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Imine allylation by allylic trimethylsilanes *via in situ* formation of *N*-tosyliminium species from carbonyl compounds and toluene-*p*-sulfonamide with $SnCl_2$ and *N*-chlorosuccinimide: regioselection and diastereoselection

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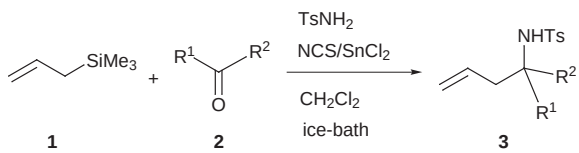
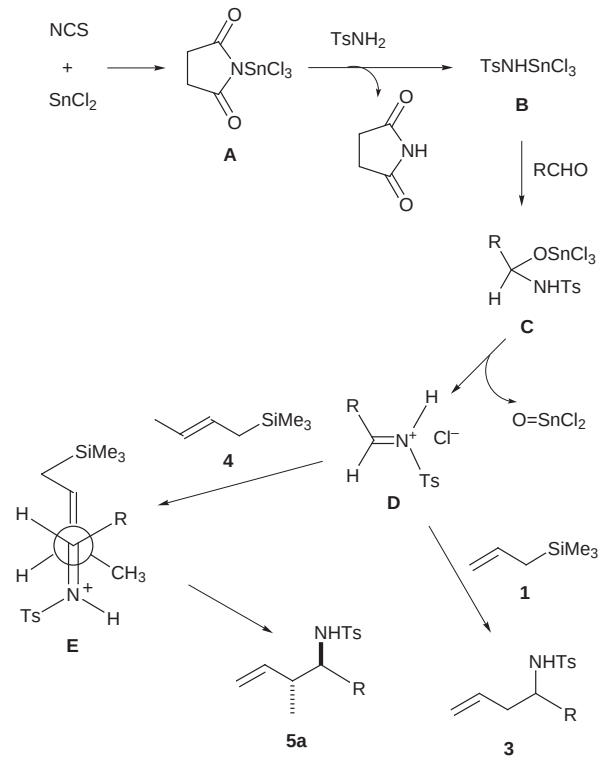
***N*-Tosyliminium species, prepared *in situ* from carbonyl compounds and $TsNH_2$ with $SnCl_2$ and *N*-chlorosuccinimide, undergo nucleophilic addition of allylic silanes (imine allylation) to produce the corresponding homoallylic amines; the imine allylation by but-2-enyltrimethylsilane with aldehydes and $TsNH_2$ 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 $SnCl_2$ 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–$SnCl_2$, aldehydes could be transformed into *N*-tosyliminium species with $TsNH_2$, 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 $SnCl_2$ (1.1 mmol), $TsNH_2$ (1 mmol) and benzaldehyde (**2**; R^1 = Ph, R^2 = H, 1 mmol) in CH_2Cl_2 (3 ml) in an ice-bath, the addition of NCS (1.1 mmol) in CH_2Cl_2 (5 ml) followed by allyltrimethylsilane (**1**, 1.5 mmol) after 2 h afforded *N*-tosyl-1-phenylbut-3-enylamine (**3**; R^1 = Ph, R^2 = 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 $TsNH_2$. 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, $TsNH_2$ reacts with **A**, derived from NCS and $SnCl_2$, 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 $TsNH_2$ 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 1



Scheme 2

Table 1 Imine allylation by **1** with **2**, $TsNH_2$, NCS and $SnCl_2$ to give **3**

Entry	R^1	R^2	*t*/h	Yield[a] (%)
1	Ph	H	6	96
2	4-ClC_6H_4	H	6	90
3	4-NCC_6H_4	H	6	92
4	4-MeC_6H_4	H	8	81
5	4-$MeOC_6H_4$	H	10	75
6	3,4-$(CH_2O_2)C_6H_3$	H	15	47
7	2-Furyl	H	15	28
8	C_6H_{13}	H	15	64
9	*c*-C_6H_{11}	H	15	70
10	$PhCH_2CH_2$	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.

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_6H_4	15	87	11 : 89
3	4-MeC_6H_4	15	73	10 : 90
4	C_6H_{13}	15	48	8 : 92
5	*c*-C_6H_{11}	15	62	9 : 91

[a] The imine allylation by **4** (1.5 mmol) was carried out with aldehydes (1 mmol), $TsNH_2$ (1 mmol), $SnCl_2$ (1.1 mmol) and NCS (1.1 mmol) in CH_2Cl_2 (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).

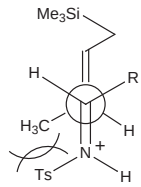
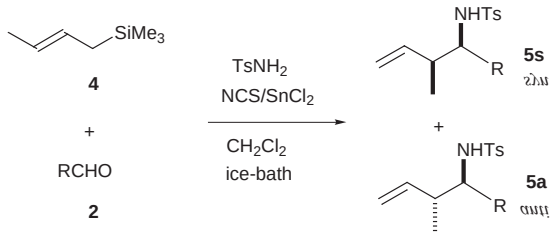


Fig. 1 Antiperiplanar transition state of **4**



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 $TsNH_2$ under the same conditions as those of **1** caused γ-*anti*-addition to afford *anti* 1-substituted 2-methylbut-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 Et_3N, with MeMgI (ref. 10).

‡ The stereochemistry was determined by comparison of ^1H NMR data of primary homoallylic amines (R = Ph, C_6H_{13}), which were produced by removal of the tosyl group (ref. 9), with those in the literature (ref. 11).

1 For a review, see: Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207.
2 For recent papers, see: D.-K. Wang, L.-X. Dai and X.-L. Hou, *Tetrahedron Lett.*, 1995, **36**, 8649; C. Bellucci, P. G. Cozzi and A. Umani-Ronchi, *Tetrahedron Lett.*, 1995, **36**, 7289; T. Basile, A. Bocoum, D. Savoia and A. Umani-Ronchi, *J. Org. Chem.*, 1994, **59**, 7766.
3 For the reaction of allylic silane and tin reagents with formaldehyde and amines, see: S. D. Larsen, P. A. Grieco and W. F. Fobare, *J. Am. Chem. Soc.*, 1986, **108**, 3512; P. A. Grieco and A. Bahsas, *J. Org. Chem.*, 1987, **52**, 1378.
4 For the reaction of allylic silanes with aldehydes and carbamates, see: S. J. Veenstra and P. Schmid, *Tetrahedron Lett.*, 1997, **38**, 997; J. S. Panek and N. F. Jain, *J. Org. Chem.*, 1994, **59**, 2674.
5 For the reaction of allyltributyltin with aldehydes and arylamines, see: S. Kobayashi, S. Iwamoto and S. Nagayama, *Synlett*, 1997, 1099.
6 For the allylation of iminiums prepared in situ from α-alkoxymethylcarbamate, see: Y. Yamamoto and M. Schmid, *J. Chem. Soc., Chem. Commun.*, 1989, 1310; N. Kise, H. Yamazaki, T. Mabuchi and T. Shono, *Tetrahedron Lett.*, 1994, **35**, 1561.
7 For the allylation of iminium species prepared *in situ* from *N*-alkyl-*N*-trifluoromethanesulfonyloxyamide, see: R. V. Hoffman, N. K. Nayar, J. M. Shankweiler and B. W. Klinekole III, *Tetrahedron Lett.*, 1994, **35**, 3231.
8 Y. Masuyama, Y. Kobayashi, R. Yanagi and Y. Kurusu, *Chem. Lett.*, 1992, 2039; Y. Masuyama, Y. Kobayashi and Y. Kurusu, *J. Chem. Soc., Chem. Commun.*, 1994, 1123.
9 For the allylation of only aromatic sulfonimines, prepared beforehand, with allylic bromides and indium, see: T. H. Chan and W. Lu, *Tetrahedron Lett.*, 1998, **39**, 8605.
10 N. Furuya and T. Sukawa, *J. Organomet. Chem.*, 1975, **96**, C1.
11 R. W. Hoffmann and A. Endersfelder, *Liebigs Ann. Chem.*, 1987, 215.

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