Trimethylsilyl Bis(trifluoromethanesulfonyl)amide as an Effective Catalyst for the Friedel-Crafts Alkylation Reaction

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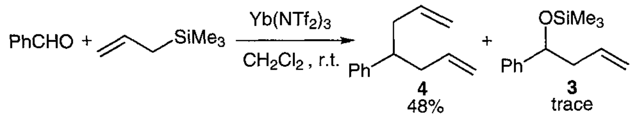
Abstract: Trimethylsilyl bis(trifluoromethanesulfonyl)amide is shown to be an effective catalyst not only for the Friedel-Crafts alkylation of an aromatic compound but also for allylation or bis-allylation of carbonyl derivatives.

The Friedel-Crafts alkylation reaction, which is one of the most important carbon-carbon bond forming processes in organic synthesis, is generally carried out by using Lewis acidic metal complexes.[1] However, there is still great demand for highly efficient catalysts employable for the Friedel-Crafts alkylation reaction under very mild conditions. We now wish to report here that trimethylsilyl bis(trifluoromethanesulfonyl)amide [$TMSNTf_2$] (**1**) is an effective catalyst not only for the Friedel-Crafts alkylation of an aromatic compound but also for the allylation or bis-allylation of carbonyl derivatives.

At the outset, ytterbium bis(trifluoromethanesulfonyl)amide, [$Yb(NTf_2)_3$] (**2**)[2] having the conjugate base of a super-acidic bis(trifluoromethanesulfonyl)imide acid ($HNTf_2$)[3] as a very weakly coordinating ligand was examined as a catalyst for allylation of benzaldehyde with allylsilane in dichloromethane. Surprisingly, the bis-allylation product (**4**) was obtained rather than the mono-allylation product (**3**) (Scheme 1). We have found that the mono-allylation intermediate, benzyl trimethylsilyl ether (**3**)[4] does provide efficiently the bis-allylation product (**4**) in the combined use of $Yb(NTf_2)_3$ (**2**) with trimethylsilyl triflate (TMSOTf) rather than the independent use thereof. These results suggest that $TMSNTf_2$ (**1**) is the actual catalyst species in the bis-allylation reaction. Thus, $TMSNTf_2$ (**1**) was prepared following the literature procedure.[5] The catalytic activity of $TMSNTf_2$ (**1**) was then examined in the bis-allylation reaction, in other words, the Friedel-Crafts-type alkylation reaction of allylsilane. Indeed, the bis-allylation product (**4**) was obtained in 49% yield.

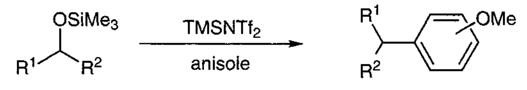


4 48%

3 trace

Scheme 1

To explore further the generality and scope of $TMSNTf_2$-catalyzed Friedel-Crafts-type alkylation reaction, we next examined the aromatic alkylation reaction (Scheme 2, Table 1). The high catalytic activity of $TMSNTf_2$ (**1**) is found in the Friedel-Crafts alkylation reaction of anisole. It is sufficient enough to use less than 10 mol% of $TMSNTf_2$ (**1**). Typical experimental procedure is as follows: To a solution of a silyl ether (1 mmol) in anisole (3 mL) was added $TMSNTf_2$ (**1**) at 0 °C. The mixture was stirred for 1 hour at room temperature, the resultant mixture was diluted with ether (5 mL) and quenched by the addition of saturated $NaHCO_3$ (10 mL). The solution was extracted three times with ether (totally 15 mL). The combined organic layer was washed with brine. The extract was then dried over $MgSO_4$ and evaporated under reduced pressure. Purification by silica gel chromatography (hexane / ethyl acetate) gave the Friedel-Crafts alkylation product of anisole.



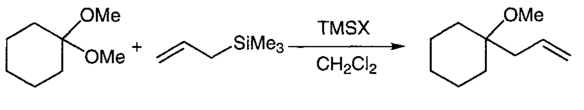
Scheme 2

Table 1. Friedel-Crafts alkylation of anisole with silyl ethers

entry	silyl ether	cat. (eq)	temp.	time (h)	yield (%)	isomer (p:o)
1	R^1=Ph,R^2=Et	0.1	r.t.	1	95	(1:0)
2	R^1=Ph,R^2=H	1	r.t.	1	89	(2:1)
3	R^1=vinyl, R^2=n-C_5H_{11}	1	r.t.	1	80[a]	(2:1)

[a] (*E*)-1-Aryl-2-octene is obtained as a sole product

It should be noted here that the silicon signal in $TMSNTf_2$ (**1**) appears much down field than those of TMSOTf[6] and $TMSN(SO_2F)_2$[7] indicating the super silylating ability of *Si*NTf_2 as compared with *Si*OTf and *Si*$N(SO_2F)_2$ (Scheme 3, Table 2): ^{29}Si nmr (neat) δ 57.2 ppm, lit.[5b] δ 55.9 ppm (tetramethylsilane in C_6D_6 as an external standard). Indeed, the allylation reaction of cyclohexanone dimethylketal with allyltrimethylsilane catalyzed by $TMSNTf_2$ (**1**) is faster than those catalyzed by TMSOTf[8] and $TMSN(SO_2F)_2$[7](entries 1 and 2 *vs*. 3).



Scheme 3

Table 2. Comparison of allylation reaction of dimethylketal with allylsilane catalyzed by TMSX

entry	TMSX (eq)	chemical shift of Si (ppm)	temp (°C)	time (h)	yield (%)
1[a]	OTf (0.01)	43.54[b]	-60 ~ -45	18	81
2[c]	$N(SO_2F)_2$ (0.05)	44.92	-78	0.75	91
3	NTf_2 (0.05)	57.2 (55.9)[d]	-78	0.25	91

[a] Ref.8. [b] Ref.6. [c] Ref.7. [d] Ref.5b

Trimethylsilyl trifluoromethanesulfonate (TMSOTf) has been widely used as a super-silylating reagent or catalyst in many organic transformations.[9] Quite recently, trimethylsilyl bis(*monofluoro*-sulfonyl)amide [$TMSN(SO_2F)_2$] was reported as a more efficient catalyst than TMSOTf.[7] Here, we have, for the first time, exemplified that the present trifluoromethyl derivative, $TMSNTf_2$ (**1**) shows a much higher catalyst activity and super-silylating ability than the monofluoro-counterpart, due to the well-known character of trifluoromethyl moiety as a higher electron-withdrawing group.

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References and Notes

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