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Trialkylsilyl triflimides as easily tunable organocatalysts for allylation and benzylation of silyl carbon nucleophiles with non-genotoxic reagents

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ABSTRACT

Trialkylsilyl triflimides generated in situ are unique catalysts for the electrophilic benzylation or allylation of trialkylsilylenol ethers or allyl trialkylsilanes with non-genotoxic alkylating reagents such as benzyl and allyl acetates. In most cases the reactions are fast at room temperature and yields are high. The reaction works particularly well with electron-rich benzyl donors including derivatives of pyrrole, indole and furane.

Acid-catalyzed alkylations of carbon nucleophiles are attractive substitutes for the classical nucleophilic S_N2-type substitution involving carbanions and alkyl halides or sulfonates.[1] They require alkylating agents (e.g., benzyl, allyl and *t*-alkyl) prone to undergo S_N1-type substitution reactions, most often after activation in situ by a Brönsted or a Lewis acid. Thus alcohols, ethers or esters which are much less genotoxic than the classical halides and sulfonates have been successfully used as precursors of the alkylating species. Acid-catalyzed benzylations and allylations of silyl nucleophiles involving benzyl or allyl alcohols and ethers or esters have received much attention in recent years.[2] However, many of the reported reactions suffer from major drawbacks such as the use of toxic metal-derived Lewis acids, significant amounts of by-products, difficulties in work-up and often experimental conditions which are incompatible with the presence of many functional groups. Recently several groups have proposed interesting approaches to overcome these problems.[3]

In 1997 we and Mikami's group independently reported that trimethylsilyl bistrifluoromethanesulfonimide ($TMSNTf_2$) was a much more efficient oxophilic catalyst than the corresponding triflate (TMSOTf) for Diels–Alder cycloadditions, ene reactions and Friedel–Crafts alkylations with alkenyloxysilanes.[4a,5a,b] This unpredicted reversal of acidity sequence in going from the protic acid to the trimethylsilyl derivative probably resulted from the size difference of the two anions: the higher I-strain of $TMSNTf_2$ thermodynamically favours the complexation with a smaller Lewis base such as a carbonyl group. Our group also made the remarkable observation that the Lewis acidity of trialkylsilyl triflimides *increased with the size of the alkyl groups* in contrast to what had always been observed for all other silylating agents.[4b] Yamamoto reported that in situ-generated $TMSNTf_2$ was a strong catalyst for the Mukayama-aldol and Sakurai–Hosomi allylation reactions.[6] Recently several groups have elegantly demonstrated the efficiency of Me_3SiNTf_2 as a catalyst for several carbon-carbon bond-forming reactions.[7] We also reported the first significant asymmetric inductions in the Diels–Alder reactions of dienes with α,β-ethylenic esters catalyzed by silylated triflimides carrying a chiral substituent on silicon.[8] Very recently List reported high asymmetric inductions in the Mukayama-aldol reaction catalyzed by a chiral binaphthyl-derived disulfonimide.[9]

We anticipated that trialkylsilyl triflimides could be attractive catalysts for allylations and benzylations of silyl nucleophiles: (1) they are easily prepared in situ from cheap and commercially available starting materials, (2) they have been shown to be good activators of esters,[4a] (3) their catalytic activity can be tuned by modifying the substituents at silicon[4b] and (4) they are tolerated by many functional groups. We selected the *p*-methoxybenzylations of trimethyl cyclohexenyloxysilane **2** and allyl trimethysilane **3** with *p*-methoxybenzyl acetate **1** as model reactions (Table 1). $TMSNTf_2$ was compared to TMSOTf and a variety of Bronsted acids. It was gratifying to observe that $TMSNTf_2$ efficiently catalyzed the reaction with both enolether **2** and allysilane **3** whether generated in situ from the instantaneous reaction of the silylated nucleophile with $HNTf_2$ (entries 1 and 9) or prepared before use (2 and 10). TMSOTf was less efficient (entries 3–5) as anticipated from the

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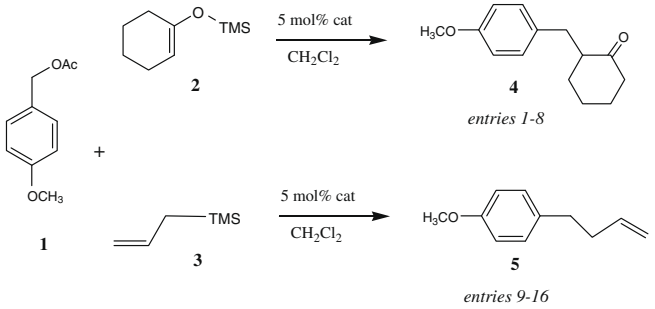
Table 1
Model reactions for the *p*-methoxybenzylation of silyl enolether **2** (entries 1–8) and allylsilane **3** (entries 9–16)[a]



Entry	Catalyst	*t* (min)	Yield[d] (%)
1	$HNTf_2$[a]	5	100
2	$TMSNTf_2$[b]	5	100
3	HOTf	5	20
4	TMSOTf	5	16
5	TMSOTf	120	90
6	CH_3SO_3H	5	0
7	CF_3COOH	5	0
8	HCl[c]	5	0
9	$HNTf_2$[a]	5	100
10	$TMSNTf_2$[b]	5	100
11	HOTf	5	19
12	TMSOTf	5	17
13	TMSOTf	120	85
14	CH_3SO_3H	5	<1
15	CF_3COOH	5	0
16	HCl[c]	5	0

[a] $HNTf_2$ was taken from a 0.5 M solution in CH_2Cl_2.
[b] $TMSNTf_2$ was prepared in situ from the addition of $HNTf_2$ to allyl trimethylsilane.
[c] HCl was taken from a 4 M solution in dioxane.
[d] Yields based on the integration of the aromatic peaks.

lower acidity of silylated triflates versus the corresponding triflimides.[4a,b] This also confirmed that the catalysts could not be the corresponding Brönsted acids because triflic acid is a stronger acid than triflimide and therefore expected to show a higher catalytic activity. The other Brönsted acids generated trimethylsilyl derivatives which were unable to catalyze the reaction (entries 6–8 and 14–16).

We then examined the scope and limitations of these reactions by varying both the substituent of the acetate and the nature of the carbon nucleophile (Table 2). A 0.5 M solution of $HNTf_2$ in dichloromethane[10] was added to the mixture of the two reagents. In a few cases (entries 22–24 and 29) additional dichloromethane was needed to favour the desired reaction over decomposition of the electrophile. Yields shown in Table 2 were measured by comparison of the integration areas of one representative proton signal of the product against C_2HCl_5 as internal standard. They were found to be reliable when compared to the isolated yields. Entries 1–5 illustrate the catalytic efficiency of in situ-generated $TMSNTf_2$ for the *p*-methoxybenzylation of various silyl nucleophiles. The reaction was not very sensitive to steric hindrance as shown by the facile alkylation of α,α′-disubstituted silyl ketene acetal **17** (95%) which created a quaternary carbon atom (entry 3). Allyl trimethylsilane **3** reacted equally well but vinyltrimethylsilane **18** yielded a complex mixture of products.

Less reactive electrophiles **6** and **7** did not react and a complex mixture of unidentified products was observed (entries 6 and 13). This probably resulted from an unfavourable competition between the desired benzylation reaction and the silylation of the enolether by the highly reactive $TMSNTf_2$ as shown by a control experiment. The catalyst could be easily tuned to overcome this problem: using a TIPS enolether generates $TIPSNTf_2$ in situ which had been shown to be a *weaker electrophile* (kinetically controlled reaction) than $TMSNTf_2$ but a *stronger Lewis acid* (thermodynamically controlled

Table 2
Electrophilic allylations and benzylations of silyl carbon nucleophiles

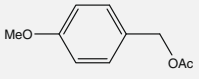
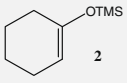
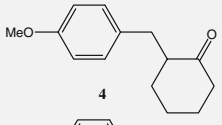
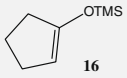
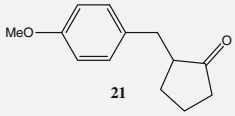
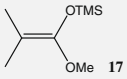
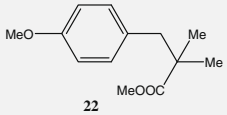
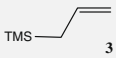
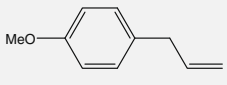
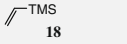
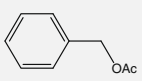
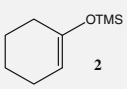
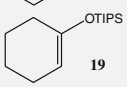
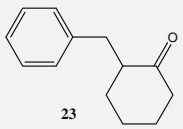
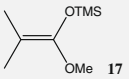
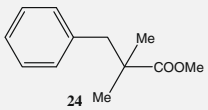
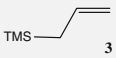
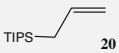
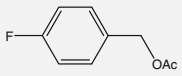
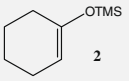
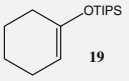
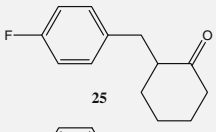
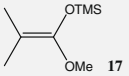
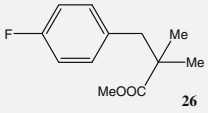
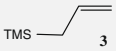
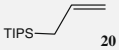
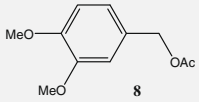
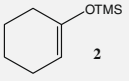
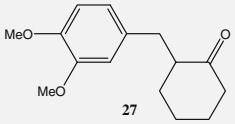
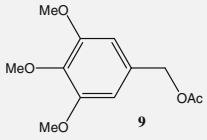
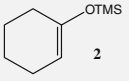
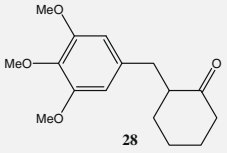
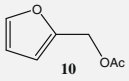
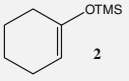
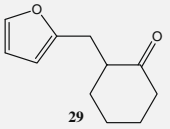
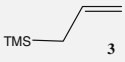
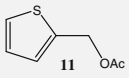
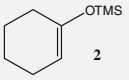
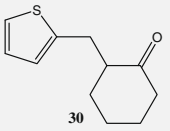
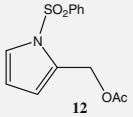
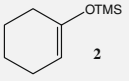
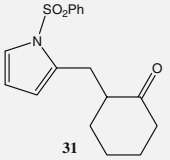
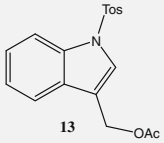
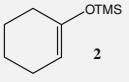
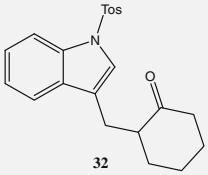
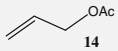
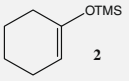
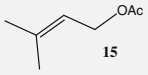
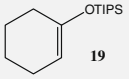
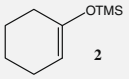
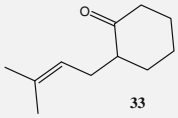
Entry	Electrophile	Nucleophile	Product	*T* (°C)	*t* (min)	% Cat	Yield[c] (%)
1[a]	 **1**	 **2**	 **4**	rt	20	5% $HNTf_2$	93 (85)
2[a]		 **16**	 **21**	rt	20	5% $HNTf_2$	93 (78)
3[a]		 **17**	 **22**	rt	20	5% $HNTf_2$	95 (83)
4[a]		 **3**	 **5**	rt	20	5% $HNTf_2$	95 (90)
5[a]		 **18**	Decomposition of anisyl acetate	rt	5	5% $HNTf_2$	0
6[a]	 **6**	 **2**	Complex mixture	rt	20	5% $HNTf_2$	0
7[a]		 **19**	 **23**	100	20	5% $HNTf_2$	85 (70)
8[a]				100	1	20% $HNTf_2$	90

Table 2 (*continued*)

Entry	Electrophile	Nucleophile	Product	T (°C)	t (min)	% Cat	Yield[c] (%)
		 17	 24				
9[a]		 3	No reaction	100	20	5% $HNTf_2$	0
10[a]			Decomposition	100	90	5% $HNTf_2$	0
11[a]		 20	No reaction	100	20	5% $HNTf_2$	0
12[a]			Decomposition	100	90	5% $HNTf_2$	0
13[a]	 7	 2	Complex mixture	rt	20	5% $HNTf_2$	0
14[a]		 19	 25	100	1	5% $HNTf_2$	78 (70)
15[a]		 17	 26	100	20	5% $HNTf_2$	88 (80)
16[a]		 3	No reaction	100	20	5% $HNTf_2$	0
17[a]			Decomposition	100	300	5% $HNTf_2$	0
18[a]		 20	No reaction	100	20	5% $HNTf_2$	0
19[a]			Decomposition	100	300	5% $HNTf_2$	0
20[a]	 8	 2	 27	rt	20	5% $HNTf_2$	95 (91)
21[a]	 9	 2	 28	rt	20	5% $HNTf_2$	90 (82)
22[b]	 10	 2	 29	rt	60	1.0% $HNTf_2$	80 (70)
23[b]		 3	Decomposition	rt	20	1% $HNTf_2$	0
24[b]	 11	 2	 30	rt	60	1.5% $HNTf_2$	88 (79)
25[a]	 12	 2	 31	rt	20	5% $HNTf_2$	96 (89)
26[a]	 13	 2	 32	rt	20	5% $HNTf_2$	95 (76)
27[a]	 14	 2	Complex mixture	rt	20	5% $HNTf_2$	0
28[a]			No reaction	90	20	5% $HNTf_2$	0

(*continued on next page*)

Table 2 (*continued*)

Entry	Electrophile	Nucleophile	Product	*T* (°C)	*t* (min)	% Cat	Yield[c] (%)
29[b]	 **15**	 **19**  **2**	 **33**	rt	20	5% $HNTf_2$	80

[a] Reaction conditions: 0.25 mmol of electrophile, 0.3 mmol of nucleophile.
[b] Reaction conditions: 0.25 mmol of electrophile, 0.5 mmol of nucleophile, in 1 mL CH_2Cl_2.[10]
[c] Yields calculated from the ^1H NMR spectra, based; in brackets yields of pure product after chromatography.

reaction): this was expected to favour the reversible complexation of the carbonyl ester over the silylation of the nucleophilic carbon atom of the enolether. It was indeed gratifying to observe that the reaction of **19** with **6** and **7** led to good yields of benzylated products (entries 7 and 14). Steric hindrance favoured the less bulky benzyl electrophile: indeed the benzylation reaction worked well with α,α′-disubstituted silyl ketene acetal **17** (entries 8 and 15). However, the less reactive allyl tri-*i*-propyl and allyl trimethylsilanes did not react at room temperature and yielded a complex mixture at higher temperatures. (entries 9–12 and 16–19). As expected the presence of additional activating methoxy groups on the phenyl ring led to excellent yields of α-benzylated cyclohexanones (entries 20 and 21).

Acetates derived from electron-rich heteroarene carbinols **10–13** were also appropriate reagents for the delivery of an HetAr-CH_2 fragment on a silyl enolether (entries 22–26). Since acetates derived from α-hydroxymethyl pyrrole and β-hydroxymethyl indole were rather unstable, we used the more stable *N*-sulfonylated derivatives.

A simple allyl group could not be transferred (entries 27 and 28) even if one uses a TIPS-derived carbon nucleophile at 90 °C. On the other hand isoprenyl acetate reacted well under standard conditions (entry 29).

We believe that these results demonstrated the efficiency of trialkylsilyl triflimides as a powerful class of catalyst for the benzylation and allylation of various classes of silyl carbon nucleophiles. The catalysts are generated in situ from the reaction of the commercially available triflimide (1–5%) with the nucleophile. Interestingly the catalytic activity can be tuned up by choosing the most appropriate alkyl substituent on silicon. Yields are high and work-up is easy. The precursors of the alkylating species are esters which are non-genotoxic. In a control experiment we showed that the corresponding benzyl alcohols could not be used since they destroy the catalyst. Also the reactions do not involve any toxic metal-containing catalyst. The reactions work particularly well with electron-rich aromatic substituents. This is interesting since the corresponding halides or tosylates are highly genotoxic. In most cases the reactions can be performed without solvent.[10] We believe that this procedure should appeal to the synthetic chemists looking for practical, safe and environmentally acceptable synthetic methods.[11]

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.03.030.

References and notes

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10. In our small-scale experiments we found more practical to use a solution of $HNTf_2$ in dichloromethane. For large-scale experiments, triflimide was introduced as a solid. Therefore, one can say that in most cases, the reaction can be performed in the absence of solvent.
11. Representative procedures: (a) *Reaction of anisyl acetate with allyltrimethylsilane*: 250 μL of a 0.5 M solution of $HNTf_2$ in CH_2Cl_2 were added to a 5-mL round-bottomed flask equipped with a magnetic stirbar and containing 410 μL of anisyl acetate (2.5 mmol) and 480 μL of allyltrimethylsilane (3.0 mmol). After 5 min the solvent was evaporated and the crude residue was purified by column chromatography (silicagel, eluent: cyclohexane/ethyl acetate 9:1) to obtain a pure yellow oil in 92% yield.
(b) *Reaction of anisyl acetate with trimethyl cyclohexenyloxysilane*: 250 μL of a 0.5 M solution of $HNNf_2$ in CH_2Cl_2 were added into a 5-mL round-bottomed flask equipped with a magnetic stirbar, 410 μL of anisyl acetate (2.5 mmol) and 583 μL of trimethyl cyclohexenyloxysilane (3.0 mmol). After 5 min the solvent was evaporated and the crude mixture was purified by column chromatography (silicagel, eluent: cyclohexane/ethyl acetate 9:1) to obtain a pure colourless oil in 85% yield.