Bis(fluorosulfuryl)imide: a Brönsted acid catalyst for the addition of allyltrimethylsilane to carbonyl compounds

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The Brönsted acid $HN(SO_2F)_2$ catalyses the addition of allyltrimethylsilane to carbonyl compounds to give the corresponding homoallylic alcohols in high yields.

The addition of allylsilanes to aldehydes and ketones is a mild method for the preparation of homoallylic alcohols.[1] This reaction is usually accomplished (except for some reactive substrates[2]) in the presence of either a stoichiometric amount of Lewis acid[3] or a catalytic amount of fluoride ion.[4] Although the later method is catalytic in nature it is not regioselective with respect to allylic inversion or retention.[4] Trimethylsilyl trifluoromethanesulfonate (TMSOTf) is a weak catalyst† but when it is mixed with $B(OTf)_3$,‡ the resultant $TMS^+B(OTf)_4^-$, is a highly efficient catalyst for this transformation[5] and can also be prepared by protodesilylation of allyltrimethylsilane with the super acid $TfOH_2^+$ $B(OTf)_4^-$.[5b] As far as we are aware Brönsted acids have not been used as a catalyst for this type of transformation because allylsilanes decompose in the presence of strong protic acids.[8] Here we report our initial results of a Brönsted acid catalysed addition of allyltrimethylsilane to carbonyl compounds using a nitrogen acid, bis(fluorosulfuryl)imide [$HN(SO_2F)_2$].

Hydrocinnamaldehyde (1.0 equiv.) was treated with allyltrimethylsilane (1.2 equiv.) in the presence of 5 mol% of $HN(SO_2F)_2$ at 0 °C and gave the corresponding pure homoallylic alcohol in 89% yield. The reaction was complete in under 5 min. as indicated by TLC. TLC showed the presence of trimethylsilyl ether **1** and a small amount of alcohol **2a**. After aqueous workup alcohol **2a** was obtained as the sole product. Presumably desilylation occurred during the workup.

Since protodesilylation by $HN(SO_2F)_2$ of allyltrimethylsilane may have occurred to give $TMSN(SO_2F)_2$, to determine the actual catalyst involved the following experiments were carried out. (*a*) The reaction of hydrocinnamaldehyde with allyltrimethylsilane in the presence of $TMSN(SO_2F)_2$[10] (5 mol%) did not give the desired product. (*b*) The same reaction when conducted in the presence of $HN(SO_2F)_2$ (5 mol%) and 2,6-di-*tert*-butyl-4-methylpyridine (15 mol%), a known proton scavanger,[7] also did not give the desired product. (*c*) The ^{19}F NMR spectra of $HN(SO_2F)_2$ and $TMSN(SO_2F)_2$ have distinct peaks at δ 58.5 and 43.0 respectively.[9,10] When a mixture of $HN(SO_2F)_2$ and allyltrimethylsilane (1 : 5) in CH_2Cl_2 at room temperature was monitored by ^{19}F NMR for 12 h, no peak corresponding to $TMSN(SO_2F)_2$ was observed. These experiments confirm that $HN(SO_2F)_2$ is the catalyst and it does not cause protodesilylation of allylsilane to give $TMSN(SO_2F)_2$. This may be due to its highly non-nucleophilic counter ion, $N(SO_2F)_2^-$, which can not remove trimethylsilyl group after the reaction of a proton with allyltrimethylsilane.

After establishing that $HN(SO_2F)_2$ is the actual catalyst involved, reactions using other aldehydes and ketones were carried out. The results are summarised in Table 1. Aldehydes underwent allylation at 0 °C to give products in high yield except for cinnamaldehyde which gave product in 50% yield with 30% recovered starting material. Some nonpolar byproducts were formed which appeared to be derived from the allylated product. Ketones underwent allylation at lower temperature (−40 °C). Acetophenone and cyclopentanone did not undergo reaction and were recovered. One can take advantage of this fact and react aldehydes in the presence of aromatic ketones and cyclopentanone. When hydrocinnamaldehyde was treated with allyltrimethylsilane in the presence of α-tetralone or cyclopentanone under standard conditions, the product derived from only hydrocinnamaldehyde was obtained and unreacted ketones were recovered.

In conclusion, this work demonstrates Brönsted acid catalysed addition of allyltrimethylsilane to carbonyl compounds to give homoallylic alcohols.§ The Brönsted acid $HN(SO_2F)_2$ used is a highly efficient catalyst and only 5 mol% is sufficient for complete conversion.

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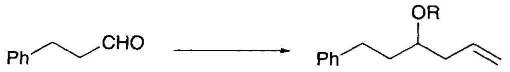
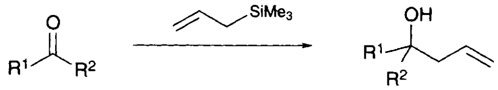


1 R = SiMe$_3$
2a R = H

Table 1 Reaction of allyltrimethylsilane with various carbonyl compounds in the presence of $HN(SO_2F)_2$[a] (5 mol%)[a]



2a–l

Entry	R¹	R²	*T*/°C	*t*/min	Product **2**	Yield[b] (%)
1	$PhCH_2CH_2$	H	0	5	**a**	89
2	*c*-C_6H_{11}	H	0	5	**b**	91
3	Bu^t	H	0	5	**c**	86
4	Ph	H	0	5	**d**	94
5	*p*-ClPh	H	0	5	**e**	92
6	*p*-$MeCO_2Ph$	H	0	5	**f**	90
7	*o*-NO_2Ph	H	0	5	**g**	90
8	*o*-MePh	H	0	5	**h**	91
9	PhCH=CH	H	−40	60	**i**	50[c]
10	$-(CH_2)_5-$		−40	60	**j**	86
11	$-(CH_2)_{11}-$		−40	60	**k**	91
12	$-(CH_2)_4-$		0	60	—	no reaction
13	C_3H_7	Me	−40	60	**l**	38[d]
14	Ph	Me	20	60	—	no reaction

[a] All reactions were carried out in 4 cm³ CH_2Cl_2/mmol of carbonyl compound under an N_2 atmosphere. [b] Isolated yields. [c] 30% starting material was recovered and the remainder nonpolar byproducts. [d] Remainder was nonpolar byproducts.

Footnotes

† Noyori reported TMSOTf to be completely ineffective for this type of allylation[6] but later Davis showed it to be a weak catalyst and the reaction of allyltrimethylsilane with benzaldehyde and hydrocinnamaldehyde occurs at a slow rate.[5a] Trifluoromethanesulfonic acid is also a weak catalyst because it generates TMSOTf by protodesilylation of allylsilane.[5b]

‡ Some triflate based organometallic reagents have been used as catalysts for the allylation of carbonyl compounds. Now it has been shown that TMSOTf is the actual catalyst involved in these cases.[7]

§ There are few examples in the literature where Brönsted acids have been used for allylation using allyltin reagents.[11]

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