hexanesulphonic acid sodium salt, which makes use of mild catalyst under solvent-free condition over the reported procedure as depicted in Scheme 1.

Here we have carried out the reaction of benzaldehyde (**1a**), aniline (**2**) and triethyl phosphite (**3**) catalyzed by 1-hexanesulphonic acid sodium salt under solvent-free condition and ultrasonic irradiation, it has been considered as a standard model reaction.

We also have studied the catalyst concentration on model reaction. We have varied the concentration of catalyst to 2, 4, 6, 8, 10, and 12 mol%. The result revealed that, when the reaction was carried out in the presence of 2, 4, 6 mol% of catalyst it gave lower yield of product even after prolonged reaction time. At the same time when the concentration of catalyst was 10 or 12 mol% we got the excellent yields of product in short span. Even after increasing the catalyst concentration the yields of the products were found to be constant. So, the use of 10 mol% of catalyst is sufficient to push the reaction forward. The obtained results summarized in Table 1.

Further, we have also studied the effect of solvents on model reaction. Here, we have kept the concentration of catalyst constant on model reaction and varied the solvents condition like water, ethanol, methanol, dichloromethane, toluene, acetonitrile and solvent-free, the observation revealed that in all the solvents the yields of the products were found to be low but in case of solvent-free condition, we got the excellent yield of product. The obtained results summarized in Table 2. We have also discussed the effect of ultrasonic irradiation. When the model reaction was carried out under conventional method it gave comparatively low yields of products, while at the same time the model reaction carried in the influence of ultrasonic irradiation it gives excellent yields of product in short reaction time (Table 3).



Scheme 1.

Table 1
Effect of catalyst concentration on model reaction.[a]

Entry	Catalyst (mol%)	Yield[b] (%)
1	2	56
2	4	63
3	6	78
4	8	85
5	10	94
6	12	94

[a] Reaction of benzaldehyde, aniline and triethyl phosphite in presence of 1-hexanesulphonic acid sodium salt under ultrasonic waves and solvent-free condition for 15 min.
[b] Isolated yield.

Table 2
Optimization of solvent effect on the model reaction.[a]

Entry	Solvent	Time (min)	Yield[b] (%)
1	Water	15	20
1	Ethanol	15	65
2	Methanol	15	52
3	Dichloromethane	15	68
4	Toluene	15	54
5	Acetonitrile	15	63
6	Solvent-free	15	94

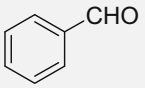
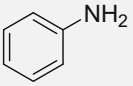
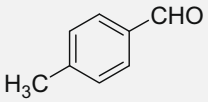
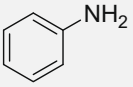
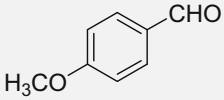
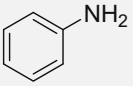
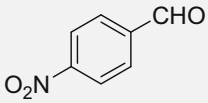
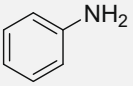
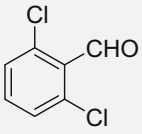
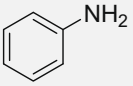
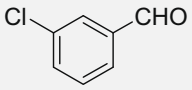
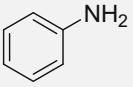
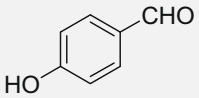
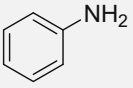
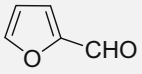
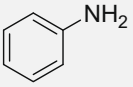
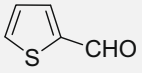
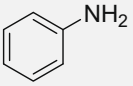
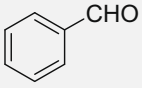
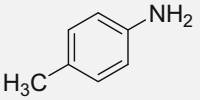
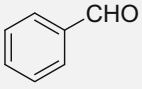
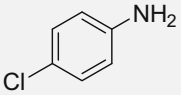
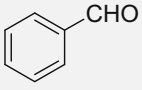
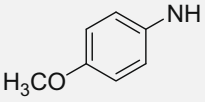
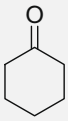
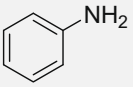
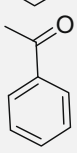
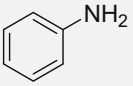
[a] Reaction of benzaldehyde, aniline and triethyl phosphite catalyzed by 1-hexanesulphonic acid sodium salt (10 mol%) under ultrasonic waves for 15 min.
[b] Isolated yield.

After optimizing the conditions, the generality of this method was examined by the reaction of several substituted aryl/heteroaryl aldehydes/ketone, amine and triethyl phosphite using 1-hexanesulphonic acid as a catalyst under ultrasound irradiation, the results are shown in Table 3. Here, we have carried out the similar reaction with various aromatic/heteroaromatic aldehydes containing electron donating or electron withdrawing functional groups at different positions but it did not showed any remarkable differences in the yields of product and reaction time. Further study of ketones revealed that it gives very low yields of products even after prolonged reaction time (Table 3, entries 13 and 14). All the synthesized compounds were characterised by spectral data and compared (MS, NMR, and IR) with authentic sample. This comparison revealed that the compounds synthesized by this newly developed method were exactly similar in all aspects to the reference compounds [18]. The developed methodology is simple and a good contribution in the field of α-aminophosphonates.

5. Conclusion

1-Hexanesulphonic acid sodium salt was found to be mild and effective catalyst in green synthesis of α-aminophosphonate under ultrasonic irradiation and solvent-free condition. The use of this catalyst provides faster conversion; greater selectivity and easy workup which make this manipulation practical and economically attractive. We believed that, sonochemical synthesis of α-aminophosphonates using 1-hexanesulphonic acid sodium salt as a catalyst promoted methodology will be a valuable contribution in the field of phosphorous chemistry as compared to the existing processes.

Table 3
Sonochemical effect on the synthesis of α-aminophosphonates.

Entry	Product	Aldehyde/ketone	Aniline	With US[a]		Without US[b]	
				Time (min)	Yield[c,d](%)	Time (min)	Yield[c,d] (%)
1	**4a**			15	94	60	75
2	**4b**			12	92	60	70
3	**4c**			12	94	60	78
4	**4d**			15	89	60	72
5	**4e**			20	87	60	68
6	**4f**			18	88	60	65
7	**4g**			15	86	60	69
8	**4h**			30	80	60	62
9	**4i**			35	82	60	65
10	**4j**			15	90	60	70
11	**4k**			20	88	60	72
12	**4l**			20	86	60	73
13	**4m**			120	43	60	30
14	**4n**			140	32	60	33

[a] Reaction of aldehyde/ketone, amine, triethylphosphite in presence of 1-hexanesulphonic acid sodium salt (10 mol%) under ultrasonic waves for 15 min.
[b] Reaction of aldehyde/ketone, amine, triethylphosphite in presence of 1-hexanesulphonic acid sodium salt (10 mol%) under stirring at ambient temperature.
[c] Isolated yield.
[d] Compounds were characterised by ^{1}H NMR, MS spectral data and were compared with the reference compounds [31].

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[31] Spectral data of reprehensive compounds (**4a**) M.P 98–100 °C ^{1}H NMR ($CDCl_3$-400 MHz): 1.13 (3H, t), 1.23 (3H, t), 3.66 (1H, ddq, J = 7.1, 11.2, 8.1 Hz), 3.97 (1H, ddq, J = 7.1, 8.1, 11.2 Hz), 4.13 (2H, m), 4.75 (1H, br, –NH), 4.78 (1H, d, J = 17.9 Hz), 6.61 (2H, d, J = 8.5 Hz), 6.70 (1H, t, J = 7.4), 7.11 (2H, t, J = 7.4), 7.26 (1H, m), 7.34 (2H, t, J = 7.4 Hz), 7.49 (2H, m); IR (KBr) cm^{-1}: 3295 (–NH), 1233 (P–O), 1103–997 (P–O–Et) Es-MI.320 (M+).