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A Rapid and Facile Synthesis of Sulphonamides Using Alumina Supported $CeCl_3.^{7H}{}_2O$-LiI Catalyst

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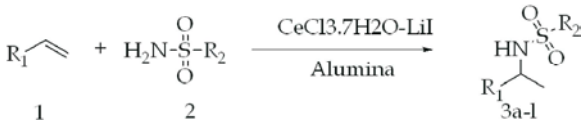
Abstract: A convenient synthesis of *N*-substituted sulphonamides was described by hydroamination reaction of vinyl arenes with sulphonamides, in which catalytic amount of Alumina supported $CeCl_3.7H_2O$-LiIwas used to afford the corresponding products in excellent yields. All the synthesised compounds were well characterized by advanced spectroscopic data. This new protocol is of interest due to stability, cost effective, short reaction time, simple work-up and excellent yields.

Key words: Vinyl arenes · Sulphonamides · Hydroamination reaction · Alumina supported $CeCl_3.7H_2O$-KI · *N*-substituted sulphonamides

INTRODUCTION

In recent years, considerable attention has been focused on the development of efficient and operationally simple protocols for hydroaminationreactions.It is one of the most useful carbon–nitrogen bond forming reactions. The hydroaminationreactions of vinyl arenes to sulphonamides have been received much interest, because a number of *N*-substituted sulphonamide derivatives occur and possess a variety of biological activities [2,3]. Several methodologies were reported by using Lewis acids for intra and intermolecular hydroamination of alkenes [4], synthesis of *N*-substituted sulphonamides using vinyl alkenes and primary sulphonamide were reported using various catalyst systems [5]. However, in spiteof their potential utility, many of these reported methodologies suffer from drawbacks such as harsh reaction conditions (strongly acidic, dry reaction conditions), prolonged reaction times, use of expensive reagents, low yields of the products, failure to provide addition product and tedious experimental procedure, difficulty of reuse, which necessitate the development of an alternative route for the synthesis of *N*-substituted sulphonamides.



Scheme-1

$CeCl_3$ (Cesium chloride) alone or along with NaI (Sodium iodide)was used to catalyse various carbon-nitrogen bond formation reactions. Increase in the catalytic activity was observed when $CeCl_3.7H_2O$ was employed along with NaI. In order to make this catalyst as strong Lewis acid system, it was supported over either Silica gel or on Neutral Alumina [6] which facilitates easy recovery and reusability [7].

MATERIALS AND METHODS

General: All chemicals and reagentsof analytical grade were purchased e from Aldrich and Merck and were used without further purification. Thin-layer chromatography (TLC) was performed on E.Merck AL silica gel 60 F254 plates and visualized under UV light. IR spectra were recorded as KBr pellet with a Perkin-Elmer spectrum gx FTIR instrument and only diagnostic and/or intense peaks

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are reported. ^{1}H NMR spectra were recorded with Varian Mercury plus 400 MHz instrument. ^{13}C NMR spectra were recorded with a Varian Gemini 100 MHz instrument. All the chemical shifts were reported in δ(ppm) using TMS as an internal standard. The ^{1}H NMR chemical shifts and coupling constants were determined assuming first-order behaviour. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad); the list of coupling constants (*J*) corresponds to the order of multiplicity assignment. Mass spectra were recorded with a PE Sciex model API 3000 instrument. All the reactions were carried out under Nitrogen atmosphere.

Preparation of Neutral Alumina Supported $CeCl_3.7H_2O$–LiI: Neutral alumina of 150 mesh, 58° A pore size (10 g) in water was added to a stirred mixture of $CeCl_3.7H_2O$ (5 g, 13.42 mmol) and LiI (1.5 g, 11.20 mmol) in acetonitrile (100 mL) and stirred for 12 hrs. The acetonitrile was evaporated under reduced pressure to dryness to yield fine powder which was stored under nitrogen in bottle.

Procedure for the Synthesis of N-Substituted Sulphonamides (3a-3l): A mixture of olefin (1) (1mmol), sulfonamide (2) (1 mmol), Alumina supported CeCl3.7H2O-LiI (10 mol %) was stirred in toluene at 80°C for a specified time. The progress of the reaction was monitored by TLC. After completion of the reaction (by TLC monitoring), the mixture was allowed to room temperature and the catalyst was separated by simple filtration.Toluene was evaporated; obtained residue was partitioned between ethylacetate and water. The organic layer was dried over anhy.Na_2SO_4 and evaporated under reduced pressure to get crude product which was purified by silica gel (100-200 mesh) column chromatography using EtOAc: hexane as eluents.

RESULTS AND DISCUSSION

In an effort to explore a novel catalyst for hydroamination of vinyl arenes (1a-g) with sulphonamides (2a-b), we have screened the model reaction of styrene (1a) with methanesulphonamide (2a) in presence of $CeCl_3.7H_2O$-LiI (Scheme-1) in various solvents such as DCM, toluene and acetonitrileunder reflux conditions and it was observed that with toluene the expected product 3a was obtained in 7 h (Table 1, entry 3).

Table 1: Selection of Solvent for the synthesis of product 3a

Entry	Solvent	Catalyst (%)	Time (h)
1	DCM	10	48*
2	Toluene	10	7
3	Acetonitrile	10	18

*Reaction not completed.

Table 2: Effect of catalyst system on hydroamination of styrene (1a) with methanesulphonamide(2a)

Entry	Catalyst	Temp°C	Time	Yield (%)
1	$CeCl_3.7H_2O$-LiI	110	7	90
2	Alumina supported $CeCl_3.7H_2O$-LiI	80	4	92
3	Silica supported $CeCl_3.7H_2O$-LiI	80	5	90

Toluene was selected as a reaction solvent. The same reaction was carried out with $CeCl_3.7H_2O$ and LiI impregnated over neutral alumina as well as Silica Gel to evaluate the effect of solid support on the catalytic activity which was presented in (Table 2). From the results in (Table 2) shows that Alumina supported $CeCl_3.7H_2O$-LiI catalyst was found to be the efficient system with 92% yield in 4 h of reaction time.

With this optimised results in hand, we have made an attempt for the synthesis of *N*-substituted sulphonamides (3a-l) utilizing 10 mol% Alumina supported $CeCl_3.7H_2O$-LiI as solid heterogeneous catalyst (Scheme-1). As expected, satisfactory results were obtained and the results are summarized in (Table 3).

Characterisation of the Synthesised Compounds (3a-l)

***N*-(1-Phenyl) Ethylmethanesulfonamide (3a):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40.7.28 (m, Ar H, 5H), 4.80 (d, J = 6.8 Hz, NH, 1H), 4.66 (qd, J = 6.8, 6.8 Hz, -$CHCH_3$, 1H), 2.62 (s, -SO_2CH_3, 3H), 1.55 (d, J = 6.8 Hz, -$CHCH_3$, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 144.2, 128.9, 127.2, 126.5, 22.4, 46.2, 42., IR (KBr cm^{-1}): 3370 (s), 1460 (m), 1430 (m), 1320 (s), 1300 (m), 1150 (s), 1110 (m), 1090 (m), 1030 (m), 990(m), 770 (s), 710 (s); ESI-MS (70 eV) *m/z* (relative intensity): (M+Na)=222.2).

***N*-(1-(*p*-tolyl) Ethyl) Methanesulfonamide (3b):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7-7.01 (m, 4H), 4.08 (q, 1H), 2.84 (s, 3H), 2.35 (s, 3H), 2.2 (d, 1H), 1.4 (d, 3H). 13C NMR (100 MHz, $CDCl_3$) δ 141,137.1, 129.2, 127, 47.4,43. 2, 25.5, 22.2., IR (cm^{-1}): 3275, 2975, 2926, 1437, 1315, 1152, 981, 819, 518. ESI-MS *m/z* (M+Na) = 236.

***N*-(1-Phenylethyl) Benzenesulfonamide (3c):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.78 (m, 2H), 7.37-7.48 (m, 3H), 7.05-7.19 (m, 5H), 5.02 (br s, 1H), 4.52 (quintet, J = 6.8Hz, 6.6Hz, 6.8 Hz, 1H), 1.454-1.42 (d, J = 6.8 Hz, 3H), 13C NMR

Table 3: Synthesis of *N*-substituted sulphonamides (3a-l) using Alumina supported $CeCl_3.7H_2O$-LiI

Entry	Compound	R_1	R_2	Time (h)	Yield(%)[a]
1	3a	Ph	Me	3.0	90
2	3b	4-MePh	Me	3.5	91
3	3c	Ph	Ph	2.5	89
4	3d	4-t-butylPh	Ph	4.0	87
5	3e	4-ClPh	Ph	3.0	86
6	3f	â-Naphthyl	Ph	3.5	92
7	3g	4-MePh	4-MePh	3.0	92
8	3h	4-t-butylPh	4-MePh	4.0	90
9	3i	1,2,3,4-tetrahydronaphthalene	4-MePh	3.5	88
10	3j	â -Naphthyl	4-MePh	3.5	91
11	3k	Ph	4-MePh	3.0	85
12	3l	2,3-dihydro-1H-indene	4-MePh	4.0	89

[a]Isolated yield of compounds

(100 MHz, $CDCl_3$) δ 23.5, 53.7, 126.1, 127.0, 127.4, 128.5, 128.8, 132.3, 140.6, 141.8., IR (KBr cm^{-1}) 3467, 2923, 2898, 1508, 1504, 1324, 1159, 1063, 1021, 810, 663, 538 HRMS-Anal.($C_{14}H_{15}NO_2S$) calcd, C: 64.34, H: 5.79, N: 5.36; found, C: 64.48, H: 5.85, N: 5.40. ESI-MI: *m/z* (M+Na) = 284.

***N*-[1-[4-(tert-Butyl) Phenyl] Ethyl]-Benzenesulfonamide (3d):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.66 (m, 2H), 7.38–7.23 (m, 3H), 7.11–6.94 (m, 4H),5.89 (d, J = 7.3 Hz, 1H), 4.51–4.3 (m, 1H), 1.41 (d, J = 7.3 Hz, 3H), 1.24 (s, 9H). 13C NMR (100 MHz, $CDCl_3$) δ 23.3, 31.1, 34.2, 53.3, 125.1, 125.7, 126.9, 128.5, 131.9, 138.6, 140.6, 150.0., IR (neat) cm^{-1}: 3276, 3061, 2962, 2868, 1512, 1447, 1323, 1165, 1091, 962, 833, 721., ESI-MS: *m/z* (M+Na) 340. HRMS m/z: calcd for $C_{18}H_{23}NO_2NaS$ [M+Na]: 340.1347, found, 340.1351.

***N*-(1-(4-Chlorophenyl) Ethyl) Benzenesulfonamide (3e):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.68 (d, J = 8Hz, 2H), 7.30-7.5 (m, 3H), 6.95-7.15 (m, 4H), 5.65-5.61 (d, J = 6.9Hz 1H), 4.5-4.35 (p, 1H), 1.41-1.37 (d, J = 7.0Hz 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 140.5, 133.4, 132.6, 129.0, 128.7, 127.7, 127.1, 53.2, 23.6., IR (KBr cm^{-1}) 3224, 3260, 2924, 2858, 1737, 1653, 1448, 1321.77, 1155, 10884, 1016, 964, 594, 543,. ESI-MS *m/z* 297 (M+H).

***N*-(1-(Naphthalen-2-yl) Ethyl) Benzenesulfonamide (3f):** ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (t, J_1 = 6 Hz, J_2 = 3.3Hz, 1H), 7.66 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 10 Hz, 2H), 7.41-7.47 (m, 3H), 7.20 (d, J = 8.7 Hz, 1H), 7.03 (d, J = 8.4 Hz, 2H), 4.92 (d, J = 7.2 Hz, 1H), 4.64 (dt, J_1 = 13.5 Hz, J_2= 6.6 Hz, 1H), 2.25 (s, 3H), 1.51 (d, J = 6.6 Hz, 3H)., ^{13}CNMR (75 MHz, $CDCl_3$): 143.1, 138.9, 137.5, 133.0, 132.6, 129.2, 128.4, 127.4, 127.0, 126.1, 125.9, 125.0, 124.0, 53.7, 23.4, 21.3., IR (KBr cm^{-1}): 3281, 3052, 2925, 2854, 1326, 1156, 1082, 748., ESI-MS *(m/z)* (M +Na) = 334.

4-methyl-*N*-(1-(p-tolyl) Ethyl) Benzenesulfonamide (3g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.655-7.634 (d, J = 8.0 Hz, 2H), 7.207- 7.185 (d, J = 8.0 Hz, 2H), 6.98 (s, 4H), 5.182-5.162 (d, J = 6.8 Hz, 1H), 4.45–4.36 (m, 1H), 2.43 (s, 3H), 2.30 (s, 3H), 1.43-1.407 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 21.3, 23.3, 53.3, 125.9, 127.0, 128.9, 129.2, 136.8, 137.6, 139.1, 142.8. IR (KBr cm^{-1}): 3253, 2921, 1647, 1514, 1433, 1324, 1158, 1083, 1021, 959, 810, 666, 538 cm^{-1}. ESI-MS (M+Na): 312. N-(1-

(4-(tert-butyl) phenyl) ethyl)-4-Methylbenzenesulfonamide (3h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 9H), 1.43 (d, J = 6.7 Hz, 3H), 2.36 (s, 3H), 4.45 (quintet, J = 6.7 Hz, 1H), 4.85 (d, J = 6.7 Hz, 1H), 7.00 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 142.2, 141.4, 136.7, 129.4, 127.2, 126.6, 124.9, 45.6, 40.7, 31.4, 24.3, 20.7., IR (neat cm^{-1}): 3255, 1376, 1160, 1078, 1026 cm^{-1}; ESI-MS *m/z* (M+Na) 354.1498,

4-methyl-*N*-(1, 2, 3, 4-tetrahydronaphthalen-1-yl) Benzenesulfonamide (3i): ^{1}H NMR (400 MHz, CDCl3): δ 7.90 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 7.30-6.85 (m, 4H), 4.85 (d, J = 6 Hz, 2H), 4.50 (m, 1H), 2.90-2.64 (m, 2H), 2.45 (s, 3H), 1.90-1.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.3, 138.0, 137.3, 135.4, 129.4, 128.2, 127.2, 126, 51.0, 30.6, 28.8, 21.5, 19.0., IR (KBr cm^{-1}): 3281, 3052, 2924, 2854, 1423, 1327, 1156, 1083, 748. EI MS *(m/z)* (M+Na) 301.

4-methyl-N-(1-(naphthalen-2-yl) ethyl)benzenesulfonamide (3j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.70 (m, 1H), 7.65-7.61 (m,2H), 7.57 (d, J = 8.3 Hz, 2H), 7.46 (s, 1H), 7.44-7.39 (m, 2H), 7.21 (dd, J = 8.5, 1.7 Hz, 1H), 6.98 (d, J = 7.8 Hz, 2H), 5.42 (br, NH, 1H), 4.62 (qd, J = 6.8, 6.8 Hz, 1H), 2.20 (s, 3H), 1.48 (d, J = 7.1 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 138.9, 137.4, 132.8, 132.4, 129.0, 128.2, 127.6, 127.3, 125.7, 126.8, 124.9, 123.9, 53.8, 23.5, 21.3., IR (KBr cm^{-1}) 3420, 1600,1430, 1320, 1310, 1300, 1150,1090, 970, 940, 810, 750, 650; ESI-MS *m*/z: 325 (M+,63), 310 (M+, 83).

4-methyl-*N*-(1-phenylethyl) Benzenesulfonamide (3k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.667-7.64 (d, 2H, J = 8.1 Hz), 7.20-7.09 (m, 7H), 5.43- 5.41(d, 1H, J = 6.9 Hz), 4.48-4.43 (m, 1H), 2.39 (s, 3H), 1.44-1.42 (d, 3H, J = 6.9 Hz)., ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 142.1, 137.6, 129.4, 128.4, 127.3, 127.0, 126.1, 53.65, 23.57, 21.46. IR (KBr cm^{-1}) 3467, 2922, 2853, 1640, 1454, 1322, 1156, 1085, 811, 664, 547., ESI-MS *m/z* 298 [M+Na].

2, 3-dihydro-*N*-tosyl-1*H*-indene-1-amine (3l): ^{1}H NMR (400 MHz, CDCl3) δ 7.87 (d, J = 8.0 Hz, 2H), 7.39-7.13 (m, 6H), 4.89–4.69 (m, 2H), 3.03-2.7 (m, 2H), 2.52 (s, 3H), 2.44-2.30 (m, 1H), 1.90-1.71 (m, 1H)., ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.7, 141.9, 138.2, 129.7, 128.2, 127.1, 126.7, 124.7, 124.0, 58.6, 34.5, 29.9, 21.4. IR (KBr cm^{-1}): 3261, 3064, 2924, 2854, 1596, 1457, 1422, 1317, 1159, 1092, 917,668 cm^{-1}. ESI-MS m/z (M+Na) = 310.

CONCLUSION

To summarise, Alumina supported $CeCl_3.7H_2O$-LiI catalyst smoothly catalyzes the hydroamination of vinyl arenes with sulphonamides leading to C–N bond, affording the desired adducts in high yields. The prominent advantages of this new protocol are short reaction times, operational simplicity, cost efficiency and high yields of product.

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REFERENCES

1. Miller, T.E., K.C. Hultzsch, M. Yus, F. Foubelo and M. Tada, 2008. Chem. Rev.
2. Xavier Giner, Carmen Najera, Gabor Kovacs, Agusti Lledos and Gregori Ujaque, 2011. Adv. Synth. Catal., 353: 3451-3466.
3. Bartoli, G., E. Marcantoni and L. Sambri, 2003. Synlett, pp: 2101-2116.
4. Bartoli, G., M. Bosco, A. Giuliani, E. Marcantoni, A. Palmieri, M. Petrini and L. Sambri, 2004. J. Org. Chem., 69: 1290-1297.
5. Dal Zotto, C., J. Michaux, A. Zarate Ruiz, E. Gayon, D. Virieux, J.M. Campagne, V. Terrasson, G. Pieters, A. Gaucher and D.J. Prim, 2011. Organomet. Chem., 696: 296-304.
6. Taylor, J.G., N. Whittall and K.K. Hii, 2006. Org. Lett., 8: 3561-3564.
7. Qian, H. and R.A. Widenhoefer, 2005. Org. Lett., 7: 2635-2638.
8. Zhang, X. and A. Corma, 2008. Dalton Trans., 7: 397-403.