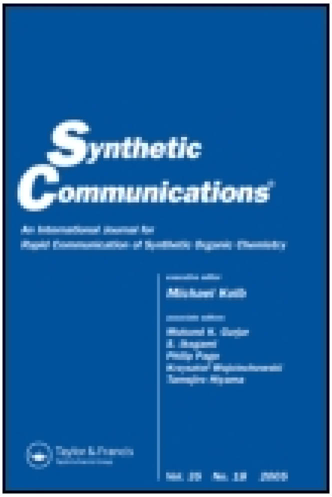

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Trimethylsilyl bis(Fluorosulfonyl)imide : An Efficient Catalyst for the Addition of Trimethylsilyl Cyanide to Carbonyl Compounds

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TRIMETHYLSILYL BIS(FLUOROSULFONYL)IMIDE : AN EFFICIENT CATALYST FOR THE ADDITION OF TRIMETHYLSILYL CYANIDE TO CARBONYL COMPOUNDS

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Abstract: In the presence of 1 mol% of trimethylsilyl bis(fluorosulfonyl)imide, trimethylsilyl cyanide adds efficiently to carbonyl compounds. The catalyst has been found to be more active than trimethylsilyl triflate for the above reaction.

Silicon based reagents have found widespread applications in organic synthesis.[1] Trimethylsilyl trifluoromethanesulfonate (TMSOTf), a derivative of oxo acid, trifluoromethanesulfonic acid has been widely used as a catalyst in many organic transformations.[2] There had been no report in the literature where a nitrogen acid derived reagent[3] was used as a catalyst in organic transformations,

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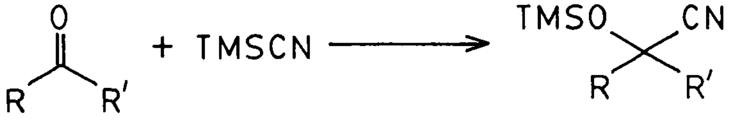
until we reported trimethylsilyl bis(fluorosulfonyl)imide [TMSN($SO_2F)_2$] **1** as an efficient catalyst for the reaction of acetals with silyl nucleophiles.[4] It was also shown to be a more efficient catalyst than TMSOTf for such type of reactions. In order to evaluate further the utility of **1**, We studied the reaction of carbonyl compounds with trimethylsilyl cyanide (TMSCN) using **1** as catalyst. Treatment of 0.5 M solution of cyclohexanone in dry CH_2Cl_2 with slight excess of TMSCN at - 78°C under nitrogen atmosphere in the presence of 1 mol% of 1 gave 1-cyano-1-trimethylsilyloxy cyclohexane in 94% yield (Table 1, entry 1). The reaction was complete in 5 min but it was continued for 30 min before quenching with pyridine. Similarly reaction of TMSCN with some other representative carbonyl compounds gave the desired product in high yields (See Table 1). A small amount of desilylated cyanohydrin was obtained in all the reactions.

To determine the catalytic efficiency of TMSN($SO_2F)_2$ as compared to TMSOTf[2b] for this reaction, a comparative study was undertaken using some slower reacting carbonyl compounds and the reactions were quenched before completion. The results are summarized in the Table II. These results clearly demonstrate that TMS N($SO_2F)_2$ is more active than TMSOTf in this case also, specially for a more demanding case of benzophenone.

Experimental Section

General Procedure : To a solution of carbonyl compound (1.0 mmol) and TMSCN (1.1 mmol) in CH_2Cl_2 (2ml) at an appropriate temperature (See Table

Table I: Reaction of TMSCN with various carbonyl compounds in the presence of 1 mol% of $TMSN(SO_2F)_2$[a]



Entry	Substrates	Temp (°C)	Time (Min)	Yield[b] (%)
1.	Cyclohexanone	-78	30	94
2.	Acetophenone	-78	45	87
3.	α-Tetralone	-78	45	98
4.	2-Cyclohexenone	-78	45	88
5.	Methyl Propyl ketone	-78	30	86
6.	Benzaldehyde	-78	15	90
7.	Mesitaldehyde	0	15	90
8.	*p*-Methoxy benzaldehyde	-78	20	84
9.	Cyclohexane carboxyaldehyde	-78	20	94
10.	Hydrocinnamaldehyde	-78	30	89
11.	Cinnamaldehyde	0	30	88

[a] Reactions were carried out in 2ml of CH_2Cl_2/mmol of carbonyl compounds under N_2 atm.

[b] Isolated yields.

Table II: Comparative study of TMSCN addition to carbonyl compounds in the presence of TMS $N(SO_2F)_2$ or TMSOTf as catalyst at 0°C

Entry	Substrates	Catalyst	Time	Ratio of Product:SM[a]
1.	Cinnamaldehyde	$TMSN(SO_2F)_2$[b]	10 min	4.5:1.0
2.	Cinnamaldehyde	TMSOTf[b]	10 min	1.5:1.0
3.	Benzophenone	$TMSN(SO_2F)_2$[c]	6 h 2	.6:1.0
4.	Benzophenone	TMSOTf[c]	6 h	1.0:7.3

[a] SM = Starting material.

[b] 1 mol% of catalyst was used.

[c] 5 mol% of catalyst was used.

I) under nitrogen atmosphere 1 mol% of $TMSN(SO_2F)_2$ was added. The reaction mixture was stirred at the same temperature for 1h and then it was quenched by adding 0.1 ml of pyridine. It was brought to the room temperature and water was added. After usual aqueous work up the product was isolated which was purified by flash chromatography.

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