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Regiospecific and Diastereoselective Crotylation of Aldimines with Crotyltrifluorosilanes Activated by Fluoride Ions[1)]

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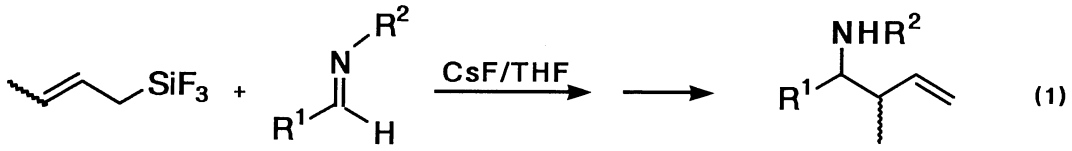
Aliphatic and aromatic aldimines are crotylated in a regiospecific and diastereoselective manner by the reaction with (E)- and (Z)-crotyltrifluorosilanes in the presence of cesium fluoride to give homoallylamines in high yields.

We have recently developed the pentacoordinate allylsilicate strategy, which provides valuable access to the regiospecific and highly stereoselective allylation of various aldehydes, α-hydroxy ketones, and α-keto-carboxylic acids.[2,3)] Much attention has been focused on regio- and stereo-controlled allylation of aldimines as new synthetic methodology for the synthesis of amines.[5)] This led us to investigate pentacoordinate silicate additions to aldimines as a potential route to homoallylamines. The reaction of crotyltrifluorosilanes[6)] with aldimines in the presence of cesium fluoride afforded the corresponding homoallylamines in high yields in a regiospecific manner like the addition to aldehydes, whereas not unexpectedly, rather drastic reaction conditions were required. The diastereoselectivity was not quite high but mostly predictable on the basis of the six-membered cyclic transition states.[7)]



(1)

1E or 1Z

2a, $R^1 = R^2 = Ph$
2b, $R^1 = Ph$, $R^2 = PhCH_2$
2c, $R^1 = Ph$, $R^2 = n\text{-}Pr$
2d, $R^1 = R^2 = n\text{-}Pr$
2e, $R^1 = i\text{-}Pr$, $R^2 = n\text{-}Pr$

3

A typical experimental procedure is as follows: A mixture of N-benzylideneaniline (**2a**, 212 mg, 1.17 mmol), (E)-crotyltrifluorosilane (**1E**, 407 mg, 2.90 mmol), and THF (5 ml) was stirred at room temperature

Table 1. Addition of Crotyltrifluorosilanes to Aldimines in the Presence of Cesium Fluoride[a)]

Entry	Aldimine	Allylsilane	Yield/%[b)]	3[c)]
				Erythro/Threo
1	PhCH=NPh (**2a**)	**1E**	94	71/29
2	**2a**	**1Z**	91	40/60
3	PhCH=NCH$_2$Ph (**2b**)	**1E**	91	73/27
4	**2b**	**1Z**	85	28/72
5	PhCH=NPr-n (**2c**)	**1E**	81	71/29
6	**2c**	**1Z**	75	28/72
7	n-PrCH=NPr-n (**2d**)	**1E**	20[d)]	71/29
8	**2d**	**1Z**	20[d)]	42/58
9	i-PrCH=NPr-n (**2e**)	**1E**	67	77/23
10	**2e**	**1Z**	66	57/43

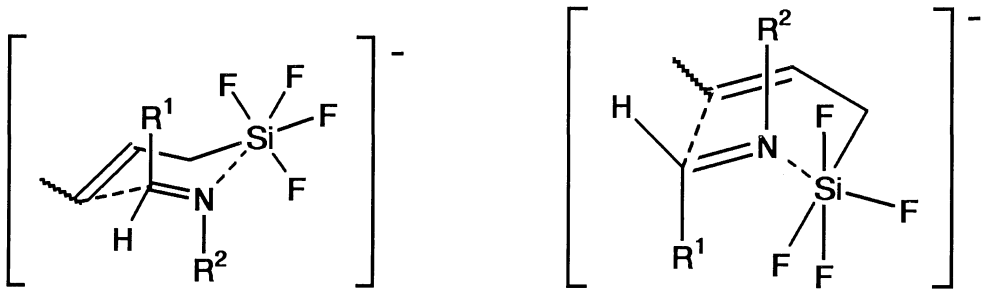
a) All reactions were carried out at room temperature for 15 h in THF. The following molar ratio of reagents was used: allylsilane/aldimine/CsF = 2/1/3-4. b) Isolated yields. c) Diastereomer ratios were determined by capillary GLC using a Shimadzu CBP1 column (25 m x 0.20 mm i.d.). d) Yield determined by GLC.

for 4 h. After addition of CsF (477 mg, 3.14 mmol), the mixture was stirred for further 12 h and then chromatographed on a short silica-gel column. Usual work-up gave pure 2-methyl-N,1-diphenyl-3-butenylamine (**3a**) in 94% yield (261 mg). The erythro/threo ratio of the products was determined to be 71/29.[8)] The results are summarized in Table 1.

The product yields were very high except for the crotylation of imines derived from linear aliphatic aldehydes, **2d**, which gave mainly undesired 2-ethyl-2-hexenal under the reaction conditions (entry 7, 8). In comparison with the similar allylation of aldehydes, the use of a larger amount of cesium fluoride than usual was required for the complete consumption of aldimines.

Expectedly, the crotylation of aldimines was regiospecific where the carbon–carbon bond formation occurred exclusively at the γ–carbon of the crotylsilanes. No regio isomers of the homoallylimines were detected by means of both glc and NMR techniques.

We have reported that the crotylation of various aldehydes (RCHO) with pentacoordinate (E)– and (Z)–crotylsilicates proceeds with very high diastereoselectivity; the facts were explained in terms of the chair–like six–membered transition states where the bulky R group of RCHO occupies preferentially the equatorial position. The preference of the cyclic transition states, rather than the acyclic transition states, was rationalized by the significant Lewis acidity of pentacoordinate silicate silicon in addition to the enhanced nucleophilicity of the allylic γ–carbon. As shown in Table 1, **1E** gave usually erythro–homoallylamines as major products, while **1Z** gave the threo–isomers favorably, irrespective to the substituents at the nitrogen. Although the diastereoselectivity was not quite high, the stereochemistry of the major isomer was predictable on the basis of the preferred conformation of the six–membered cyclic transition states as proposed for the allylation of aldimines with allylboron reagents.[7] Thus, the major product would be obtained via a chair–like transition structure **A**. Lower diastereoselectivity for the crotylation of aldimines than that of aldehydes would be due to the requirement that the bulky R^1 groups in the aldimines are forced to occupy the axial position in the transition structure, since the silicate silicon should coordinate the nitrogen syn to the R^1 group in the trans geometry of the aldimines. The competitive reaction via a boat–like transition–structure **B** leads to the minor product.



A B

Rather unexpected diastereoselectivity was found in the reaction of **1Z** with N–isobutylidenepropylamine which gave the erythro–isomer as a major product. Because in the transition state, both chair and boat cyclohexane–like transition states are energetically disfavored, the third route via the acyclic transition state may contribute to give the erythro product preferably. There is much yet to be understood about the controlling factors of the stereochemical outcome of the crotylation of aldimines via the cyclic transition states. It may be possible to control the diastereoselectivity of crotylation of aldimines by modifying the substituents at the nitrogen.[8]

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6) (E)- and (Z)-crotyltrifluorosilanes used in the present work were prepared in the purity of more than 99 %, respectively, by using the reported methods.[2] The E/Z isomer ratios were determined by GLC with capillary column.

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8) The products were identified by using ^{1}H and ^{13}C NMR and low- and high-resolution mass spectroscopy. The erythro/threo ratios were determined by capillary GLC.

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