Synthesis of N-sulfonylimines using $CeCl_3$ under neutral conditions

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An efficient and environmentally benign method for the synthesis of N-sulfonylimines is reported. Condensation of aryl sulfonamides with different aromatic aldehydes and ketones gave N-sulfonylimines in good to excellent yields in the presence of 10 mol% $CeCl_3$ as catalyst. This method can be used with both aldehydes and ketones.

Keywords: N-sulfonylimines, aldehydes, cerium(III) chloride, condensation

N-Sulfonylimines are important precursors for the preparation of synthetic intermediates. because they are one of the electron deficient imines that are stable enough to be isolated but sufficiently reactive to be useful intermediates.[1] They have been used in numerous reactions such as Diels–Alder,[2] nucleophilic addition,[3] ene,[4] and radical reactions.[5] In addition, they are important precursors for the preparation of reactive aziridines[6,7] imidazolines,[8] and N-sulfonyloxaziridines.[9]

Recently, attention has been paid to the development of efficient methods for the preparation of N-sulfonylimines. A number of methods for the synthesis of N-sulfonylimines have been reported. These have involved catalysis with Lewis acid,[10] titanium tetrachloride,[11] tellurium,[12] ruthenium,[13] Montmorillonite K-10,[14] oxidation with m-CPBA,[15] catalysis with zeolite,[16] DBU,[17] Pd,[18] Tf_2O,[19] and rearrangements of sulfinate esters of oximes,[20] imine-transfer reaction,[21,22] and microwave facilitated acid catalysis.[23] However, these methods suffer from some limitations, such as a poor scope, unsatisfactory yields, expensive reagents and difficult scale-up. The requirements for environmentally benign and efficient chemical processes in recent years have led to the search for clean, high-yielding, and economical reduction methods.

Cerium(III) chloride has become an attractive candidate for use as a Lewis acid in organic chemistry since it is inexpensive, environmentally friendly and readily available, and involves simple reaction conditions.[24] We now describe a very simple, general and highly efficient synthesis method for the preparation of N-sulfonylimines in the presence of $CeCl_3$ in relatively high yields.

Results and discussion

We initially attempted to synthesise N-sulfonylimine using a $CeCl_3$ catalysed procedure as a new and efficient method for the preparation of sulfonylimines. The reaction of the benzaldehyde with 4-toluenesulfonamide was chosen as a model. Our catalytic system consisted of commercially available metallic salts. Among the different salt precursors tested, the best result was achieved when the reaction was performed in presence of 10 mol% $CeCl_3$. GC showed that the yield obtained was 93%. Interestingly, the conversion was 81% when $CeCl_3 \cdot 7H_2O$ was used, which shows the Lewis acid ability of $CeCl_3$ was far better. Control experiments in the absence of $CeCl_3$ showed that the reaction of benzaldehyde and 4-toluenesulfonamide did not occur. In general, the optimised conditions for the synthesis of N-tosylaldimines were 1 equiv. of aldehyde and 1 equiv. of N-tosylamide in the presence of 10 mol% of $CeCl_3$ in ethyl acetate at 50 °C for 6h.

A variety of aldehydes and N-sulfonylamides were tested under the optimised conditions using 10 mol% $CeCl_3$ as catalyst (Table 1). In general, all the reactions were successful. According to Table 1, aromatic aldehydes with electron-donating groups such as the methyl group were converted to the corresponding N-tosylaldimines in good yields (Table1, entry 4). Substrates with electron-withdrawing groups such as nitro, chloro and bromo had a reduced yield (Table 1, entries 1, 2, 3 and 6). 3-Phenyl-propenal also gave the desired product in high yield (Table 1, entry 7). When 2-furaldehyde was used, low yield was obtained in 65% (Table 1, entry 8).

We have also studied the reaction of sulfonamide with ketones which were converted to the corresponding N-sulfonylimines. In these reactions, the overall yields were not as high as those obtained from the aldehydes (Table 1, entries 9 and 10).

We observed that the reaction of 4-toluenesulfonamide with aldehydes was better than the other sulfonamides, due to the difference of nucleophilicity of the amino groups (Table 1, entries 5, 11 and 12).

It turned out that $CeCl_3$ catalysed condensation could be adapted for use with various aromatic aldehydes.

In conclusion, we have developed a new procedure for the synthesis of N-sulfonylimines of aromatic aldehydes in the presence of catalytic amounts of 10 mol% of $CeCl_3$ which has less environmental impact and is an easier method. The process is suitable for synthesis of a range of N-sulfonylimines and is amenable to larger scale preparations.

Experimental

All chemicals (AR grade) were obtained from commercial resources and used without further purification. Gas chromatography (GC) analysis was performed on an Agilent GC-6820 chromatograph equipped with a 30m×0.32mm×0.5μm HP-Innowax capillary column and a flame ionisation detector. GC-MS spectra were recorded on Thermo Trace DSQ GC-MS spectrometer using TRB-5MS (30m × 0.25mm × 0.25μm) column. Progress of the reactions was followed by TLC using silica-gel polygrams SIL G/UV 254 plates. Column chromatography was performed using Silicycle (0.2–0.3mm) silica gel. ^1H NMR spectra were obtained using a Bruker DRX 500 (500 MHz) spectrometer in $CDCl_3$ with TMS as the internal standard. All products are known. Products were also identified by melting point which were determined using XT-4 apparatus and are not corrected.

General procedure: 4-Toluenesulfonamide (1 mmol) and benzaldehyde (1 mmol) in ethyl acetate (5 mL) and $CeCl_3$ (0.0246 g, 0.1 mmol) was then added and the mixture was stirred at 50 °C for 6h. The aqueous solution was extracted with ethyl acetate (3×10 mL) and the product was purified on a small silica gel column with EtOAc: petroleum ether (1:10) as eluent.

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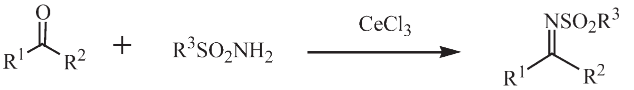
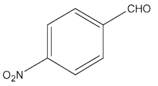
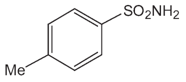
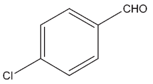
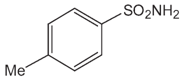
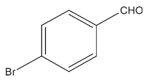
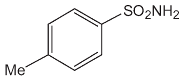
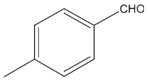
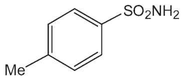
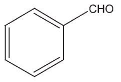
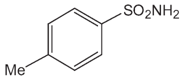
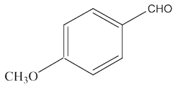
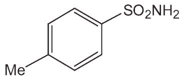
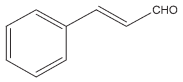
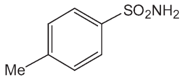
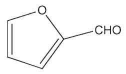
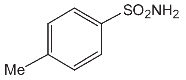
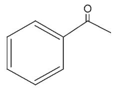
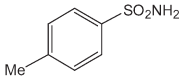
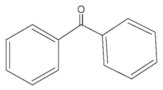
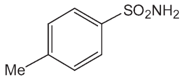
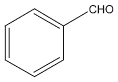
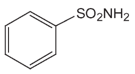
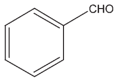
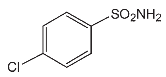


Table 1 Preparation of N-sulfonylimines by using $CeCl_3$[a]

Entry	Aldehyde(R^1, R^2)	Sulfonylamide(R^3)	Yield/%[b]	M.p./°C	Lit. value [Ref.]/°C
1			85	204–205	205[13]
2			86	176–177	175[13]
3			81	180–182	180–182[14]
4			91	113–114	114–116[14]
5			90	113–114	114–115[15]
6			70	130–131	128–129[15]
7			90	117–118	117–118[16]
8			65	99–101	100–101[16]
9			50[c]	88–90	89–90[17]
10			40[c]	99–101	100–101[18]
11			70	82–83	82–83[19]
12			40	104–105	104–106[25]

[a] Reaction conditions: N-tosylamide (1 mmol); aldehydes (1 mmol); $CeCl_3$ (10 mol%); solvent (5 mL); at 50 °C; 6 h.
[b] Isolated yields.
[c] Reflux for 10h.

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