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N-trimethylsilyl-bis(trifluoromethanesulfonyl)imide : a Better Carbonyl Activator than Trimethylsilyl Triflate.

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Dedicated to Professor Waldemar Adam on the occasion of his 60th birthday

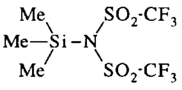
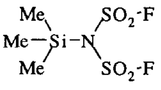
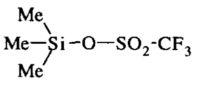
Abstract : N-trimethylsilyl-bis(trifluoromethanesulfonyl)imide (TMSNTf$_2$) was readily prepared from allyltrimethylsilane and bis(trifluoromethanesulfonyl)imide. It was shown to complex carbonyl groups much more effectively than trimethylsilyl triflate. As a result, TMSNTF$_2$ was found to be superior to TMSOTf as a catalyst for the Diels-Alder reaction of methyl acrylate with various dienes. © 1997 Elsevier Science Ltd.

Complexation of a carbonyl compound with a Lewis acid is a simple and much used method for the activation of dienophiles and enophiles. Transfer of chirality from the Lewis acid catalyst to the product has also been very successful in many instances and is becoming the strategy of choice for asymmetric Diels-Alder reactions.[1] However, problems can be encountered when the diene partner itself is sensitive to Lewis acids. Thus we found that 1- and 2-azadienes often decomposed when exposed to a dienophile in the presence of the commonly used Lewis acid catalysts.[1e,2]

A first solution to this problem was found by running the reactions of 1-aza- and 2-azadienes in concentrated organic solutions of lithium bis(trifluoromethanesulfonyl)imide, LiNTf$_2$, a safe substitute for lithium perchlorate.[3] We also showed that trialkylsilyl triflates were suitable catalysts for the reaction of α,β-unsaturated tertiary amides with 2-azadienes.[4] No degradation of the sensitive 2-azadienes was observed under these conditions. However, no catalytic effect was observed with the corresponding esters which have a much less basic carbonyl group.[4c] A more powerful silylating agent was thus required.

The comparison of ^{29}Si chemical shifts[5] of compounds 1-3 led us to the conclusion that TMSNTf$_2$[6] should exhibit a stronger Lewis acidity as compared to TMSOTf 2 and TMSN(SO$_2$F)$_2$ 3 (Table 1).[7] There was already evidence that compound 3 was superior to TMSOTf for the activation of ketones[8] and acetals[3b]. However, compound 3 is not very stable at room temperature.[5a] A much higher Lewis acidity should be expected for TMSNTf$_2$, which should also be thermally more stable (no possibility of F$^-$ release).

Table 1 : ^{29}Si Chemical Shifts (in ppm) of TMS-X compounds.

 $Me_3Si-N(SO_2CF_3)_2$	 $Me_3Si-N(SO_2F)_2$	 $Me_3Si-O-SO_2CF_3$
1	3	2
55.9 [5a]	44.9 [5b]	43.5 [5c]

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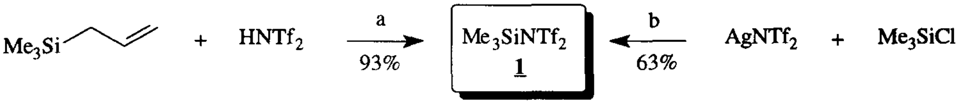
Compound 1 can be readily prepared by reacting $HNTf_2$ with allyltrimethylsilane (Scheme 1). An earlier synthesis involved the reaction of the silver salt of $HNTF_2$ with trimethylsilylchloride.[5a] Compound 1 is a colourless, moisture sensitive liquid.

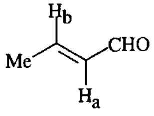
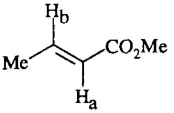


Conditions : (a) neat, rt, 1h, distillation; (b) neat, rt, 2.5 h protected from light, distillation.

Scheme 1

The ability of $TMSNTf_2$ and TMSOTf to complex trans-crotonaldehyde and trans-methyl crotonate was examined by ^1H NMR following the procedure described earlier by Childs *et al.*[9] (Table 2).

Table 2 : ^1H Chemical shift difference ($\Delta\delta$ in ppm) of carbonyl compounds on complexation with 1 and 2 in $CDCl_3$.

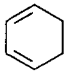
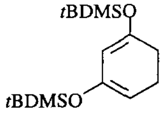
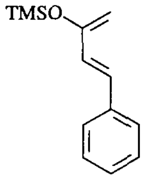
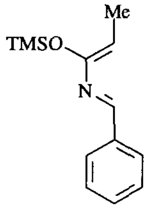
Carbonyl compound		*Catalyst*	
		$TMSNTf_2$ 1	TMSOTf 2
	$\Delta\delta(H_a)^{a,b}$	0.80	0.03
	$\Delta\delta(H_b)^{a,b}$	1.81	0.06
	$\Delta\delta(H_a)^{a,c}$	0.37	0.00
	$\Delta\delta(H_b)^{a,c}$	0.85	0.01

(a) $CHCl_3$ (7.24 ppm) as internal reference; (b) spectrum recorded at -40° C; (c) spectrum recorded at 0° C.

These results confirm our prediction that $TMSNTf_2$ 1 should exhibit an enhanced Lewis acidity as compared to TMSOTf 2. This is dramatically illustrated by a comparison of the catalytic effects of 1 and 2 on the Diels-Alder reactions of methyl acrylate with various dienes (Table 3). No catalysed reaction was observed with TMSOTf even in the presence of highly activated dienes.[10] In some cases, degradation of the diene was observed. On the other hand, under the same conditions, $TMSNTf_2$ was found to efficiently catalyse the cycloadditions.

In all cases, the cycloadditions were highly endo-selective. In the case of dienes of entries C and E, this endo-selectivity is in contrast to the kinetic exo-selectivity observed for the thermal reactions.[11, 4c] This stereochemical dichotomy between the thermal and $TMSNTf_2$ catalysed reactions parallels that observed for the reactions of the same dienes with N,N-dimethylacrylamide, and can be ascribed to electrostatic attraction favouring the endo transition state.[4a,b]

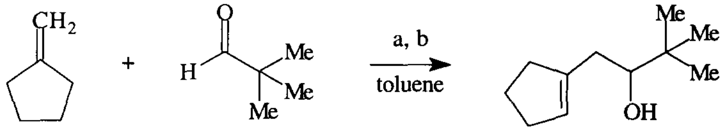
Table 3 : Cycloadditions of methyl acrylate in toluene with 10 mol% catalyst.

Entry	*Diene*	*addition T°*	*Conditions*	*Catalyst*	*Yield (%)*[a]	*Endo : Exo*[b]
A		0° C	0°C - 20 min	TMSOTf $TMSNTf_2$	< 5 83	13.3 : 1 24 : 1
B		0° C	0°C - 60 min	TMSOTf $TMSNTf_2$	0 92	- 49 : 1
C		0° C	RT - 60 min	TMSOTf $TMSNTf_2$	0 76	- 24 : 1
D		-50° C	RT - 60 min	TMSOTf $TMSNTf_2$	0 91	- ≥ 99 : 1
E		0° C	0°C - 90 min	- TMSOTf $TMSNTf_2$	<5 <5 74	1 : 2 1 : 2 2 : 1

(a) total yield of pure adducts; (b) Endo/Exo ratios were determined by gas chromatography or ^{1}H NMR on the crude mixture.

We have explored briefly the potential of $TMSNTf_2$ as a catalyst for the ene reaction (Scheme 2). Here also, $TMSNTf_2$ was found to be much superior to TMSOTf.

Further applications of N-silylated bis(trifluoromethanesulfonyl)imide are being examined with the goal of developing efficient and mild catalysts of reactions triggered by carbonyl groups.



Catalyst	*Yield of 4 (%)*
$TMSNTf_2$ 1	44
TMSOTf 2	0

Conditions : a) 1 or 2 (1 eq.) and 2,6-bis(*tert*-butyl)-4-methylpyridin (1 eq.); b) CF_3CO_2H

Scheme 2

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