

Imine allylation by allylic trimethylsilanes *via in situ* formation of *N*-tosyliminium species from carbonyl compounds and toluene-*p*-sulfonamide with SnCl₂ and *N*-chlorosuccinimide: regioselection and diastereoselection

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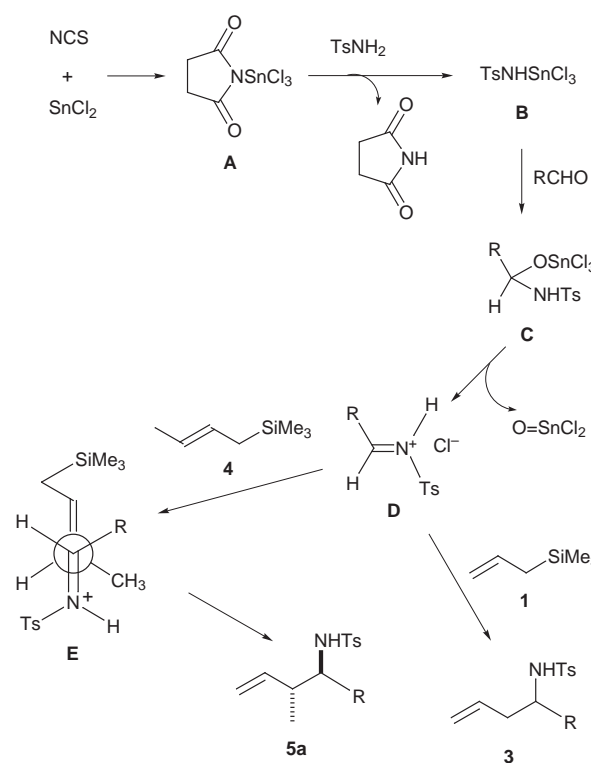
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N-Tosyliminium species, prepared *in situ* from carbonyl compounds and TsNH₂ with SnCl₂ and *N*-chlorosuccinimide, undergo nucleophilic addition of allylic silanes (imine allylation) to produce the corresponding homoallylic amines; the imine allylation by but-2-enyltrimethylsilane with aldehydes and TsNH₂ leads to regio- and diastereoselection to produce *anti* 1-substituted 2-methylbut-3-enylamines.

Lewis acid-catalysed allylations of imines or iminium species with allylic silane or tin reagents are one of the most effective methods for the introduction of an amino group into carbon skeletons.^{1,2} However, some imines and iminium species are unstable to water or heat, and their purification is difficult *via* recrystallization, distillation and chromatography. The allylation of imines or iminium species, prepared *in situ* from carbonyl compounds and amines, would therefore be a synthetically useful strategy.^{3–7} We have reported that *N*-chlorosuccinimide (NCS) and SnCl₂ can be utilized for the aldol-type reaction of isopropenyl acetate with oxycarbenium ions derived from either aldehydes with alcohols or lactols.⁸ A key step in the aldol-type reaction is probably the formation of alkoxytrichlorotins, which react with aldehydes to form oxycarbenium ions. We hoped that, using NCS–SnCl₂, aldehydes could be transformed into *N*-tosyliminium species with TsNH₂, in analogy to alcohols giving oxycarbenium ions, and that the *N*-tosyliminium species could undergo nucleophilic addition with allylic silanes (imine allylation).⁹

As a consequence of the investigation of imine allylation by allyltrimethylsilane **1** with benzaldehyde and some amines under various conditions, it was proved that starting with a solution of SnCl₂ (1.1 mmol), TsNH₂ (1 mmol) and benzaldehyde (**2**; R¹ = Ph, R² = H, 1 mmol) in CH₂Cl₂ (3 ml) in an ice-bath, the addition of NCS (1.1 mmol) in CH₂Cl₂ (5 ml) followed by allyltrimethylsilane (**1**, 1.5 mmol) after 2 h afforded *N*-tosyl-1-phenylbut-3-enylamine (**3**; R¹ = Ph, R² = H) in a 96% yield (Scheme 1). Benzylamine, benzamide, and *tert*-butyl carbamate were ineffective in the reaction under the same conditions as those used with TsNH₂. This allylation probably needs amines or amides bearing an acidic proton on nitrogen for the formation of the trichlorotin amide; as shown in Scheme 2, TsNH₂ reacts with **A**, derived from NCS and SnCl₂, to form **B**, which undergoes nucleophilic addition to benzaldehyde (R = Ph) to form **C** followed by **D**. The imine allylation by **1** with various carbonyl compounds and TsNH₂ was carried out under the same conditions as those for benzaldehyde described above. Representative results are summarized in Table 1. Any aldehyde,

including aromatic aldehydes bearing either an electron-withdrawing group (entries 2 and 3) or an electron-donating group (entries 4–6), aliphatic aldehydes (entries 8–10) and an α,β-unsaturated aldehyde (entry 11) can be used in the imine allylation. In the cases of aldehydes bearing a coordinate group,

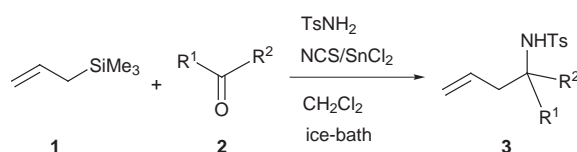


Scheme 2

Table 1 Imine allylation by **1** with **2**, TsNH₂, NCS and SnCl₂ to give **3**

Entry	R ¹	R ²	t/h	Yield ^a (%)
1	Ph	H	6	96
2	4-ClC ₆ H ₄	H	6	90
3	4-NCC ₆ H ₄	H	6	92
4	4-MeC ₆ H ₄	H	8	81
5	4-MeOC ₆ H ₄	H	10	75
6	3,4-(CH ₂ O ₂)C ₆ H ₃	H	15	47
7	2-Furyl	H	15	28
8	C ₆ H ₁₃	H	15	64
9	<i>c</i> -C ₆ H ₁₁	H	15	70
10	PhCH ₂ CH ₂	H	10	86
11	PhCH=CH	H	15	52
12		(CH ₂) ₄	20	26
13		(CH ₂) ₅	20	38
14	Ph	Me	20	17

^a Isolated yields.



Scheme 1

Table 2 Diastereoselective imine allylation by but-2-enyltrimethylsilane **4** to give **5**^a

Entry	R	t/h	Yield ^b (%)	5s : 5a ^c
1	Ph	6	91	11 : 89
2	4-ClC ₆ H ₄	15	87	11 : 89
3	4-MeC ₆ H ₄	15	73	10 : 90
4	C ₆ H ₁₃	15	48	8 : 92
5	c-C ₆ H ₁₁	15	62	9 : 91

^a The imine allylation by **4** (1.5 mmol) was carried out with aldehydes (1 mmol), TsNH₂ (1 mmol), SnCl₂ (1.1 mmol) and NCS (1.1 mmol) in CH₂Cl₂ (3 ml) by the same method as that for the allylation by **1**. ^b Isolated yields. ^c The ratio was determined by ¹H NMR (JEOL GX-270).

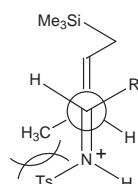
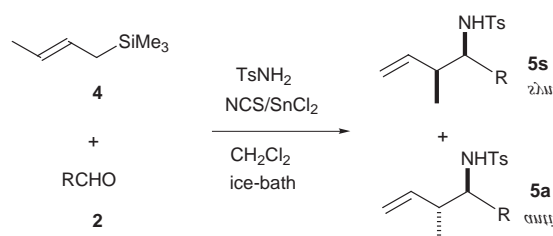


Fig. 1 Antiperiplanar transition state of **4**



Scheme 3

3,4-methylenedioxybenzaldehyde and furan-2-carbaldehyde exhibited low yields (entries 6 and 7), and pyridine-2-carbaldehyde did not react under the given conditions. Ketones can also undergo the imine allylation to be converted into the corresponding homoallylic amines in unsatisfactory yields (entries 12–14).

The imine allylation of but-2-enyltrimethylsilane (**4**)[†] with some aldehydes and TsNH₂ under the same conditions as those of **1** caused γ -anti-addition to afford *anti* 1-substituted 2-me-

thylbut-3-enylamines **5a** in good yields, as summarized in Table 2 (Scheme 3).[‡] The γ -anti-addition probably occurs *via* an acyclic antiperiplanar transition state (**E**) between **4** and **D** (Scheme 2), due to steric hindrance between the tosyl group and the methyl group (Fig. 1).^{4,9}

Notes and references

[†] But-2-enyltrimethylsilane (**4**; *E*:*Z* = 86 : 14) was prepared by the reaction of but-2-enyltrichlorosilane, derived from 1-chlorobut-2-ene and trichlorosilane with CuCl and Et₃N, with MeMgI (ref. 10).

[‡] The stereochemistry was determined by comparison of ¹H NMR data of primary homoallylic amines (R = Ph, C₆H₁₃), which were produced by removal of the tosyl group (ref. 9), with those in the literature (ref. 11).

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