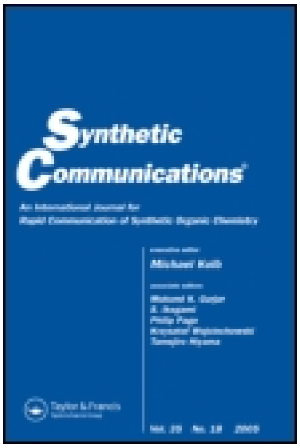

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Efficient and Convenient Procedure for Preparation of *N*-Sulfonylimines Catalyzed by Montmorillonite K-10

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Abstract: A general and practical chemical route to the synthesis of *N*-sulfonylimines using montmorillonite K-10 as the catalyst is described. This method provides several advantages such as operational simplicity, short reaction time, using of inexpensive materials, noncorrosivity, lack of pollution, and high yields.

Keywords: Aldehydes, montmorillonite K-10, *N*-sulfonylimines, sulfonamides

INTRODUCTION

During the past several years, *N*-sulfonylimines have attracted strong interest because of their broad uses: they can be used as powerful synthetic intermediates[1,2] and they can also be used in numerous reactions such as inverse electron-demand Diels–Alder reactions,[3–5] addition reactions as carbonyl equivalents,[6] and in ene reactions.[7] Various methods are available for the construction of *N*-sulfonylimines involving the rearrangement of oxime *O*-sulfinates,[8] Lewis acid- or solid acid-catalyzed reactions of sulfonamides with aldehydes or acetals,[9–13] utilization of tellurium metal and chloramines T,[14] addition of *N*-sulfinyl sulfonamides to aldehydes in the presence of $BF_3 \cdot Et_2O$,[15] use of methyl orthosilicate,[16] halogen-mediated conversion

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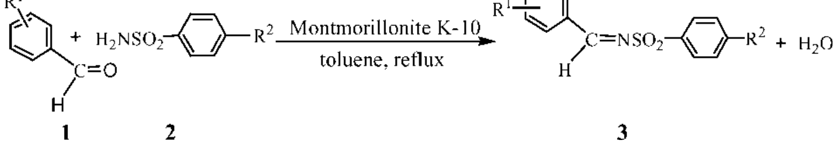
of *N*-(trimethylsilyl)imines in the presence of corresponding sulfonyl chloride,[17] and catalysis by HCOOH and $NaHCO_3$.[18] Each of these methods has its own merit, but some of these methods are plagued by the limitation of long reaction times, expensive and hazardous reagents, cumbersome experimental 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.

Montmorillonite K-10 is a type of acidic stratified silicate mineral with a three-layer structure with an ideal chemical formula of $(Al_{2\text{-}y}Mg_y)Si_4O_{10}(OH)_2 \cdot nH_2O$. In montmorillonite clay, one octahedral aluminate layer is sandwiched between two octahedral silicate layers. The interlayer cations are exchangeable, which allows alteration of the acidic nature of the material by a simple ion-exchange procedure. Both Brönsted and Lewis acidic catalytic sites are available, and its natural occurrence as well as its ion-exchange properties make it a useful catalyst. Up to now, montmorillonite and in particular montmorillonite K-10 have been used as efficient acidic catalysts for many organic transformations, such as substitution[19] and acetalization.[20] This prompted us to initiate a systematic investigation on montmorillonite K-10–catalyzed synthesis of *N*-sulfonylimines (Scheme 1), and herein we disclose our results.

Montmorillonite K-10 was purchased from Aldrich. The catalyst has surface area of $220–270\,m^2g^{-1}$ and a bulk density of $300–370\,g\,l^{-1}$. The montmorillonite K-10 was activated at 120°C over night prior to use.

In a typical general experimental procedure, a solution of aldehydes and sulfonamide was heated in refluxing toluene in the presence of a catalytic amount of montmorillonite K-10 for a certain period of time required to complete the reaction, and the corresponding *N*-sulfonylimines were obtained in good to excellent yields. The results are summarized in Table 1.

To study the generality of this process, several examples illustrating this method for the synthesis of those *N*-sulfonylimines were studied. As shown in Table 1, the effect of electrons and the nature of aldehydes on the aromatic ring did not show strongly obvious effects in terms of yields under this reaction condition. The reaction proceeded smoothly in refluxing toluene to give the corresponding products **3** in high yields. Mention must be made here that the conversion rate of *p*-toluenesulfonamide with aldehydes was a little higher than benzenesulfonamide. For example, the reaction yield of



Scheme 1.

Table 1. Synthesis of *N*-sulfonylimines catalyzed by montmorillonite

Entry	R^1	R^2	Product	Time (min)	Yield (%)[a]	Mp (°C) Found	Mp (°C) Reported
1	H	4-CH_3	**3a**	50	93	105–106	110[17]
2	H	H	**3b**	45	88	135	139–141[10]
3	4-CH_3	4-CH_3	**3c**	65	91	114–116	116–118[13]
4	4-CH_3	H	**3d**	50	86	133–135	136[18]
5	4-CH_3O	4-CH_3	**3e**	70	92	127–128	128–129[14]
6	4-CH_3O	H	**3f**	75	86	140–142	145[18]
7	2-HO	4-CH_3	**3g**	75	86	120	125[18]
8	2-HO	H	**3h**	85	62	117–119	119–120[13]
9	3,4-(OCH_2O)	4-CH_3	**3i**	50	90	117–118	114–116[14]
10	4-Cl	4-CH_3	**3j**	50	85	172–173	172–173[13]
11	4-Cl	H	**3k**	60	83	190–192	127–130[10]
12	3-Cl	4-CH_3	**3l**	50	83	98	
13	3-Cl	H	**3m**	60	90	103	102–104[13]
14	2,4-Cl_2	4-CH_3	**3n**	55	87	110	112–113[13]
15	2,4-Cl_2	H	**3o**	50	87	113–115	
16	2-Cl	4-CH_3	**3p**	50	94	129–130	128–129[10]
17	4-Br	4-CH_3	**3q**	45	96	180–182	182–185[14]
18	3-NO_2	4-CH_3	**3r**	80	92	143–145	143–145[10]
19	3-NO_2	H	**3s**	90	91	134	

[a] Yield of pure isolated products.

4-chlorobenzaldehyde (1.00 mmol) with $C_6H_5SO_2NH_2$ (1.00 mmol) was 83% yield in refluxing toluene for 60 min, but it increased to 85% from 4-chlorobenzaldehyde (1.00 mmol) with $4\text{-}CH_3C_6H_4SO_2NH_2$ (1.00 mmol) for refluxing for 50 min.

We examined several experiments and found that the effect of the catalyst and the molar ratio showed crucial effects on these conversions. As a model reaction, the reaction of 2-chlorobenzaldehyde with *p*-toluenesulfonamide catalyzed by montmorillonite K-10 in refluxing toluene was investigated. The results are summarized in Table 2.

As shown in Table 2, the catalyst plays a crucial role in the success of the reaction in terms of the rate and the yields. 2-Chlorobenzaldehyde reacted with *p*-toluenesulfonamide in the presence of 50 mg of montmorillonite K-10 to give the product **3p** in modest yield (87%) in refluxing toluene after 50 min of reaction time. Increasing the catalyst to 70, 80, and 90 mg results in accelerating the reaction yields to 89%, 92%, and 94% respectively. Higher amounts of the catalyst did not improve the results to a greater extent. Thus, 90 mg of montmorillonite K-10 was chosen as a quantitative catalyst for these reactions. In addition, the catalyst was easily regenerated by washing with toluene followed by drying at 120°C for 2 h, and it could be reused five times without significant loss of activity.

In conclusion, we have provided a facile and efficient method for the synthesis of *N*-sulfonylimine catalyzed by montmorillonite K-10. This method possesses these advantages of operational simplicity, short reaction time, use of inexpensive materials, noncorrosivity, lack of pollution, and high yields.

EXPERIMENTAL

Melting points are uncorrected. The new compounds prepared were characterized by ^1H NMR, IR, and element analyses and are described in the

Table 2. Effect of catalyst on the reaction of 2-chlorobenzaldehyde with *p*-toluenesulfonamide

Montmorillonite	Yield (%)
50	87
70	89
80	92
90	94
100	91
120	85
150	83

experimental section. Liquid aldehydes were purified by distillation before use. IR spectra were recorded on a Bio-rad FIS-40 spectrometer (KBr). ^{1}H NMR spectra were measured at 400 MHz on an Avance-400 spectrometer using TMS as internal standard and $CDCl_3$ as solvent.

General Procedure for the Preparation of *N*-Sulfonylimines

A mixture of aldehyde (1.00 mmol), sulfonamide (1.00 mmol), montmorillonite K-10 (90 mg), and toluene (5 ml) was stirred under refluxing for 45–90 min (Table 1) in a Dean-Stark apparatus. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled, and montmorillonite K-10 was filtered off with toluene washing. The solvent was evaporated under reduced pressure to provide the crude product, and the crude product was purified by recrystallization with hexane–ethyl acetate mixture or by flash chromatography on silica gel (Et_2O–hexane as eluent) to give the pure product.

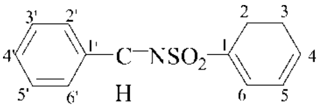
The number of carbon atom in aryl is shown in Scheme 2.

Data

3l: IR (KBr), ν (cm^{-1}) 3090, 1680, 1605, 1566, 1553, 1497, 1333, 1166, 805, 746, 694. ^{1}H NMR ($CDCl_3$) δ (ppm) 9.00 (s, 1H, HC=N), 7.96 (s, 1H, 2′-ArH), 7.90 (d, 2H, $J = 8.4$ Hz, 2,6-SO_2ArH), 7.79 (d, 1H, $J = 7.6$ Hz, 6′-ArH), 7.58 (d, 1H, $J = 8.0$ Hz, 4′-ArH), 7.46 (t, H, $J = 8.0$ Hz, 5′-ArH), 7.37 (d, 2H, $J = 8.0$ Hz, 3,5-SO_2ArH), 2.47 (s, 3H, CH_3). Anal. calcd. for $C_{14}H_{12}NO_2SCl$: C, 57.24; H, 4.12; N, 4.77. Found: C, 57.11; H, 4.05; N, 4.92.

3o: IR (KBr), ν (cm^{-1}) 3108, 2890, 1691, 1593, 1546, 1485, 1315, 1160, 820, 754, 694. ^{1}H NMR ($CDCl_3$) δ (ppm) 9.47 (s, 1H, HC=N), 8.12 (d, 1H, $J = 8.8$ Hz, 6′-ArH), 8.03 (d, 2H, $J = 8.0$ Hz, 2,6-SO_2ArH), 7.67 (d, 1H, $J = 7.2$ Hz 5′-ArH), 7.58 (t, 2H, $J = 8.4$ Hz, 3,5-SO_2ArH), 7.53 (s, 1H, 3′-ArH), 7.34 (d, 1H, $J = 8.8$ Hz, 4-SO_2ArH). Anal. calcd. for $C_{13}H_9NO_2SCl_2$: C, 49.70; H, 2.89; N, 4.46. Found: C, 49.89; H, 2.78; N, 4.35.

3s: IR (KBr),ν (cm^{-1}) 3050, 1698, 1601, 1541, 1496, 1334, 1163, 806, 750, 696. ^{1}H NMR ($CDCl_3$) δ (ppm) 9.16 (s, 1H, HC=N), 8.80 (s, 1H, 2′-ArH), 8.47 (d, 1H, $J = 8.0$ Hz, 6′-ArH), 8.27 (d, 1H, $J = 7.6$ Hz, 4′-ArH), 8.05



Scheme 2.

(d, 2H, $J = 7.6\,\mathrm{Hz}$, 2,6-SO_2ArH), 7.69 (m, 2H, 4-SO_2ArH and 5′-ArH), 7.60 (t, 2H, $J = 8.0\,\mathrm{Hz}$, 3,5-SO_2ArH). Anal. calcd. for $C_{13}H_{10}N_2O_4S$: C, 53.79; H, 3.47; N, 9.65. Found: C, 53.65; H, 3.53; N, 9.53.

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