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Short Communication

N-Sulfonylation of amines, imides, amides and anilides using *p*-TsCl in presence of atomized sodium in EtOH–THF under sonic condition

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ABSTRACT

A simple, facile and an efficient procedure for the *N*-sulfonylation of amines, imides, amides and anilides using *p*-TsCl in the presence of atomized sodium in a mixture of EtOH–THF under sonic condition is developed. The method is rapid, mild and inexpensive; yields are high and the reactions go to completion within 2–8 min.

1. Introduction

In recent times many areas of chemical synthesis have been investigated under the influence of ultrasound [1]. Sonic condition modifies both organic and inorganic materials [2,3]. Use of ultrasound is one such application in organic chemistry which offers unique and facile routes to a variety of organic reactions [4,5]. Cavitation occurs when ultrasonic waves are transmitted through a liquid medium which will generate extreme environment like high local pressure and temperature; and thus great heating and cooling effects are possible under sonic condition [6,7]. Conventional chemical reactions under such extraordinary conditions will progress even faster and also some reactions which are impossible under normal condition can take place under sonication. Usually sonication is carried out at a lower external temperature compared to usual thermal methods, under sonic condition the possibility of formation of undesired products is less [8]. The sonic reactions are cleaner, hence, are green and are generally faster [9].

While biologically active compounds are in great demand, sulfonamides are one such class of organic compounds which are extremely useful pharmaceutical chemicals because they exhibit a wide range of biological activities such as anticancer, anti-inflammatory and antiviral functions [10]. Since under mild conditions sulfonamides can be recovered easily from the reaction mixture they are used as protecting groups for the —NH— functionality [11]. Several drugs including therapeutic agents for Alzheimer's disease [12], inhibitors of tRNA synthetases, antibacterial agents [13], prostaglandin F1α sulfonamides for the potential treatment of osteoporosis [14], antagonists for angiotensin II [15], and leukotriene D4-receptors [16] possess the *N*-sulfonyl moiety. Protocols documented in the literature for the *N*-sulfonylation involves use of metal oxides (MgO, Ag_2O, CuO, ZnO), Zn–Al hydrotalcite, CsF–Celite as catalysts and *N*-chlorosulfonyl carbamate (CSC) [17]. However, the reported methods suffer from one or the other drawbacks such as formation of by-products, harsh conditions [18], use of toxic solvents and reagents, longer reaction durations and involve tedious work-up procedures [19]. Sulfonylation of amines in the presence of a base still remains the choice because of the high efficiency and simplicity of the reaction [20]. Therefore, developing a general, mild, simple, efficient and rapid method for *N*-sulfonylation of amines, amides, imides and anilides is necessary.

Various organic reactions have been carried out and several organic molecules have been synthesized by employing sodium in THF under sonication [21]. A thorough literature survey revealed that, there are no reports on the application of atomized sodium in THF under sonication for the sulfonylation reactions. In continuation of our work on the synthesis of organic molecules under ultrasonic condition [22–24], we, herein, report a simple, rapid and economical method for the *N*-sulfonylation of amines, imides,

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amides and anilides by *p*-TsCl using atomized sodium in a mixture of EtOH–THF under ultrasonic condition (35 kHz). The process is mild and inexpensive, the yields are very high and the reactions go to completion within 2–8 min as shown in the Scheme 1.

2. Results and discussion

In order to develop a new and simple method for the *N*-sulfonylation of amines, imides, amides and anilides by *p*-TsCl, we started our investigations with various catalysts in various solvents under different reaction conditions. For this purpose the reaction of aniline was taken up as a standard. Initially we selected a series of metals and conducted the above reaction to get high yield of the desired product with atomized sodium in THF. The results of this study are presented in Table 1.

In order to verify whether the sulfonylation of aniline is possible with a base, we carried out the reaction with 10 mol% NaOMe, and found that, only 40 % product was obtained under sonic condition in EtOH–THF after 8 min.

Further, to verify whether THF is a suitable solvent or not, various solvents were selected and the reactions were carried out at different reaction conditions (25 °C, MW and ultrasound). Initially, the reaction was carried out under solvent-free condition and it was observed that, the yield of 4-methyl-*N*-phenylbenzenesulfonamide was very low (Table 2, entry a). Moderate yields were obtained when THF was used at 25 °C, MW (160 W, 70 °C) and under sonication. It was found that, 25 °C and MW (160 W, 70 °C) are time consuming when compared to the sonic reaction (Table 2, entry k). Under sonic condition, best yields were obtained when atomized sodium in EtOH–THF was used (Table 2, entry m), and the product was obtained in 3 min.

For optimizing the amount of atomized sodium, we then, worked with different amounts of atomized sodium and the results are presented in the Table 3. From Table 3 it is clear that, 2 mg atom of the metal is essential for the present reaction (entry e) to give the product in excellent yield.

The amount of EtOH and THF required to give the maximum yield of the product is found to be 2 mL and 1 mL respectively, results of this study are presented in the Table 4 (entry m).

From the data presented in the Tables 1–4 it is also clear that, *N*-sulfonylation under the influence of ultrasound at 35 kHz is efficient and gives very high yield of the product in short duration. It was also found that, this method does not require excess amount of amine when compared to other methods. In order to verify the generality of the method, several substituted anilines were treated with *p*-TsCl in the presence of atomized sodium in EtOH–THF to get the respective products in excellent yield within 03 min. The results of these studies are presented in Table 5(entries a–h). In order to verify the applicability of the method for the *N*-sulfonylation of amines, imides, amides and anilides; different amines, imides, amides and anilides were also treated with the above reagents to get the corresponding products in very high yields under the influence of ultrasound at 35 kHz as shown in the Table 5(entries a–r).

3. Experimental

All the reagents used were commercially available and all the solvents were distilled before use. EtOH and THF were distilled and dried over magnesium metal and sodium metal respectively. All microwave assisted reactions were studied using Catalyst CATA-Sc, Indian make Microwave reactor. All the ultrasonic reactions were studied using SIDILU, Indian make sonic bath working at 35 kHz (constant frequency) at 25 °C (maintained by circulating water continuously); and the reactions were followed by SHIMADZU QP 5050A GC-MS instrument (EI) equipped with a 30 m long and 0.32 mm dia BP-5 column with the column temperature program 80–15–250 °C. IR, ^{1}H NMR and ^{13}C NMR spectra were recorded on Nicolet 400D FT-IR, Bruker AMX (300 MHz) and (100 MHz) instruments respectively.

3.1. Preparation of atomized sodium [25]

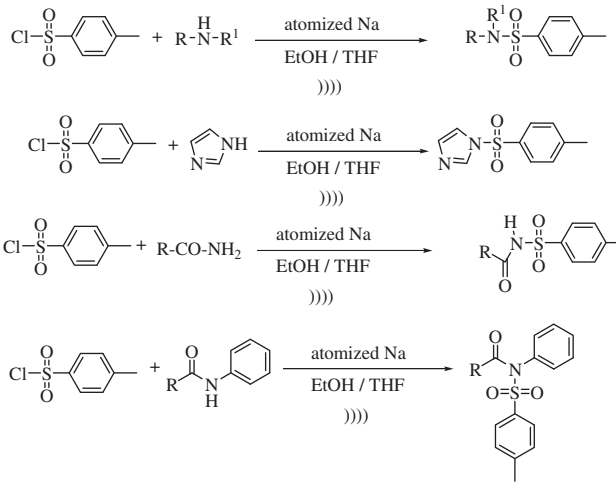
20 g of clean sodium metal was weighed under dry ether and introduced into a B24 standard joint 1000 mL round bottomed flask containing about 200 mL sodium-dried xylene fitted with an air condenser and the flask was placed on a sand bath. The flask was sufficiently enveloped with a dry cloth, and the sand bath was heated cautiously, and the ring of condensed vapor of the xylene was carefully watched. When the ring of condensed vapor had raised within 2.5 cm from the neck of the flask the flame beneath was extinguished. The condenser was then removed and a B24 stopper was fixed, the flask was wrapped with a pre-dried cloth; the stopper was then held firmly in place through the enveloping cloth and shaken vigorously for 30–60 s (in observation until the molten sodium was converted into a fine dispersion). Immediately the stopper was removed and the flask was placed on the cork ring. The atomized sodium was obtained in the form of small spheres depending upon the time and rapidity of shaking. When the contents cooled to room temperature, the xylene was decanted and the sodium was washed with sodium-dried ether. Finally, the atomized sodium was covered with absolute ether.

3.2. General procedure for the N-sulfonylation

A mixture of amine, imide, amide or anilide (2.5 mmol), *p*-TsCl (2.5 mmol), atomized sodium (2.0 mg atom), EtOH (2 mL), THF (1 mL) was sonicated in a sonic bath working at 35 kHz (constant frequency) maintained at 25 °C by circulating water for an appropriate time (Table 5). After the completion of the reaction [TLC, (eluent: 8–10 % ethyl acetate in light petrol)], the organic matter was filtered, washed with water (5 mL) and ether (3 mL); and then extracted with ether (5 mL × 3), and dried over anhydrous Na_2SO_4. The desired *N*-sulfonylated product was obtained after the removal of the solvent under vacuum.

4. Effect of ultrasound on the reaction

Organic reactions not only get accelerated under the influence of ultrasound, the number of steps involved can also be reduced, and cruder reagents can also be used under sonic condition. These accomplishments by ultrasound are attributed to the phenomenon of acoustic cavitation [26], and the primary chemical reactions are due to the transient state of high temperatures and pressures generated during the acoustic cavitation [27]. Cavitation depends on whether the system is liquid–liquid or liquid–solid. The present reaction is an example of a three-phase system: the liquid phase (reagents in solvents), solid phase (atomized sodium), and the gas phase (dissolved gases in the liquid phase) [28]. Cavitation near extended liquid–solid interfaces is very different from cavitation in pure liquids [29]. Under the influence of ultrasound the bubble collapse becomes non-spherical near the surface of the solid atomized sodium, and near the surface of the vessel, and produces millions of high-speed liquid jets. These jets and shock waves cause damage to the surface of the metal (erosion), thereby increasing the reactivity of the chemical reaction by increasing the surface area of the metal. The created high-speed jets can reach velocities of hundreds of meters per second and further fragmentation of the metal sodium may also occur due to cavity collapse in the liquid (solvent), which may be responsible for the higher rates of the reactions [30]. We



Scheme 1. *N*-Sulfonylation of amines, imides, amides and anilides by *p*-TsCl.

found that, the polar aprotic, low boiling, high cavitation energy solvent system EtOH–THF is useful for the present sonic reaction [31–33].

5. Mechanism

The best result was obtained by using 0.8 equivalents (2 mg atom) of atomized sodium, and the use of 0.2 equivalents (0.5 mg atom) of atomized sodium also gave 70 % yield of the product (Table 3, entries b and e respectively). This clearly indicates that, atomized sodium acts as catalyst. In such case, it is doubtful that, catalytic amount of sodium can promote the present reaction due to the following reasons:

1. Sodium reacts with ethanol to give sodium ethoxide, which can act as a base. In contrast, the reaction also proceeded in THF. This fact makes the role of sodium in the present reaction ambiguous.
2. Typically, more than equimolar amount of base is required to trap the HCl generated in the reaction of amine with tosyl chloride. If the atomized sodium acts as a base, more than equimolar amount of sodium would have been required for the reaction to go to completion.
3. Sodium is generally used as a one-electron reductant, and it is unlikely that, sodium acts as a Lewis acid. It is thus possible to explain the present reaction using a one-electron reduction mechanism. Hence, the following three probable mechanisms which may operate in the present reaction are envisaged.

Table 1
A comparative study on the synthesis of 4-methyl-*N*-phenyl-benzenesulfonamide with different metals in THF.[a]

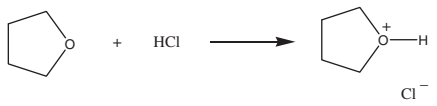
Entry	Metal[b]	Time (min)))))	Yield (%)[c,d]
a	Sodium	30–40	63
b	Atomized sodium	10–20	75
c	Aluminium	12–20	15
d	Zinc	12–20	17
e	Iron	12–20	20
f	Copper	12–20	5

[a] Aniline (2.5 mmol), *p*-TsCl (2.5 mmol) in THF (3 mL).
[b] 2 mg atom.
[c] Isolated yields.
[d] Characterized by IR and comparison with authentic sample on TLC.

Firstly, atomized sodium may react with tosyl chloride by a single electron transfer to give the tosyl free radical under sonic condition. This radical may react with an amine, imide, amide or an anilide to give the respective sulfonylated product as shown in the Scheme 2.

Secondly, sodium may react with EtOH to give sodium ethoxide, which may react with the HCl formed during the course of sulfonylation.

Finally, THF itself may react with the HCl formed during the course of the reaction and promote the sulfonylation as shown below.



As catalytic amount of atomized sodium is sufficient to bring about the present reaction in EtOH–THF medium, we feel that, all the above three possible pathways may operate simultaneously to give the product in excellent yield under the said reaction conditions.

6. Spectral data [34]

6.1. 4-Methyl-N-phenylbenzenesulfonamide (Table 5, entry a)

IR (KBr): ν 540, 682, 823, 890, 1080, 1165, 1495, 1600, 1612, 3270 cm^{-1};
^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.56 (s, 1H), 7.13–7.06 (m, 3H), 7.24–7.21 (m, 4H), 7.72–7.65 (m, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 121.3, 125.1, 127.3, 129.2, 129.6, 136.0, 136.7, 143.8 ppm;
MS (70 eV), *m*/*z*: 247 [M^+].

6.2. N-(2′-chlorophenyl)-4-methylbenzenesulfonamide (Table 5, entry b)

IR (KBr): ν 540, 682, 823, 890, 1080, 1165, 1495, 1600, 1612, 3270 cm^{-1};
^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.95 (s, 1H), 7.04 (t, J = 4.2 Hz, 1H), 7.26–7.21 (m, 4H), 7.67–7.64 (m, 3H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 122.2, 124.9, 125.6, 127.1, 127.7, 129.2, 130.0, 133.3, 135.7, 144.0 ppm;
MS (70 eV), *m*/*z*: 281 [M^+].

6.3. N-(3′-chlorophenyl)-4-methylbenzenesulfonamide (Table 5, entry c)

IR (KBr): ν 540, 682, 823, 890, 1080, 1165, 1495, 1600, 1612, 3270 cm^{-1};
^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 6.98 (d, J = 4.3 Hz, 1H), 7.04 (d, J = 4.2 Hz, 1H), 7.15–7.11 (m, 3H), 7.24 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 118.9, 120.9, 125.1, 127.4, 129.7, 130.3, 134.9, 135.7, 137.9, 144.3 ppm;
MS (70 eV), *m*/*z*: 281 [M^+].

6.4. N-(4′-chlorophenyl)-4-methylbenzenesulfonamide (Table 5, entry d)

IR (KBr): ν 675, 800, 900, 1020, 1100, 1148, 1245, 1280, 1311, 1360, 1500, 1665, 3302 cm^{-1};

Table 2
Effect of nature of solvent on the synthesis of 4-methyl-*N*-phenylbenzenesulfonamide under different reaction conditions with atomized sodium.

Entry	Solvent[a]	At (25 °C)		MW		))))	
		Time (min)	Yield (%)[b,c,d]	Time (min)	Yield (%)[b,c,d]	Time (min)	Yield (%)[b,c,d]
a	No solvent	360–480	ND	60–80	5	60–80	ND
b	Acetone	360–480	ND	60–80	ND	50–60	12
c	Acetonitrile	360–480	ND	60–80	ND	50–60	5
d	Chloroform	360–480	5	60–80	20	50–60	23
e	DCE	360–480	5	60–80	20	50–60	25
f	DCM	360–480	12	60–80	20	50–60	25
g	Ethanol	360–480	25	60–80	40	60–80	35
h	Ether	360–480	5	60–80	10	60–70	10
i	Hexane	360–480	10	60–80	17	30–40	20
j	Methanol	360–480	25	60–80	30	60–80	30
k	THF	360–480	40	60–80	55	10–20	75
l	Xylene	360–480	5	60–80	5	50–60	5
m	EtOH–THF[e]	360–480	75	60–80	75	3	92

ND: not detected.
[a] 3 mL.
[b] Isolated yields.
[c] Characterized by IR and by comparison with authentic sample on TLC.
[d] Aniline (2.5 mmol), *p*-TsCl (2.5 mmol).
[e] EtOH (2 mL)–THF (1 mL).

Table 3
Amount of atomized sodium required for the synthesis of 4-methyl-*N*-phenylbenzenesulfonamide under sonic condition.

Entry	Amount of atomized sodium (mg atom)	Time (min)))))	Yield (%)[a,b,c]
a	0	50	ND
b	0.5	30	70
c	1	20	75
d	1.5	20	80
e	2	3	92[c]
f	2.5	3	92
g	3	8	90

ND: not detected.
[a] Isolated yields; after silica gel column chromatography.
[b] Characterized by IR and by comparison with authentic samples on TLC.
[c] Aniline (2.5 mmol), *p*-TsCl (2.5 mmol) in EtOH (2.0 mL)–THF (1.0 mL) under sonic condition (35 kHz).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 6.62 (d, J = 8.5 Hz, 2H), 7.36 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 8.17 (s, br, 1H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 122.9, 127.6, 129.1, 129.4, 130.8, 135.2, 135.7, 144.2 ppm;
MS (70 eV), m/z: 281 [M^+].

6.5. N-(4′-bromophenyl)-4-methylbenzenesulfonamide (Table 5, entry e)

IR (KBr): ν 663, 798, 911, 1015, 1111, 1162, 1261, 1283, 1320, 1355, 1512, 1655, 3313 cm^{-1};
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H), 6.52 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.3 Hz, 2H), 8.27 (s, br, 1H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 118.2, 122.8, 127.0, 129.5, 132.1, 135.4, 138.0, 143.9 ppm;
MS (70 eV), m/z: 326 [M^+].

6.6. N-(4′-methoxyphenyl)-4-methylbenzenesulfonamide (Table 5, entry f)

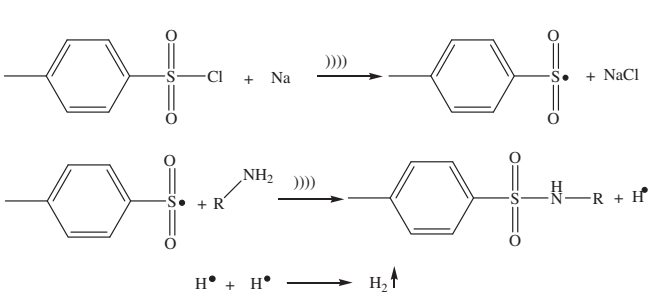
IR (KBr): ν 678, 802, 900, 1022, 1100, 1153, 1250, 1275, 1312, 1395, 1500, 3249 cm^{-1};

Table 4
Amount of EtOH and THF required for the synthesis of 4-methyl-*N*-phenylbenzenesulfonamide.

Entry	EtOH (mL)	THF (mL)	Time (min)))))	Yield (%)[a,b,c]
a	0.5	0.5	50	75
b	1	0.5	50	78
c	1.5	0.5	50	80
d	2	0.5	50	85
e	2	0.5	40	82
f	2.5	0.5	50	82
g	2	1	50	92
h	2	1	40	92
i	2	1	30	92
j	2	1	20	92
k	2	1	10	92
l	2	1	5	92
m	2	1	3	92
n	2	1.5	3	92
o	2	1.5	10	92

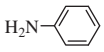
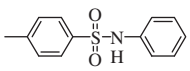
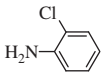
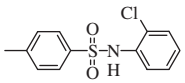
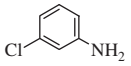
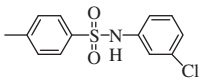
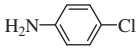
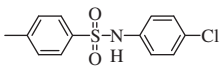
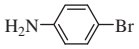
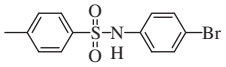
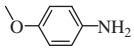
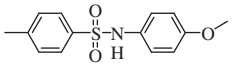
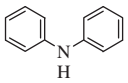
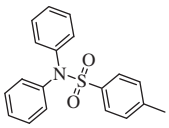
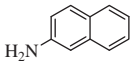
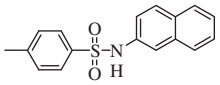
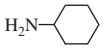
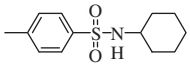
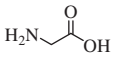
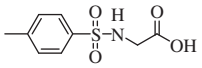
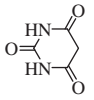
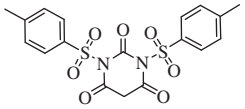
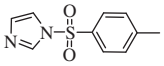
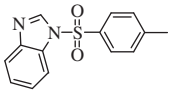
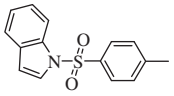
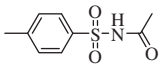
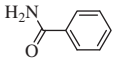
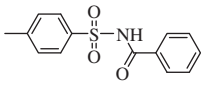
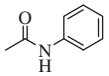
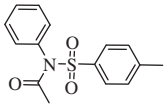
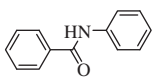
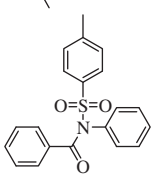
[a] Isolated yields.
[b] Characterized by IR and by comparison with authentic samples on TLC.
[c] Aniline (2.5 mmol), *p*-TsCl (2.5 mmol) and atomized sodium (2 mg atom) under sonic condition (35 kHz).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H), 3.76 (s, 3H), 6.30 (s, 1H), 6.77–6.75 (m, 2H), 6.97–6.95 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 55.4, 114.4, 125.4, 127.4, 129.0, 129.7, 136.0, 143.6, 157.9 ppm;
MS (70 eV), m/z: 277 [M^+].



Scheme 2. A plausible free-radical mechanism for atomized sodium catalyzed sulfonylation.

Table 5
N-Sulfonylation of amines, imides, amides and anilides with *p*-TsCl in the presence of atomized sodium in a mixture of EtOH–THF under ultrasonic condition.

Entry	Amine/imide/amide/anilide	Product	Reaction time (min)	Yield[a] (%)
a			3	92
b			4	90
c			6	90
d			4	90
e			4	92
f			4	90
g			5	88
h			6	90
i			3	88
j			4	89
k			5	88[†]
l			2	92
m			3	92
n			3	88
o			7	86
p			8	85
q			6	85
r			7	83

[a] Isolated yields.
[†] Novel compound.

6.7. N,N-(diphenyl)-4-methylbenzenesulfonamide (Table 5, entry g)

IR (KBr): ν 665, 785, 930, 1040, 1120, 1155, 1245, 1288, 1357, 1557, 1612, 3500 cm^{-1};
^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 7.13–7.06 (m, 6H), 7.24–7.21 (m, 6H), 7.72–7.65 (m, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 118.3, 119.1, 127.2, 129.4, 129.7, 136.7, 141.6, 143.2 ppm;
MS (70 eV), *m*/*z*: 323 [M^+].

6.8. N-(2′-naphthyl)-4-methylbenzenesulfonamide (Table 5, entry h)

IR (KBr): ν 670, 785, 909, 1035, 1113, 1145, 1242, 1265, 1348, 1530, 1595, 3209 cm^{-1};
^1H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 6.81 (br s, 1H, NH), 7.51–7.34 (m, 7H, Ar–H), 7.83–7.73 (m, 4H, Ar–H), ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 108.4, 118.1, 121.4, 124.6, 125.3, 126.5, 126.8, 127.2, 127.9, 129.4, 133.7, 136.7, 141.6, 142.6 ppm;
MS (70 eV), *m*/*z*: 297 [M^+].

6.9. N-(cyclohexyl)-4-methylbenzenesulfonamide (Table 5, entry i)

IR (KBr): ν 855, 1250, 1365, 1450, 1572, 1660, 2862, 3048, 3362 cm^{-1};
^1H NMR (300 MHz, $CDCl_3$): δ 1.30–1.09 (m, 5H), 1.54–1.51 (m, 5H), 2.23 (s, 3H), 3.13 (m, 1H), 4.6 (br s, 1H), 7.80–7.50 (m, 4H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 22.9, 24.3, 28.0, 32.9, 42.7, 127.2, 129.4, 136.7, 141.6 ppm;
MS (70 eV), *m*/*z*: 253 [M^+].

6.10. N-(4′-methylbenzenesulfonyl) glycine (Table 5, entry j)

^1H NMR (300 MHz, $CDCl_3$): δ 2.00 (s, 1H, —NH), 2.35 (s, 3H), 4.10 (s, 2H), 7.34 (d, J = 8.4 Hz, 4H, Ar–H),7.81 (d, J = 8.7 Hz, 4H, Ar–H), 11.0 (s, 1H, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 46.4, 127.2, 129.4, 136.7, 141.6, 173.2 ppm;
MS (70 eV), *m*/*z*: 229 [M^+].

6.11. 1,3-Di-p-tosyl-pyrimidine-2,4,6-(1H,3H,5H)-trione (Table 5, entry k)

^1H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H, —C<u>H</u>$_3$), 2.45 (s, 3H, —C<u>H</u>$_3$), 3.27 (d, J = 8.1 Hz, 2H, —C<u>H</u>$_2$), 7.36–7.43 (m, 4H, Ar–H), 7.64–7.74 (m, 4H, Ar–H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 27.6, 38.1, 123.3, 129.7, 136.7, 143.3, 158.4, 170.5 ppm;
MS (70 eV), *m*/*z*: 436 [M^+].

6.12. N-(4′-methylbenzenesulfonyl) imidazole (Table 5, entry l)

IR (KBr): ν 520, 693, 850, 1000, 1195, 1262, 1578, 1654, 3050, 3110, 3163, 3515 cm^{-1};
^1H NMR (300 MHz, DMSO): δ 2.38 (s, 3H, —C<u>H</u>$_3$), 7.41 (d, J = 8.4 Hz, 2H, Ph), 7.70–7.64 (m, 4H), 9.21 (d, J = 29.6 Hz,1H, imidazole) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 124.3, 127.8, 128.2, 130.1, 134.9, 139.2, 143.4 ppm;
MS (70 eV), *m*/*z*: 222 [M^+].

6.13. N-(4′-methylbenzenesulfonyl) benzimidazole (Table 5, entry m)

^1H NMR (300 MHz, DMSO): δ 2.47 (s, 3H), 7.06 (d, J = 9.3 Hz, 1H, Ar–H), 7.18–7.23 (m, 2H, Ar–H), 7.46 (d, J = 4.8 Hz, 2H, Ar–H), 7.64 (d, J = 7.2 Hz, 1H, Ar–H), 7.71 (d, J = 9.9 Hz, 2H, Ar–H), 8.16 (s, 1H, =N—C—H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 27.6, 114.9, 123.5, 128.0, 129.8, 132.0, 133.7, 136.2, 140.9, 144.7 ppm;
MS (70 eV), *m*/*z*: 272 [M^+].

6.14. N-(4′-methylbenzenesulfonyl) indole (Table 5, entry n)

^1H NMR (300 MHz, DMSO): δ 2.35 (s, 3H), 6.40 (m, 1H), 7.10–7.00 (m, 2H), 7.30 (m, 1H), 7.40–7.34 (m, 3H), 7.60 (m, 1H), 7.81 (m, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 102.4, 111.1, 118.3, 119.0, 120.1, 122.2, 128.0, 128.2, 130.1, 134.9, 136.0, 143.4 ppm;
MS (70 eV), *m*/*z*: 271 [M^+].

6.15. N-p-tosylacetamide (Table 5, entry o)

^1H NMR (300 MHz, DMSO): δ 2.02 (s, 3H, —CH_3), 2.35 (s, 3H), 7.34 (m, 2H), 7.81 (m, 2H), 8.00 (s, 1H, NH) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 24.3, 127.2, 129.4, 136.7, 141.6, 173 ppm;
MS (70 eV), *m*/*z*: 213 [M^+].

6.16. N-p-tosylbenzamide (Table 5, entry p)

^1H NMR (300 MHz, DMSO): δ 2.29 (s, 3H), 7.47–7.43 (m, 2H), 7.52–7.49 (m, 2H), 7.86 (m, 5H), 8.00 (s, 1H, —NH) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 127.2, 127.5, 128.9, 129.4, 132.2, 134.2, 136.7, 141.6, 170 ppm;
MS (70 eV), *m*/*z*: 275 [M^+].

6.17. N-phenyl-N-p-tosylacetamide (Table 5, entry q)

^1H NMR (300 MHz, DMSO): δ 2.02 (s, 3H), 2.35 (s, 3H), 7.00 (m, 1H), 7.34–7.24 (m, 4H), 7.64 (m, 2H), 7.81 (m, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 24.3, 121.6, 124.4, 127.2, 129.0, 129.7, 130.3, 136.7, 141.6, 168 ppm;
MS (70 eV), *m*/*z*: 289 [M^+].

6.18. N-phenyl-N-p-tosylbenzamide (Table 5, entry r)

^1H NMR (300 MHz, DMSO): δ 2.35 (s, 3H), 7.00 (m, 1H), 7.24 (m, 2H), 7.34 (m, 2H), 7.51–7.44 (m, 3H), 7.64 (m, 2H), 7.81 (m, 2H), 7.95 (m, 2H) ppm;
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 121.6, 124.4, 127.2, 127.5, 127.7, 128.9, 129.0, 129.4, 132.2, 134.2, 136.7, 141.6, 165 ppm;
MS (70 eV), *m*/*z*: 351.42 [M^+].

7. Conclusions

In conclusion, a rapid, simple, convenient, cost effective *N*-sulfonylation of amines, imides, amides and anilides by *p*-TsCl in the presence of atomized sodium in EtOH–THF under ultrasonic condition is developed. The reaction is facile, involves simple workup, uses readily available chemicals and gives high yield of the products in short reaction duration. The method is green as it involves the use of an energy efficient technique.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ultsonch.2015.01.018.

References

[1] T.J. Mason, J.P. Lorimer, Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry, Ellis Harwood, Chichester, UK, 1988.

[2] K.S. Suslick, Ultrasound: Its Chemical, Physical and Biological Effects, VCH Publishers, New York, 1988.

[3] K.S. Suslick, G. Price, Applications of ultrasound to materials chemistry, Annu. Rev. Mater. Sci. 29 (1999) 295.

[4] (a) T.J. Mason, D. Peters, Practical Sonochemistry, second ed., Ellis Horwood, London, 2002;
(b) K.S. Suslick, Sonochemistry and sonoluminiscence, in: The Encyclopedia of Physical Science and Technology, third ed., vol. 17, Academic Press: San Diego, 2001.;
(c) J.L. Luche, Synthetic Organic Sonochemistry, Plenum Press, New York, 1998.

[5] (a) T.J. Mason, Sonochemistry and the environment – providing a "green" link between chemistry, physics and engineering, Ultrason. Sonochem. 14 (2007) 476;
(b) E. Kimmel, Cavitation bioeffects, Crit. Rev. Biomed. Eng. 34 (2006) 105;
(c) K.S. Suslick, Sonochemistry in comprehensive coordination chemistry, vol. 2, Elsevier Science, New York, 2003, p. 731;
(d) S.J. Putterman, K.R. Weninger, Sonoluminescence. How bubbles turn sound into light, Ann. Rev. Fluid Mech. 32 (2000) 445.

[6] K.S. Suslick, Sonochemistry, Science 247 (1990) 1439.

[7] K.S. Suslick, D.A. Hammerton, R.E. Cline, Sonochemical hot spot, J. Am. Chem. Soc. 108 (1986) 5641.

[8] J.P. Lorimer, T.J. Mason, Sonochemistry. Part 1-The physical aspects, Chem. Soc. Rev. 16 (1987) 239.

[9] H. Mehrabi, Ultrasound-assisted synthesis of aromatic 1,2-diketones from oximinoketones under neutral conditions in aqueous media, Ultrason. Sonochem. 19 (2012) 125.

[10] (a) C.T. Supuran, A. Casini, A. Scozzafava, Protease inhibitors of the sulfonamide type: anticancer, antiinflammatory, and antiviral agents, Med. Res. Rev. 5 (2003) 535;
(b) A. Scozzafava, T. Owa, A. Mastrolorenzo, C.T. Supuran, Anticancer and antiviral sulfonamides, Curr. Med. Chem. 10 (2003) 925;
(c) W.G. Harter, H. Albrect, K. Brady, B. Caprathe, J. Dunbar, J. Gilmore, S. Hays, C.R. Kostlan, B. Lunney, N. Walker, The design and synthesis of sulfonamides as caspase-1 inhibitors, Bioorg. Med. Chem. Lett. 14 (2004) 809;
(d) N.S. Reddy, M.R. Mallireddigari, S. Cosenza, K. Gumireddy, S.C. Bell, E.P. Reddy, M.V. Reddy, Synthesis of new coumarin 3-(N-aryl) sulfonamides and their anticancer activity, Bioorg. Med. Chem. Lett. 14 (2004) 4093;
(e) B.R. Stranix, J.F. Lavallee, G. Sevigny, J. Yelle, V. Perron, N. Leberre, D. Herbart, J.J. Wu, Lysine sulfonamides as novel HIV-protease inhibitors: *N*-epsilon-acyl aromatic α-amino acids, Bioorg. Med. Chem. Lett. 16 (2006) 3459.

[11] (a) H. Nishida, T. Hamada, O. Yonemitsu, Hydrolysis of tosyl esters initiated by an electron transfer from photoexcited electron-rich aromatic compounds, J. Org. Chem. 53 (1988) 3386;
(b) W. Yuan, K. Fearson, M.H. Gelb, Synthesis of sulfur-containing phospholipid analogues as mechanistic probes of phospholipase A2 catalysis, J. Org. Chem. 54 (1989) 906;
(c) J.F. O'Connell, H. Rapoport, 1-Benzenesulfonyl- and 1-*p*-toluenesulfonyl-3-methylimidazolium triflates: efficient reagents for the preparation of arylsulfonamides and arylsulfonates, J. Org. Chem. 57 (1992) 4775;
(d) S. Chandrasekhar, S. Mohapatra, Asymmetric synthesis of anti-convulsive drug (*S*)-Vigabatrin, Tetrahedron Lett. 39 (1998) 6415.

[12] T. Hasegawa, H. Yamamoto, A practical synthesis of optically active (R)-2-propyloctanoic acid: therapeutic agent for Alzheimer's disease, Bull. Chem. Soc. Jpn. 73 (2000) 423.

[13] M.G. Banwell, C.F. Crasto, C.J. Easton, A.K. Forrest, T. Karoli, D.R. March, L. Mensah, M.R. Nairn, P.J. O'Hanlon, M.D. Oldham, W. Yue, Analogues of SB-203207 as inhibitors of tRNA synthetases, Bioorg. Med. Chem. Lett. 10 (2000) 2263.

[14] Y. Wang, D.L. Soper, M.J. Dirr, M.A. Delong, B. De, J.A. Wos, The synthesis and human FP receptor binding affinity of 13,14-dihydroprostaglandin F1α sulfonamides: potential treatments for osteoporosis, Chem. Pharm. Bull. 48 (2000) 1332.

[15] L.L. Chang, W.T. Ashton, K.L. Flanagan, T.B. Chen, S.S. O'Malley, G.J. Zingaro, P.K.S. Siegl, S.D. Kivlighn, V.J. Lotti, R.S.L. Chang, W.J. Greenlee, Triazolinone biphenyl sulfonamides as angiotensin II receptor antagonists with high affinity for both the AT_1 and AT_2 types, J. Med. Chem. 37 (1994) 4464.

[16] J.H. Musser, A.F. Kreft, R.H.W. Bender, D.M. Kubrak, D. Grimes, R.P. Carlson, J.M. Hand, J. Chang, *N*-[(arylmethoxy)phenyl] carboxylic acids, hydroxamic acids, tetrazoles, and sulfonyl carboxamides. Potent orally active leukotriene D4 antagonists of novel structure, J. Med. Chem. 33 (1990) 240.

[17] (a) C.G. Frost, J.P. Hartley, D. Griffin, Catalytic arylation of sulfamoyl chlorides: a practical synthesis of sulfonamides, Synlett 2002 (1928) 11;
(b) H.H. Kang, H.S. Rho, D.H. Kim, S.-G. Oh, Metal oxide in aqueous organic solution promoted chemoselective *N*-sulfonylation of hydrophilic amino alcohols, Tetrahedron Lett. 44 (2003) 7225;
(c) G.A. Meshram, V.D. Patil, A simple and efficient method for sulfonylation of amines, alcohols and phenols with cupric oxide under mild conditions, Tetrahedron Lett. 50 (2009) 1117;
(d) F. Tamaddon, M.A. Reza Sabeti, A.A. Jafari, F. Tigir, E. Keshavarz, ZnO and ZnO-nanoparticles: efficient and reusable heterogeneous catalysts for one-pot synthesis of N-acylsulfonamides and sulfonate esters, J. Mol. Catal. A: Chem. 41 (2011) 41;
(e) M. Mokhtar, T.S. Saleh, N.S. Ahmed, S.A. Al-Thabaiti, R.A. Al-Shareef, An eco-friendly *N*-sulfonylation of amines using stable and reusable Zn–Al–hydrotalcite solid base catalyst under ultrasound irradiation, Ultrason. Sonochem. 18 (2011) 172;
(f) F. Tamaddon, A. Nasiri, S. Farokhi, CsF–Celite as an efficient heterogeneous catalyst for sulfonylation and desulfonylation of heteroatoms, Catal. Commun. 12 (2011) 1477;
(g) C. Barbey, R. Bouasla, M. Berredjem, N. Dupont, B. Retailleau, M. Lecouvey, N.E. Aouf, Synthesis and structural study of new substituted chiral sulfamoyl oxazolidin-2-ones, Tetrahedron 68 (2012) 9125;
(h) R. Sridhar, B. Srinivas, V. Pavan Kumar, M. Narender, K. Rama Rao, β-Cyclodextrin-catalyzed monosulfonylation of amines and amino acids in water, Adv. Synth. Catal. 2007 (1873) 349;
(i) M. Jafarpour, A. Rezaeifard, M. Aliabadi, Catalytic activity of silica gel in the synthesis of sulfonamides under mild and solvent-free conditions, Appl. Catal. A Gen. 358 (2009) 49;
(j) S. Lakrout, H. K'tir, A. Amira, M. Berredjem, N.-E. Aouf, A simple and eco-sustainable method for the sulfonylation of amines under microwave-assisted solvent-free conditions, RSC Adv. 4 (2014) 16027.

[18] A. Yasuhara, M. Kameda, T. Sakamoto, Selective monodesulfonylation of *N*, *N*-disulfonylarylamines with tetrabutylammonium fluoride, Chem. Pharm. Bull. 47 (1999) 809.

[19] J.G. Kim, D.O. Jang, Mild and efficient indium metal catalyzed synthesis of sulfonamides and sulfonic esters, Synlett 18 (2007) 2501.

[20] K.K. Anderson, D.N. Jones, Comprehensive Organic Chemistry, Pergamon Press, Oxford, 1979. 3.

[21] J.L. Luche, Synthetic Organic Sonochemistry, Plenum Press, New York, 1998. pp. 178–179, 183, 189–190, 220–221.

[22] S. Sudha, M.A. Pasha, Ultrasound assisted synthesis of tetrahydrobenzo[c]xanthene-11-ones using CAN as catalyst, Ultrason. Sonochem. 19 (2012) 995.

[23] M.A. Pasha, S. Nagashree, $Ni(NO_3)_2{\cdot}6H_2O/I_2$/water: a new, mild and efficient system for the selective oxidation of alcohols into aldehydes and ketones under sonic condition, Ultrason. Sonochem. 20 (2013) 810.

[24] (a) M.A. Pasha, S. Nagashree, A one-pot three-component synthesis of 4,6-diarylpyrimidin-2(1*H*)-ones (DAPMs) using atomized sodium in THF under sonic condition, Ultrason. Sonochem. 21 (2014) 1279;
(b) M.A. Pasha, S. Nagashree, Baeyer condensation: a facile synthesis of triarylmethanes using atomized sodium in THF under sonic condition, Int. J. Res. Chem. Environ. 3 (2013) 54–58.

[25] B.S. Furniss, A.J. Hannaford; P.W.G. Smith; A.R. Tatchell, Vogel's Text Book of Practical Organic Chemistry, fifth ed., Longman, 1989, 4.2, 463.

[26] T.J. Mason, Chemistry with Ultrasound, Published for the Society of Chemical Industry, Elsevier Science Publisher Ltd., England, 1990.

[27] A. Kotrorearou, G. Mills, Hoffmann MR, ultrasonic irradiation of p-nitrophenol in aqueous solution, J. Phys. Chem. 95 (1991) 3630–3638.

[28] J.L. Luche, A few questions on the sonochemistry of solutions, Ultrason. Sonochem. 4 (1997) 211–215.

[29] T.G. Leighton, The Acoustic Bubble, Academic, London, 1994.

[30] M.A. Pasha, S. Nagashree, Baeyer condensation: a Facile Synthesis of Triaryl methan-es using atomized Sodium in THF under Sonic Condition, Int. J. Res. Chem. Environ. 55 (2013) 54–58.

[31] J.L. Luche, Synthetic organic sonochemistry, Plenum Press, New York, 1998. pp. 236, 10–15, 188, 242, 177.

[32] S.D. Howkins, Solid erosion in low-amplitude sound fields, J. Acoust. Soc. Am. 39 (1966) 55.

[33] K. Sollner, Notes on the dispersion of solids in liquids by ultrasonic waves, Trans. Faraday Soc. 34 (1938) 1170–1174.

[34] (a) M.A. Pasha, M.B.M. Reddy, Cs_2CO_3 catalysed rapid and efficient conversion of amines into sulfonamides; alcohols and phenols into sulfonic esters, Phosphorus, Sulfur, and Silicon, 2011, 186, 1867–1875 and references cited therein.;
(b) Y.-C. Teo, F.-F. Yong, Efficient Ligand Free copper-catalyzed *N*-arylation of sulfonamides, Synlett 6 (2011) 837–843.