Chiral sulfoxides as activators of allyl trichlorosilanes in the stereoselective allylation of aldehydes†

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Chiral aryl methyl sulfoxides proved to be efficient activators in the asymmetric allylation of aldehydes with allyl trichlorosilanes. High enantioselectivity was found in the case of electron-poor aldehydes. The high levels of diastereoselectivity and the detection of nonlinear effects have allowed the elucidation of some mechanistic aspects of the reaction.

Introduction

Within the last two decades, asymmetric organocatalysis based on the activation of suitable organosilanes with neutral Lewis bases has attracted the interest of many research groups.[1] One of the most investigated reactions is represented by the allylation of carbonyl compounds with allyl trichlorosilane to obtain chiral homoallylic alcohols.[2] In this context, a variety of chiral catalysts, such as formamides,[3] phosphoramides,[4] pyridine *N*-oxides[5] and phosphines oxides,[6] have been synthesized allowing the achievement of efficient and stereoselective procedures.

From a mechanistic point of view, the activation of the allylating agent by strong Lewis bases was attributed to the formation of a hypervalent silicon compound capable of reacting with suitable electrophiles.[1,7] Furthermore, the high levels of diastereoselectivity, often observed with substituted allyl trichlorosilanes (such as *E*- and *Z*-crotyl trichlorosilanes) proved to be in agreement with a reaction path involving an allylating group transfer through a cyclic six-membered transition state.[8]

Rather surprisingly, especially in consideration of their broad employment in asymmetric synthesis both as chiral ligands and auxiliaries, poor attention has been paid in the past years to sulfoxides,[9] typical neutral Lewis bases, as possible activators of allyl trichlorosilanes in allylation reactions.[10] In fact, only recently Massa *et al.*[11] reported an asymmetric procedure, based on the use of chiral methyl *p*-tolyl sulfoxide, for the allylation of aldehydes with allyl trichlorosilane. Nevertheless, a large amount of activator was required (up to 3 eq.) and moderate yields and enantiomeric excesses (e.e.s) were observed.

No significant improvement was obtained by the contemporary Rowland's procedure,[12] which involved the use of sulfoxides incorporating oxazoline moieties, since homoallylic alcohols were isolated in good yields but rather low e.e.s. In the attempt to get a heterogeneous catalyst, chiral sulfoxides were covalently bonded to mesoporous silica (SBA-15):[13] unfortunately, the resulting solid catalyst exhibited poor efficiency and enantioselectivity.

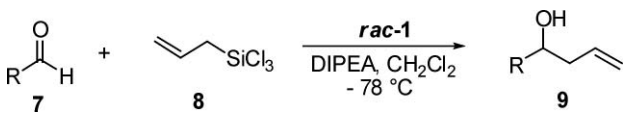
More conveniently, the easy access to a novel chiral tetradentate bis-sulfoxide has been exploited for the achievement of a new procedure characterized by a much lower activator loading (0.2–0.3 eq.) and significantly increased yields and e.e.s.[14]

Furthermore, taking advantage of our previous report, Liao *et al.* examined the catalytic activity of a series of mono- and bidentate aryl *t*-butyl sulfoxides;[15] it has to be noted that moderate to high yields and enantioselectivity could again be attained in the presence of a large amount of Lewis bases (3 eq.) and allyl trichlorosilane (up to 3 eq.), provided that an α-benzyloxy-phenyl *t*-butyl sulfoxide was used as an activator. A mechanistic investigation indicated that the activation took place by coordination of only one molecule of aryl *t*-butyl sulfoxide to the silicon atom, resulting in the formation of a pentacoordinate Si intermediate in the stereodetermining step.[15]

Stimulated by our previous results, the catalytic properties of a variety of easily available sulfoxides were submitted to an extensive investigation leading to the achievement of a very satisfactory procedure for the stereoselective allylation of aldehydes and, furthermore, to the elucidation of some mechanistic aspects concerning the effective catalytic species.

Results and discussion

In the early phase, commercially available racemic methyl *p*-tolyl sulfoxide, *rac*-**1**, was used as an activator of the allylating agent **8** (Scheme 1) and benzaldehyde was chosen as the representative substrate.



Scheme 1

Under the conditions reported in Scheme 1 and Table 1 (entries 1–3) the activator loading proved to be the crucial factor: in fact, 3 eq. of *rac*-**1** were required for the formation of the homoallylic alcohol **9a** with very high efficiency.

The procedure proved to be successful, with aromatic aldehydes bearing both electron-donor and electron-withdrawing substituents (entries 4, 6 and 7), as well as heteroaromatic (entry 5), α,β-unsaturated (entry 8) and aliphatic aldehydes (entry 9).

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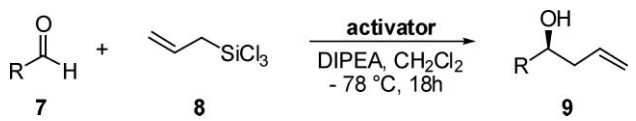
Table 1 Allylation of RCHO with allyltrichlorosilane catalyzed by racemic methyl *p*-tolyl sulfoxide

Entry	R (**7**)	*rac*-**1**(eq.)	*t*/h	**9**	Yield (%)[a]
1	Ph (**7a**)	1	8	**9a**	49
2	Ph (**7a**)	2	8	**9a**	84
3	Ph (**7a**)	3	8	**9a**	99
4	4-$MeOC_6H_4$ (**7b**)	3	18	**9b**	78
5	5-NO_2-2-Furyl (**7c**)	3	4	**9c**	92
6	4-CNC_6H_4 (**7d**)	3	18	**9d**	64
7	2-$MeOC_6H_4$ (**7e**)	3	18	**9e**	79
8	PhCH=CH (**7f**)	3	18	**9f**	81
9	$PhCH_2CH_2$ (**7g**)	3	18	**9g**	80
10[b]	Ph (**7a**)	3	18	**9a**	94
11	$Ph(CH_3)CHCHO$ (**7h**)	3	28	**9h**	71[c]

[a] All the yields refer to isolated chromatographically pure compounds whose structures were confirmed by analytical and spectroscopic data. [b] The reaction was carried out by using 3 equiv. of DMSO. [c] d.r. 65/35, determined by ^{1}H-NMR and ^{13}C-NMR analysis on the crude reaction mixture.

Interestingly, the steric hindrance in proximity of the reaction site, as in entry 11, did not prevent the formation of the homoallylic alcohol **9h** occurring (71% yield) although a poor diastereoselectivity was observed (65/35 d.r.). Furthermore, more prolonged reaction times were required by using dimethyl sulfoxide as activator (entry 10).

Our efforts were then focused on the achievement of the asymmetric version of the allylation procedure and, therefore, the influence exerted by a set of chiral activators was examined (Scheme 2). It has to be noted that, while methyl *p*-tolyl sulfoxide is commercially available in both the enantiomerically pure forms, highly enantioenriched sulfoxides **2–6** were synthesized by a catalytic enantioselective oxidation of the corresponding sulfides performed with a very convenient, recent, modification of the original Modena's protocol[16] and directly used in the optical purity indicated in Fig. 1.



Scheme 2

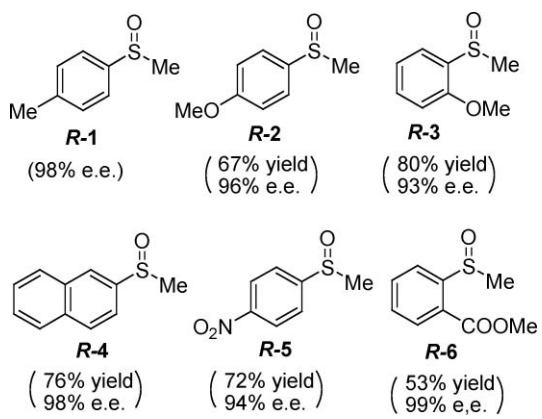


Fig. 1 Structures of aryl methyl sulfoxides.

The experiments performed on benzaldehyde **7a** in the presence of *R*-**1**, as Lewis base, confirmed the strict dependence of the efficiency of the process on the amount of activator, while, conversely, only moderate, comparable e.e.s were usually observed (entries 1–3, Table 2). More interestingly, the electronic properties of the used aldehydes played a determining role as regards the stereochemical aspects. In fact, while the presence of an electron-donor in the *para* position of the aromatic ring (entry 4) caused a slight decrease in the level of enantioselectivity with respect to entry 3, the reaction on the electron-poor aldehyde **7c** (entry 5) took place in a much more satisfactory way, leading to the homoallylic alcohol **9c** in 99% yield and significantly enhanced e.e. (83% e.e.). The same difference in the stereochemical outcome could be appreciated by using the more Lewis basic sulfoxides *R*-**2** (entries 6 and 7) and *R*-**3** (entries 8 and 9) as well as the more hindered *R*-**4** (entries 10 and 11). Furthermore, the significantly lower Lewis basicity, deriving from the presence of a nitro group in the *para* position, as in *R*-**5**, can be considered responsible of the complete failure of the procedure both on aldehyde **7a** and **7c**. Conversely, a milder electron-withdrawing group, although situated in proximity of the sulfoxide moiety, such as the carbomethoxy substituent in *R*-**6**, did not seem to affect the preparative and stereochemical outcome (entry 12).

Table 2 Asymmetric allylation of RCHO with allyltrichlorosilane catalyzed by chiral aryl methyl sulfoxides

Entry	R	**Activator**[a] (equiv.)	**9**	Yield (%)[b]	e.e. (%)[c]
1	Ph (**7a**)	***R*-1** (1)	**9a**	59	56
2	Ph (**7a**)	***R*-1** (2)	**9a**	89	58
3	Ph (**7a**)	***R*-1** (3)	**9a**	99	59
4	4-$MeOC_6H_4$ (**7b**)	***R*-1** (3)	**9b**	78	53
5	5-NO_2-2-Furyl (**7c**)	***R*-1** (3)	**9c**	99	83
6	Ph (**7a**)	***R*-2** (3)	**9a**	91	50
7	5-NO_2-2-Furyl (**7c**)	***R*-2** (3)	**9c**	97	85
8	Ph (**7a**)	***R*-3** (3)	**9a**	95	47
9	5-NO_2-2-Furyl (**7c**)	***R*-3** (3)	**9c**	99	81
10	Ph (**7a**)	***R*-4** (3)	**9a**	91	50
11	5-NO_2-2-Furyl (**7c**)	***R*-4** (3)	**9c**	95	82
12	5-NO_2-2-Furyl (**7c**)	***R*-6** (3)	**9c**	94	84

[a] *R*-**5** is not soluble in CH_2Cl_2 at −78 °C. [b] All the yields refer to isolated chromatographically pure compounds whose structures were confirmed by analytical and spectroscopic data. [c] e.e.s have been determined by chiral HPLC.

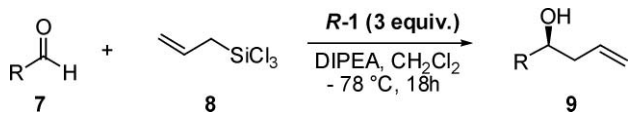
On the grounds of the results reported in Table 2, most of the chiral sulfoxides used proved to be employable in the asymmetric allylation of aldehydes with allyl trichlorosilane, affording the homoallylic alcohols in not significantly different yields and e.e.s. Consequently, the scope of the protocol was checked by using the commercially available and relatively cheap methyl *p*-tolyl sulfoxides *R*-**1** and *S*-**1**.

Therefore, a variety of aldehydes were submitted to treatment with **8** in the presence of *R*-**1** under the conditions reported in Scheme 3 and Table 3. As regards aromatic substrates, very high yields were usually observed, while electron-poor aldehydes afforded the best results from the stereochemical point of view. Particularly, the presence of a strong electron-withdrawing substituent on the aromatic (entries 2, 3) and heteroaromatic ring (entries 6, 7 and 9, 10) resulted in the highest e.e.s (up to 86% e.e.). Interestingly, the steric hindrance caused by the $-NO_2$ group situated in proximity of the reaction site, as in **7j**, did not affect its reactivity, although a slightly lower enantioselectivity

Table 3 Asymmetric allylation of aldehydes with allyltrichlorosilane catalyzed by chiral methyl *p*-tolyl sulfoxide

Entry	R	9	Yield (%)[a]	e.e. (%)[b]
1	Ph (**7a**)	***S*-9a**	99	59
2	4-$NO_2C_6H_4$ (**7i**)	***S*-9i**	97	82
3	2-$NO_2C_6H_4$ (**7j**)	***S*-9j**	97	72
4	4-$CF_3C_6H_4$ (**7k**)	***S*-9k**	83	66
5	4-FC_6H_4 (**7l**)	***S*-9l**	96	62
6	5-NO_2-2-Furyl (**7c**)	***S*-9c**	99	83
7[c]	5-NO_2-2-Furyl (**7c**)	***R*-9c**	99	–86
8	4-CNC_6H_4 (**7d**)	***S*-9d**	65	67
9	5-NO_2-2-Thienyl (**7m**)	***S*-9m**	80	82
10[c]	5-NO_2-2-Thienyl (**7m**)	***R*-9m**	80	–84
11	4-$MeOC_6H_4$(**7b**)	***S*-9b**	78	53
12	4-$MeSC_6H_4$(**7n**)	***S*-9n**	72	65
13	$PhCH_2CH_2$ (**7g**)	***R*-9g**	78	72

[a] All the yields refer to isolated chromatographically pure compounds whose structures were confirmed by analytical and spectroscopic data. [b] e.e.s have been determined by chiral HPLC. [c] The reactions were performed by using *S*-**1**



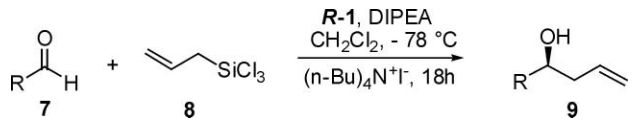
Scheme 3

was observed in comparison to the isomeric 4-nitro-derivative **7i** (compare entries 2 and 3).

Furthermore, as regards electron-rich aldehydes **7b** and **7n**, the experiments reported in entries 11 and 12, confirmed the notable influence exerted by the electronic effects of the substituents. In fact, the attainment of higher e.e.s for substrate **7n** can be reasonably explained with the lower overall electron-donor effect of the MeS– group with respect to the MeO– group. As is well known, most of the protocols available for the allylation of aliphatic aldehydes have often given rather unsatisfactory results leading to the corresponding homoallylic alcohols in modest yields and/or e.e.s. To our delight, under the usual conditions, 3-phenyl propionaldehyde **7g** was converted into product **9g** in 78% yield and 72% e.e., which can be considered among the best values reported for allylation with allyl trichlorosilane promoted by mono- and bidentate Lewis bases.

The possibility to recover *R*-**1** in almost quantitative yield and unchanged optical purity by silica gel column chromatography was conveniently exploited by using the same sulfoxide batch more times.

Taking advantage of a recent report pointing out the beneficial effect exerted by the use of tetrabutylammonium salts on the rate of allylation of aldehydes promoted by O-donor ligands,[17] the improvement of our protocol was attempted by performing the reaction in the presence of $(n\text{-}Bu)_4N^+I^-$ under the conditions depicted in Scheme 4 and Table 4.



Scheme 4

Table 4 Asymmetric allylation of aldehydes with allyl trichlorosilane catalyzed by chiral methyl *p*-tolyl sulfoxide in the presence of $(n\text{-}Bu)_4N^+I^-$

Entry	R	9	Yield (%)[a]	e.e. (%)[b]
1	Ph (**7a**)	***S*-9a**	99	60
2	5-NO_2-2-Furyl (**7c**)	***S*-9c**	99	90
3	4-CNC_6H_4 (**7d**	***S*-9d**	76	72
4	5-NO_2-2-Thienyl (**7m**)	***S*-9n**	87	85
5	$PhCH_2CH_2$ (**7g**)	***R*-9g**	80	74
6[c]	$PhCH_2CH_2$ (**7g**)	***S*-9g**	82	–76

[a] All the yields refer to isolated chromatographically pure compounds whose structure were confirmed by analytical and spectroscopic data. [b] e.e.s have been determined by chiral HPLC. [c] The reaction was performed by using *S*-**1**.

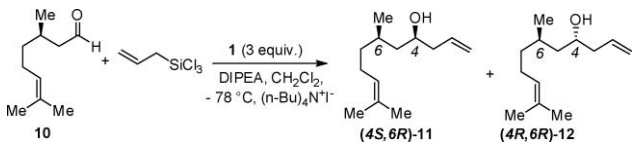
Table 5 Allylation of *R*-citronellal **10** with allyltrichlorosilane catalyzed by methyl *p*-tolyl sulfoxide

Entry	**1**	Yield (%)[a]	(**4*S*,6*R*)-11**/(**4*R*,6*R*)-12** d.r.[b]
1	***rac*-1**	57	58/42
2	***R*-1**	63	33/67
3	***S*-1**	55	75/25

[a] The values reported refer to the overall yield of the diastereoisomeric mixture, whose efficient separation by chromatography proved to be unsuccessful in spite of several attempts. [b] Diastereoisomeric ratios were determined by ^{1}H-NMR and ^{13}C-NMR on the crude mixtures.

Indeed, although no modification of the reaction rate was caused by the additive, the formation of alcohols **9** from aromatic (entries 1, 3), hetero-aromatic (entries 2, 4) and aliphatic aldehydes (entries 5, 6) was usually found to occur with comparable yields and, most of all, slightly enhanced e.e.s (~5%).

Some experiments, performed on the commercially available *R*-citronellal **10** and reported in Scheme 5 on Table 5, pointed out that the stereochemical outcome could be notably affected by the β-situated stereogenic center.



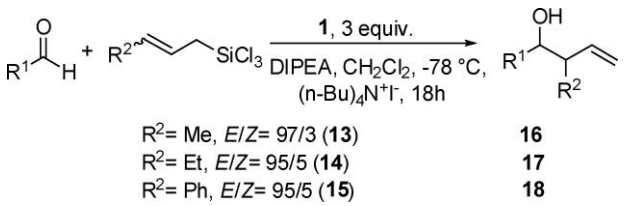
Scheme 5

The usual treatment with allyl trichlorosilane in the presence of *rac*-**1** furnished the allylation product in overall 57% yield and poor diastereoisomeric ratio (58/42 dr).

The employment of enantiopure *R*-**1** and *S*-**1** resulted in the increase of diastereoselectivity and, rather interestingly, reverse diastereoisomeric ratios in entries 2 and 3. The separation of the diastereoisomeric mixtures by chromatographic techniques proved to be very problematic and only in the case of entry 2 a very laborious silica gel chromatography allowed the isolation of the less abundant diastereoisomer, as pure compound, in rather low yield (10%). ^{1}H NMR analysis (400 MHz) of the corresponding *R*-(–)- and *S*-(+)-α-methoxy-(trifluoromethyl)phenylacetic acid esters allowed the assignment of the 4*S*, 6*R* configuration to the less abundant diastereoisomer **11**. The consequent attainment of the predominant product as the (4*R*,6*R*)-**12** isomer disclosed the

deep influence exerted by the stereogenic center, as emphasized by the reversal of the usual sense of asymmetric induction.

Successively, in order to broaden the scope of the protocol, an investigation was aimed to evaluate the reactivity of substituted allyl trichlorosilanes of type **13–15**, Scheme 6, easily accessible by a known procedure[4i,5f] as predominantly *E* geometrical isomers. Preliminarily, the feasibility of the reaction was checked on benzaldehyde **7a** by using dimethyl sulfoxide and *rac*-**1** as activators, and *E*-crotyl silane, **13**, as allylating agent. Rather satisfactorily, the formation of the corresponding alcohol **16a** took place in rather good yields and very high diastereoselectivity in both cases (entries 1 and 2, Table 6). The achievement of the asymmetric version was then attempted under the optimized conditions of Table 4 and, to our delight, the crotylation occurred with good to high yields, high diastereoselectivity and moderate to high e.e.s (up to 87%) with aliphatic aldehydes (entries 12, 13), as well as hetero-aromatic (entries 4, 5 and 8, 9) and, most importantly, both electron-rich and electron-poor aldehydes (entries 3, 6, 7, 10, 11). It has to be noted that the enhanced steric hindrance in proximity of the reaction site of ethyl- and phenyl-substituted trichlorosilanes *E*-**14** and *E*-**15** did not affect either the level of diastereoselectivity or enantioselectivity of the process, although a slight lowering of efficiency was usually observed (respectively, entries 14–19 and 20–25). From a mechanistic point of view, the results reported in Table 6 are in complete agreement with the typical reaction path, already proposed for related Lewis bases, involving closed, chair-like transition states of type A and B characterized by the presence of hypervalent penta- or hexacoordinated silicon species (Fig. 2).[8]



Scheme 6

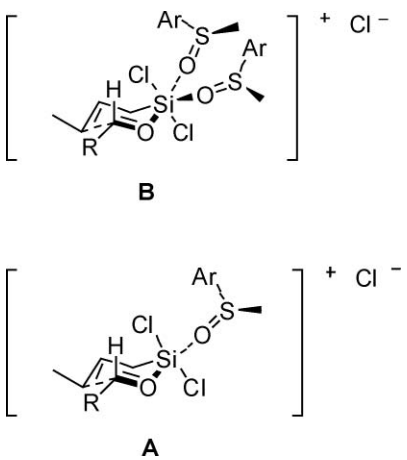


Fig. 2

In the past two decades the detection of non-linear effects (NLE)[18] has proven to be a powerful tool for the elucidation of mechanistic aspects of an asymmetric process, especially as regards

Table 6 Asymmetric allylation of aldehydes with differently substituted allyltrichlorosilanes catalyzed by chiral methyl *p*-tolyl sulfoxide in presence of $(n\text{-Bu})_4N^+I^-$

Entry	R^1	R^2	Prod.	Yield (%)[a]	e.e. (%)[b]	d.r.[c]
1[d]	Ph	Me	**16a**	81	—	3 : 97
2[e]	Ph	Me	**16a**	84	—	3 : 97
3[f]	Ph	Me	**16a**	88	68	3 : 97
4[f]	5-NO_2-2-Furyl	Me	**16b**	70	87	3 : 97
5[g]	5-NO_2-2-Furyl	Me	**16b**	75	–87	3 : 97
6[f]	4-$MeOC_6H_4$	Me	**16c**	71	70	3 : 97
7[g]	4-$MeOC_6H_4$	Me	**16c**	79	–77	3 : 97
8[f]	5-NO_2-2-Thien.	Me	**16d**	77	82	3 : 97
9[g]	5-NO_2-2-Thien.	Me	**16d**	81	–84	3 : 97
10[f]	2-$MeOC_6H_4$	Me	**16e**	67	58	3 : 97
11[g]	2-$MeOC_6H_4$	Me	**16e**	73	–60	3 : 97
12[f]	$C_6H_5CH_2CH_2$	Me	**16f**	67	64	3 : 97
13[g]	$C_6H_5CH_2CH_2$	Me	**16f**	69	–64	3 : 97
14[f]	Ph	Et	**17a**	71	72	5 : 95
15[g]	Ph	Et	**17a**	80	–72	5 : 95
16[f]	5-NO_2-2-Furyl	Et	**17b**	78	86	5 : 95
17[g]	5-NO_2-2-Furyl	Et	**17b**	77	–85	5 : 95
18[f]	4-$MeOC_6H_4$	Et	**17c**	58	74	5 : 95
19[g]	4-$MeOC_6H_4$	Et	**17c**	58	–80	5 : 95
20[f]	Ph	Ph	**18a**	61	68	<1 : 99
21[g]	Ph	Ph	**18a**	64	–70	<1 : 99
22[f]	5-NO_2-2-Furyl	Ph	**18b**	68	97	<1 : 99
23[g]	5-NO_2-2-Furyl	Ph	**18b**	69	–97	<1 : 99
24[f]	4-$MeOC_6H_4$	Ph	**18c**	65	66	<1 : 99
25[g]	4-$MeOC_6H_4$	Ph	**18c**	67	–66	<1 : 99

[a] All the yields refer to isolated chromatographically pure compounds whose structures were confirmed by analytical and spectroscopic data. [b] e.e.s have been determined by chiral HPLC and they are referred to the major diastereoisomer. [c] Diastereoisomeric ratios are referred to as *syn*/*anti* diastereisomers. [d] The reaction was carried out using 3 equiv. of DMSO. [e] The reaction was performed using ***rac*-1**. [f] The reaction was carried out using ***R*-1** as activator. [g] The reaction was carried out by using ***S*-1** as activator.

the recognition of the effective catalytic species. Consequently, benzaldehyde was submitted to allylation under the typical conditions in the presence of variously enantioenriched *R*-**1** and, differently from Liao's[15] finding, a slightly positive deviation was observed (Fig. 3).

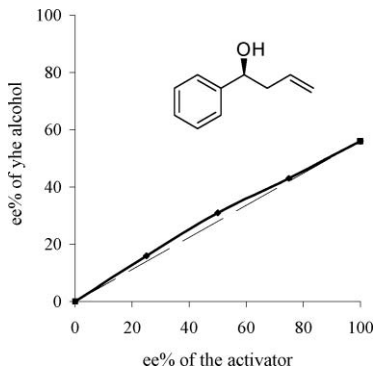


Fig. 3

A more convincing result was obtained by reacting the heteroaromatic aldehyde **7c** with allyltrichlorosilane under the same conditions as benzaldehyde. In fact, as depicted in Fig. 4, a more significant positive deviation could be observed.

Therefore, these results can be reasonably considered to be in agreement with a chair-like transition state involving the

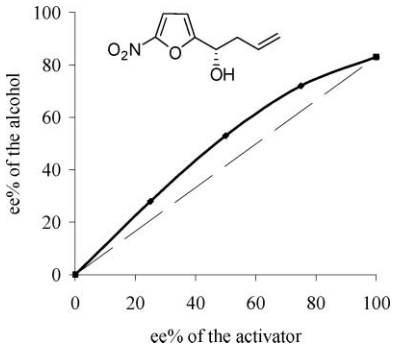


Fig. 4

coordination of two molecules of sulfoxide to the silicon atom and, consequently, the formation of a hexa-coordinate Si intermediate in the stereodetermining step, as reported in Fig. 2B.

Conclusions

An easy and general procedure for the attainment of enantioenriched homoallylic alcohols by the allylation of aldehydes with allyl trichlorosilanes was based on the use of methyl aryl sulfoxides as activators. Very high levels of enantioselectivity could be observed for aromatic and heteroaromatic aldehydes having a strong electron-withdrawing substituent. The use of tetrabutylammonium iodide, as additive, resulted in an appreciable increase of the yields and e.e.s. Furthermore, the protocol was successfully employed in the case of substituted allyl trichlorosilanes, so that the corresponding alcohols could be isolated in high diastereoselectivity and moderate to high enantioselectivity (up to 97% e.e.). Finally, as regards the mechanistic aspects, the detection of (+)-NLE supported the involvement of the coordination of two sulfoxide molecules to the silicon atom in a close chair-like transition state.

Acknowledgements

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Notes and references

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