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Selectfluor™-Catalyzed Synthesis of N-Sulphonyl Imines

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A new and simple synthesis of N-sulphonyl imines has been accomplished by reaction of sulphonamides with aryl aldehydes in the presence of Selectfluor™ under solvent-free conditions.

Key Words: N-Sulphonyl imine, Sulphonamide, Selectfluor™, Solvent-free.

INTRODUCTION

N-Sulphonyl imines have proven to be useful intermediates in organic synthesis[1]. They are used in numerous reactions such as inverse electron-demand Diels-Alder reactions[2], addition reactions as carbonyl equivalents[3] and in ene reactions[4]. There are several methods available for the preparation of N-sulphonyl imines including rearrangement of oxime O-sulphlnates[5], Lewis acid- or solid acid-catalyzed reactions of sulphonamides with aldehydes or acetals[6], utilization of tellurium metal and chloramines T[7], halogen-mediated conversion of N-(trimethylsilyl) imines in the presence of corresponding sulphonyl chloride[8] or two step synthesis using sulphamic acid[9]. Each of these methods has its own merit, but some of these methods are plagued by the limitation of long reaction times, expensive and hazardous reagents, cumber some experimental conditions and requiring use of a microwave oven. Consequently, there is scope for further renovation toward mild conditions, increased of variation of the substituents in the components and better yields.

Selectfluor™ (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octanebis (tetrafluoro-borate)) (Fig. 1) is a commercially available, stable, nonvolatile, nonhygroscopic and easy to handle solid and is more widely used for site-selective fluorination of a variety of carbonyl compounds. Selectfluor™ is a low-cost readily available acidic material and recently it has been employed as an efficient Lewis acid catalyst for the synthesis of 14-aryl-14*H*-dibenzo[a,j]xanthenes[10a], substituted coumarins[10b], 9-aryl-1,8-dioxooctahydroxan-thanes[10c], β-hydroxy thiocyanates[10d], and β-acetamido ketones[10e]. In continuation of our work to bring in and develop new synthetic methodologies[11], we report that a new and simple Selectfluor™-catalyzed synthesis of N-sulphonyl imines by reaction of sulphonamides with aryl aldehydes under mild conditions (**Scheme-I**).

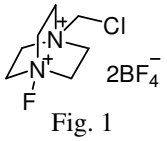
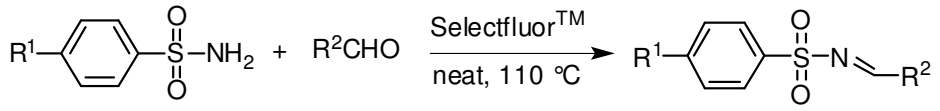


Fig. 1



1 **2** **3**

Scheme-I

EXPERIMENTAL

NMR spectra were determined on Bruker AV-400 spectrometer at room temperature using TMS as internal standard, coupling constants (*J*) were measured in Hz; IR spectra were determined on FTS-40 infrared spectrometer; elemental analysis were performed by a Vario-III elemental analyzer; melting points were determined on a XT-4 binocular microscope and were uncorrected; commercially available reagents were used throughout without further purification unless otherwise stated.

General procedure for the preparation of 4: A mixture of the aldehyde (1 mmol), sulphonamide (1 mmol) and selectfluor™ (0.1 mmol) was stirred at 110 °C for the appropriate time (Table-1). Completion of the reaction was monitored by TLC. The material was cooled to 25 °C and after addition of water the mixture was stirred for 5 min. The solid so obtained was filtered off and recrystallized with hexane-ethyl acetate mixture. The structure of the products was conflrmed by NMR, IR and comparison with authentic samples obtained commercially or prepared by reported methods. The spectral data of some new N-sulphonyl imines are given below:

TABLE-1
SYNTHESIS OF (E)-N-BENZYLIDENEBENZENESULPHONAMIDE UNDER VARIOUS CONDITIONS*

Entry	Selectfluor™ (mol (%))	Temperature (°C)	Time (h)	Yield (%)**
1	0	110	3	12
2	5	110	2	67
3	10	Room temp.	3	52
4	10	50	3	59
5	10	90	2	74
6	10	100	1	80
7	10	110	1	89
8	10	120	1	89
9	10	130	1	88
10	15	100	1	87
11	15	110	1	88
12	20	110	1	85

*Reaction conditions: benzenesulphonamide (1 mmol); benzaldehyde (1 mmol); neat.
**Isolated yield.

(E)-N-(2-Fluoro-benzylidene)benzene sulphonamide (4h): White crystals, IR (KBr, ν_{max}, cm^{-1}): 1648 (C=N), 1325 (S=O); ^1H NMR ($CDCl_3$, 400 MHz) δ 9.41 (s, 1H), 8.08 (d, 1H, *J* = 8.0 Hz), 7.91 (d, 2H, *J* = 8.4 Hz), 7.60-7.48 (m, 3H), 7.35 (t, 2H, *J* = 7.6 Hz), 7.22 (t, 1H, *J* = 7.6 Hz); Anal. calcd. (%) for $C_{13}H_{10}NO_2SF$: C 59.30, H 3.83, N 5.32, S 12.18; found. (%): C 59.42, H 3.90, N 5.26, S 12.09.

(E)-N-(2,4-Dibromobenzylidene)-4-methylbenzene sulphonamide (4q): White crystals, IR (KBr, ν_{max}, cm^{-1}): 1652 (C=N), 1312 (S=O); ^1H NMR ($CDCl_3$, 400 MHz) δ 9.42 (s, 1H), 8.10 (d, 1H, *J* = 8.4 Hz), 7.89 (d, 1H, *J* = 8.0 Hz), 7.46 (s, 1H), 7.40 (d, 2H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.0 Hz), 2.44 (s, 3H); Anal. calcd. (%) for $C_{14}H_{11}NO_2SBr_2$: C 40.31, H 2.66, N 3.36, S 7.69; found. (%): C 40.26, H 2.49, N 3.41, S 7.72.

RESULTS AND DISCUSSION

In order to optimize the reaction conditions, we first examined the amount of catalyst and the reaction temperature, the reaction of benzene sulphonamide with benzaldehyde to the corresponding (E)-N-benzylidenebenzene sulphonamide was studied under solvent-free conditions in the presence of Selectfluor™ at different temperatures. The results are summarized in Table-1. As shown in Table-1, the reaction using 10 % mmol Selectfluor™ at 110 °C proceeded in highest yield.

After optimization of the reaction conditions, the reactions of sulphonamides were examined with various structurally diverse aldehydes (Table-2). As it is clear from Table-2, the reactions proceeded efflciently and the desired products were obtained in good to high yields. Aromatic aldehydes containing both electron-withdrawing and electron-donating substituents afforded the corresponding N-sulphonyl imines in good yields. However, aryl aldehydes possessing electron-withdrawing or hindered substituents generally necessitates longer reaction times and decreased the reaction yields (Table-2, entries 2, 3, 6-9, 11 and 14).

Mention must be made here that the yields of N-sulphonyl imines obtained from the reaction of 4-methylbenzene sulphonamide with aldehydes were higher than benzene sulphonamide (for comparison Table-2). The reaction is highly regioselective forming (E)-N-sulphonyl imines as the products. The structures of the products were established from their spectral properties (IR, ^1H NMR and elemental analysis) and also by comparison with available literature data. The N-sulphonylimines have C=N bond stretching frequencies in the range of 1690-1595 cm^{-1}. These compounds have a characteristic imino resonance in their ^1H NMR spectra at δ = 9.0-9.5. This methodology offers significant improvements with regard to the scope of this transformation and simplicity in operation.

Conclusion

In conclusion, we have demonstrated a simple, cost-effective and efficient alternative method for the preparation of N-sulphonyl imines by the reaction of sulphonamides with aryl aldehydes at 110 °C under solvent-free conditions using selectfluor™ as catalyst. Prominent among the advantages of this method are operational simplicity, good yields in short reaction times, solvent-free conditions and easy workup procedure employed.

TABLE-2
PREPARATION OF N-SULPHONYL IMINES CATALYZED BY SELECTFLUOR™*

Entry	R^1	R^2	Time (h)	Product	m.p. (°C) (Lit.)	Yield (%)**
1	H	C_6H_5	1.0	**4a**	75-77 (77-78)[6h]	88
2	H	4-Cl-C_6H_4	2.0	**4b**	132-133 (131-133)[6k]	84
3	H	4-Br-C_6H_4	2.0	**4c**	204-205 (206-208)[6h]	85
4	H	4-MeO-C_6H_4	1.5	**4d**	132-133 (130-132)[6h]	87
5	H	4-Me-C_6H_4	1.0	**4e**	112-114 (114-116)[6k]	88
6	H	3-NO_2-C_6H_4	2.0	**4f**	115-116 (113-114)[6f]	76
7	H	4-NO_2-C_6H_4	2.0	**4g**	162-164 (161-163)[6h]	72
8	H	2-F-C_6H_4	1.5	**4h**	121-124	83
9	H	2,4-Cl_2-C_6H_3	2.0	**4i**	121-122 (123-124)[6h]	80
10	CH_3	C_6H_5	1.0	**4j**	109-110 (108-109)[6h]	93
11	CH_3	4-Cl-C_6H_4	1.5	**4k**	169-170 (171-173)[6h]	85
12	CH_3	4-MeO-C_6H_4	1.0	**4l**	125-126 (127-129)[6k]	89
13	CH_3	4-Me-C_6H_4	1.0	**4m**	113-115 (112-114)[6h]	88
14	CH_3	4-NO_2-C_6H_4	1.5	**4n**	159-160 (163-164)[6k]	86
15	CH_3	2-Cl-C_6H_4	1.0	**4o**	128-130 (128-129)[6h]	83
16	CH_3	2,5-MeO-C_6H_3	1.5	**4p**	122-123 (124-126)[6h]	85
17	CH_3	2,4-Br-C_6H_3	1.5	**4q**	118-120	79
18	CH_3	2-Furyl	2.0	**4r**	99-100 (100-101)[6h]	85
19	CH_3	3-Thiophenyl	2.0	**4s**	124-126 (127-129)[6h]	83
20	CH_3	$CH_3(CH_2)_5CH_2$	2.0	**4t**	138-139 (136-137)[6k]	76

*Reaction conditions: sulfonamide (1 mmol); aldehyde (1 mmol); Selectfluor™ (0.1 mmol); 110 °C; neat. **Isolated yield.

TABLE-3
EFFECT OF CATALYST ON THE REACTION OF
BENZENESULPHONAMIDE WITH BENZALDEHYDE

Entry	Reagent and conditions	Time (min)	Yield (%)	Ref.
1	Silica chloride, solvent-free, 120 ºC	180	75	6a
2	$Si(OEt)_4$, 160 ºC	360	68	6b
3	$CaCO_3$, K10 Clay, $CH(OMe)_3$, Microwave	6	69	6c
4	$TiCl_4$, NEt_3, 0 ºC, CH_2Cl_2	25	58	6d
5	P_2O_5/SiO_2, solvent-free, 110 ºC	120	88	6e
6	ZrO_2, $S_2O_8^{2-}$, Microwave	9	89	6k
7	MgO, solvent-free, Microwave	8	87	6f
8	ZnO, solvent-free, 110 ºC	240	90	6g
9	Selectfluor™, solvent-free, 110 ºC	60	89	–

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REFERENCES

1. (a) R. Bloch, *Chem. Rev.*, **98**, 1407 (1998); (b) S.M. Weinreb, *Top. Curr. Chem.*, **190**, 131 (1997).
2. (a) R. Albrecht and G. Kresze, *Chem. Ber.*, **97**, 490 (1964); (b) D.L. Boger, W. L. Corbett, T. Curran and A.M. Kasper, *J. Am. Chem. Soc.*, **113**, 1713 (1991); (c) M.D. Alexander, R.E. Anderson, J. Sisko and S.M. Weinreb, *J. Org. Chem.*, **55**, 2563 (1990).
3. J. Sisko and S.M. Weinreb, *J. Org. Chem.*, **55**, 393 (1990).
4. (a) D.M. Tschaen, E. Turos and S.M. Weinreb, *J. Org. Chem.*, **49**, 5058 (1984); (b) M.J. Melnick, A.J. Freyer and S.M. Weinreb, *Tetrahedron Lett.*, **29**, 3891 (1988).
5. D.L. Boger and W.L. Corbett, *J. Org. Chem.*, **57**, 4777 (1992).
6. (a) A. Hasaninejad and H. Sharghi, *Phosphorus Sulfur Silicon Rel. Elem.*, **182**, 873 (2007); (b) B. Love, P.S. Raje and T.C. Williams, *Synlett*, 493 (1994); (c) A. Vass, J. Dudas and R.S. Varma, *Tetrahedron Lett.*, **40**, 4951 (1999); (d) W.B. Jennings and C.J. Lovely, *Tetrahedron*, **47**, 5561 (1991); (e) A. Hasaninejad, A. Zare, H. Sharghi and M. Shekouhy, *ARKIVOC*, **11**, 64 (2008); (f) A. Hasaninejad, A. Zare, A.R.M. Zare, A. Parhami, H. Sharghi and A. Khalafi-Nezhad, *Phosphorus Sulfur Silicon Rel. Elem.*, **183**, 2769 (2008); (g) M. Hosseini-Sarvari and H. Sharghi, *Phosphorus Sulfur Silicon Rel. Elem.*, **182**, 2125 (2007); (h) A. Hasaninejad and A. Zare, *J. Sulfur Chem.*, **28**, 357 (2007); (i) H. Sharghi, M. Hosseini-Sarvari and S. Ebrahimpourmoghaddam, *ARKIVOC*, **15**, 255 (2007); (j) T.-S. Jin, M.-J. Yu and L.-B. Liu, *Synth. Commun.*, **36**, 2339 (2006); (k) T.S. Jin, G.L. Feng, M.N. Yang and T.S. Li, *Synth. Commun.*, **34**, 1277 (2004); (l) A. Zare, A.R. Moosavi-Zare, A. Hasaninejad, A. Parhami, A. Khalafi-Nezhad and M.H. Beyzavi, *Synth. Commun.*, **39**, 3156 (2009).
7. B.M. Trost and C. Marrs, *J. Org. Chem.*, **56**, 6468 (1991).
8. G.I. Georg, G.C.B. Harriman and S.C. Peterson, *J. Org. Chem.*, **60**, 7366 (1995).
9. A. Vass, J. Dudas and R.S. Varma, *Tetrahedron Lett.*, **40**, 4951 (1999).
10. (a) P.S. Kumar, B.S. Kumar, B. Rajitha, P.N. Reddy, N. Sreenivasulu and Y.T. Reddy, *ARKIVOC*, **12**, 46 (2006); (b) B.S. Kumar, Y.T. Reddy, P.N. Reddy, P.S. Kumar and B. Rajitha, *J. Heterocycl. Chem.*, **43**, 477 (2006); (c) M.R.P. Heravi, *J. Iran. Chem. Soc.*, **6**, 483 (2008); (d) J.S. Yadav, B.V.S. Reddy and C.S. Reddy, *Tetrahedron Lett.*, **45**, 1291 (2004); (e) V.S. Shinu, B. Sheeja, E. Purushothaman and D. Bahulayan, *Tetrahedron Lett.*, **50**, 4838 (2009).
11. (a) L.Q. Wu, C.G. Yang, C. Zhang, L.M. Yang, *Bull. Korean Chem. Soc.*, **30**, 1665 (2009); (b) L.Q. Wu, C.G. Yang, C. Zhang and L.M. Yang, *Lett. Org. Chem.*, **6**, 234 (2009); (c) L.Q. Wu, C.G. Yang, C. Zhang and L.J. Yang, *Phosphorus Sulfur Silicon Rel. Elem.*, **185**, 903 (2010).

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