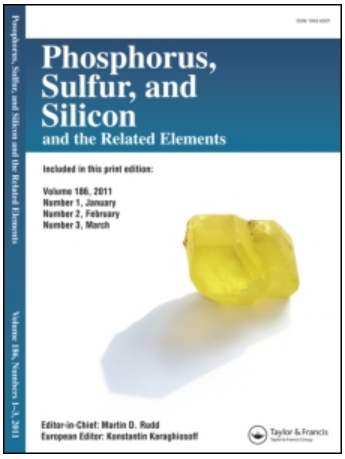

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A Convenient and Efficient Method for the Preparation of *N*-Sulfonyl Aldimines from Aromatic Aldehydes under Solvent-Free Conditions

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A Convenient and Efficient Method for the Preparation of *N*-Sulfonyl Aldimines from Aromatic Aldehydes under Solvent-Free Conditions

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Condensation of a variety of aromatic aldehydes with sulfonamides in the presence of silica chloride by heating afforded novel functionally varied aromatic N*-sulfonyl aldimines in good to excellent yields.*

Keywords *N*-sulfonyl aldimine; sulfonamides; silica chloride; solvent-free

INTRODUCTION

Sulfonyl imines are versatile synthetic intermediates in organic synthesis and have industrial applications.[1,2] They are activated imines in which the limitations of aldimine functionality such as low electrophilicity of azomethine carbon and the tendency of enolizable imines to undergo deprotonation rather than addition can be circumvated.[3] They are excellent substrates in aziridination,[4] oxaziridination,[5] olefination reactions,[6] nucleophilic additions,[7] reductions,[8] and aza Diels-Alder reactions.[9] Several synthetic methods for the preparation of *N*-sulfonyl imines have been found in the literature.[5,10–19] Most of them involve the condensation of aldehydes with sulfonamides in the presence of strong Lewis acids.[10,12,17,18] In many cases such strongly acidic conditions are not compatible with other functionality present in a given substrate, and some methods need a two-step procedure or they are expensive methods and generate toxic byproducts.

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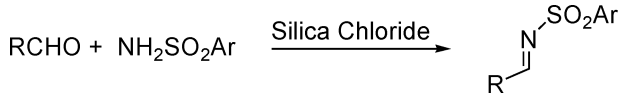
However, some methods require prior preparation such as oxime, sulfinyl imine, and/or aziridine.[11,15,19] Therefore, it seems highly desirable to find simple, efficient, economical, and green chemistry protocols for synthesis of a wide range of *N*-sulfonyl imines without the requirement of toxic or otherwise hazardous reagents. Solvent-free organic reactions have been applied as useful protocol in organic synthesis.[20] A solid-state technique under thermal conditions often leads to shorter reaction times, increased yields, and easier work-up; it matches with green chemistry protocols; and it may enhance the regio- and stereoselectivity of reactions.[20]

Because of the convenience of solid reagents, such as ease of handling, low costs, and ease of work-up of the reaction products, the use of heterogeneous reagents from functional group transformation is of value to synthetic organic chemists.[21] Nevertheless, a literature survey shows that little attention has been paid to the use of heterogeneous reagents for preparation of *N*-sulfonyl imines.

RESULTS AND DISCUSSION

In extension of our previous studies on the application of silica chloride and developing solvent-free conditions in organic synthesis,[22,23] we describe here an efficient and operationally simple method for synthesis of *N*-sulfonyl aldimines in one step without any solvent. In this method, various *N*-sulfonyl imines were obtained from the reaction of aryl aldehyde and sulfonamide (Scheme 1). Silica chloride was obtained from the reaction of silica gel (item 7731 for TLC from Merck, Darmstadt, FRG) and thionyl chloride according to a literature procedure.[24]

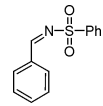
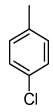
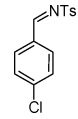
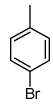
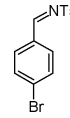
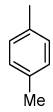
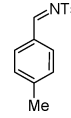
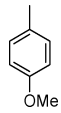
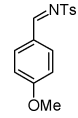
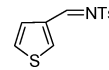
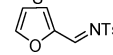
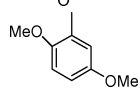
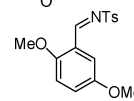
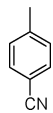
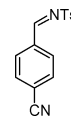
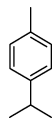
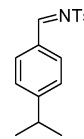


SCHEME 1

We found heating (110–120°C) an approximately equimolar mixture of an aldehyde and sulfonamide in the presence of silica chloride between 3–5 h resulted in the formation of sulfonyl aldimines in good to excellent yield. The results of the reaction of aryl aldehydes with sulfonamides in the presence of silica chloride are summarized in Table I.

Aromatic aldehydes containing both electron-withdrawing and -donating substituents afforded the corresponding sulfonyl imines in high yields (Table I). The lower reactivity of the arylaldehydes containing electron-withdrawing or hindered substituents (Table I, entries 9

TABLE I Conversion of Aldehydes into *N*-Sulfonyl Imines in the Presence of Silica Chloride at 120°C

Entry	R	Ar	Product	Time (h)	Yield (%)[a]
1		*p*-tolyl		3	75
2		phenyl		3.5	70
3		*p*-tolyl		3	76
4		*p*-tolyl		3	78
5		*p*-tolyl		3	71
6		*p*-tolyl		3.5	68
7		*p*-tolyl		3	73
8		*p*-tolyl		3	70
9		*p*-tolyl		4	56
10		*p*-tolyl		3.5	65
11		*p*-tolyl		3	61
12		*p*-tolyl		3	69

[a]Isolated Yield.

and 11) generally necessitated longer reaction times. These indicate that electron-donating groups increased the reaction speed as well as reaction yields. Mention must be made here that the conversion rate of *p*-toluenesulfonamide with aldehydes was a little higher than benzene sulfonamide (for comparison, see Table I, entries 1 and 2).

The *N*-sulfonyl imines were readily separated from the byproducts of the reaction, allowing their isolation in a high state of purity and in good yield.

The crude products could be purified by recrystallization (see Table I and Experimental section).

This chemistry was applied unsuccessfully toward the synthesis of enolizable *N*-sulfonyl aldimines, and unfortunately this method shares a common limitation with several other methods of *N*-tosylaldimine synthesis[10,12,17,18] in that it does not appear to be applicable to the synthesis of *N*-tosyl aldimines derived from aldol condensations being obtained instead. Methods of overcoming this limitation are currently under investigation.

This method possesses advantages of facile work-up, it is nonpolluting and of low cost, and it has easy availability of the catalyst and good yield.

EXPERIMENTAL

Melting points determined in open capillary tubes in a Buchi-535 circulating oil melting point apparatus without further corrections. Infrared spectra were obtained using a Perkin Elmer 781 and a Shimadzu FT-IR 8300 spectrophotometer, and NMR spectra were recorded on a Bruker Avance DPX-250 (^{1}H NMR 250 MHz and ^{13}C NMR 62.9 MHz) spectrometer in pure deuterated solvents with tetramethyl silane as an internal standard. Elemental analyses were performed at the National Oil Co. of Iran, Tehran Research Center, Iran.

Typical Procedure

General Procedure for Preparation of Silica Chloride (SiO_2-Cl)[24]

To an oven-dried (120°C, vaccum) silica gel (10 g) in a round bottomed flask (250 mL) equipped with a condenser and a drying tube was added thionyl chloride (40 mL), and it was refluxed for 48 h. The unreacted thionyl chloride was distilled off. The resulting white-grayish powder was flame dried and stored in a tightly capped bottle. This silica chloride can be used for months without loosing its activity.

General Procedure for Synthesis of N-Sulfonyl Imines

In a 100-mL single-necked flask equipped with magnetic stirring bar and short-path distilling head were placed equivalent amounts (typically 5 mmol) of the appropriate sulfonamide and aldehyde. The reaction mixture was heated at about 120°C in an oil bath, and after 10 min the appropriate amount of silica chloride (3 g) was added to it, stirring was continued for about 3 h, at which time the reaction was allowed to cool to r.t. The solid mixture and the solid materials were removed through a Celite pad and washed with acetone (50 mL). The solvent was evaporated with a rotary evaporator, and the solid product was dissolved in warm ethylacetate (10 mL), treated with n-hexane (35–50 mL), and allowed to stand at r.t. for 5–6 h. During this time crystals formed, which were collected by filtration, washed with n-hexane, and dried.

Selected Spectral Data for Sulfonyl Imines

N-Benzylidene-4-methyl-benzenesulfonamide (1)[25]

White solid; m.p. 108°C (lit.,[25] 109°C); ^{1}H NMR ($CDCl_3$, 250 MHz): 2.33 (s, 3H), 7.25 (d, J = 8.2 Hz, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.51(t, J = 6.2 Hz, 1H), 7.80–7.84 (m, 4H), 8.99 (S, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 21.97, 128.42, 129.89, 130.26, 131.61, 135.39, 140.21, 145.07, 170.69. IR (KBr): 1650, 1570, 1380, 1320, 1160 (cm^{-1}).

N-Benzylidenebenzenesulfonamide (2)[25]

m.p. 77–80°C ^{1}H NMR ($CDCl_3$, 250 MHz): 7.61 (m, 6H), 8.02 (m, 4H), 9.05 (s, 1H).

N-(4-chlorobenzylidene)-4-methyl-benzenesulfonamide (3)[10]

White needles; m.p. 172–173°C (lit.,[10] 172–173°C); ^{1}H NMR ($CDCl_3$, 250 MHz): 2.46 (s, 3H), 7.15 (d, J = 9.1 Hz, 2H), 7.38 (d, J = 9.0 Hz, 2H), 7.86 (dd, J = 8.9 Hz, 4H), 9.01 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 22.04, 128.53, 129.98, 130.25, 131.24, 132.73, 135.32, 141.80, 145.17, 169.02.

N-(4-bromobenzylidene)-4-methyl-benzenesulfonamide (4)[17]

White powder; m.p. 181–183°C; ^{1}H NMR ($CDCl_3$, 250 MHz): 2.50 (s, 3H), 7.26–7.85 (m, 8H), 9.04 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 22.69, 125.02, 128.60, 129.48, 131.18, 131.26, 133.87, 167.69.

N-(4-methyl-benzylidene)-4-methyl-benzenesulfonamide (5)[25]

White powder; m.p. 112–114°C; ^{1}H NMR ($CDCl_3$, 250 MHz): 2.42 (s, 6H), 7.26 (d, J = 7.5 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 7.5 Hz,

2H), 7.90 (d, J = 7.5 Hz, 2H), 8.96 (S, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 22.01, 126.78, 128.38, 129.98, 130.17, 130.33, 131.80, 135.74, 144.87, 170.42.

N-(4-methoxy-benzylidene)-4-methyl-benzenesulfonamide (6)[25]

White powder; m.p. 126–128°C; ^{1}H NMR ($CDCl_3$, 250 MHz): 2.36 (s, 3H), 3.78 (s, 3H), 6.93 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 7.81 (d, J = 7.5 Hz, 2H), 7.85 (d, J = 7.6 Hz, 2H), 8.90 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 22.44, 56.58, 115.51, 125.95, 128.69, 130.40, 134.55, 136.59, 145.17, 166.20, 170.15.

4-methyl-N– thiophen-3-ylmethylene-benzenesulfonamide (7)

White needles; m.p. 127–129°C; ^{1}H NMR ($CDCl_3$, 250 MHz): 2.43 (s, 3H), 7.29–8.15 (m, 7H), 9.01 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 22.02, 126.85, 128.20, 128.39, 130.19, 135.72, 137.42, 138.63, 144.91, 163.55. Anal. calcd for $C_{12}H_{11}NO_2S_2$: C, 54.32; H, 4.18, N, 5.28; found: C, 54.43; H, 4.09, N, 5.46.

N-Furan-2-ylmethylene-4-methyl- benzenesulfonamide (8)[25]

Brown powder; m.p. 100–101°C; ^{1}H NMR ($CDCl_3$, 250 MHz): 2.32 (s, 1H), 6.76-7.75 (m, 7H), 8.83 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 22.53, 112.57, 115.42, 126.65, 128.63, 130.98, 148.36, 151.59, 154.39, 157.07.

N-(2, 5-dimethoxy-benzylidene)-4-methyl-benzenesulfonamide (9)

M.p. 124–126°C ^{1}H NMR (DMSO-d^6, 250 MHz): 2.39 (s, 3H), 3.69 (s,3H), 3.93 (s, 3H), 7.14–7.82 (m, 7H), 9.30 (s, 1H). ^{13}C NMR (DMSO-d^6, 62.9 MHz): 21.00, 55.53, 56.24, 110.16, 114.28, 119.78, 125.17, 127.58, 130.01, 134.88, 144.47, 153.08, 156.44, 165.54. Anal. calcd. for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.37, N, 4.39; found: C, 60.03; H, 5.49; N, 4.46.

N-(2-chloro-benzylidene)-4-methyl-benzenesulfonamide (10)[10]

White needles; m.p. 126–128°C (lit.[10]; 128–129°C); ^{1}H NMR ($CDCl_3$, 250 MHz): 2.43 (s, 3H), 7.29–7.90 (m, 8H), 9.13 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 22.64, 126.90, 128.54, 129.10, 129.51, 131.17, 131.86, 134.48, 137.06, 168.12.

N-(4-Cyanobenzylidene)-4-methyl-benzenesulfonamide (11)[19]

White needles; m.p. 172–173°C; ^{1}H NMR ($CDCl_3$, 250 MHz): 2.35 (s, 3H), 7.28 (d, J = 10.2 Hz, 2H), 7.66–7.96 (m, 6H) 8.97 (s, 1H). ^{13}C

NMR ($CDCl_3$, 62.9 MHz): 21.68, 117.70, 126.32, 128.29, 129.92, 130.01, 131.34, 132.76, 135.89, 145.30, 168.16.

N-(4-Isoperopyl-benzylidene)-4-methyl-benzenesulfonamide (12)

^{1}H NMR ($CDCl_3$, 250 MHz): 1.20 (d, j = 7 Hz, 6H), 2.33 (s, 3H), 2.93 (m, 1H), 7.18–7.80 (m, 8H), 8.91 (s, 1H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 22.43, 22.45, 32.91, 126.08, 126.70, 128.59, 129.32, 130.31, 130.95, 132.91, 156.73, 171.43. Anal. calcd. for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65; found: C, 67.81; H, 6.26; N, 4.52.

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