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Stereohomogeneous Synthesis of (E)- and (Z)-Crotyltrifluorosilanes and Highly Stereoselective Allylation of Aldehydes[1]

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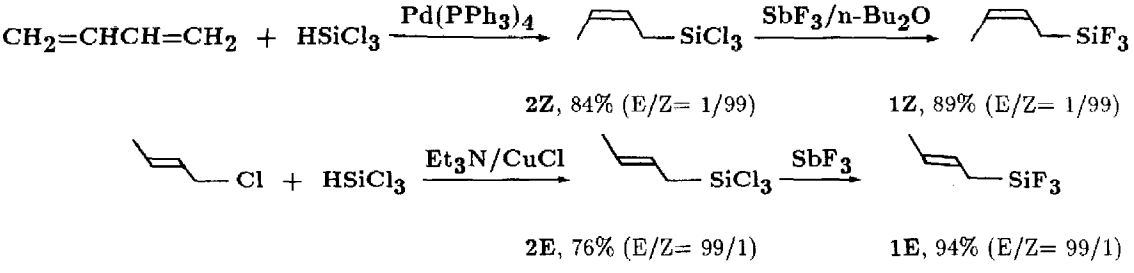
Summary: Stereohomogeneous (E)- and (Z)-crotyltrifluorosilanes were prepared and used for the highly diastereoselective synthesis of threo- and erythro-β-methylhomoallyl alcohols, respectively, from aldehydes in the presence of fluoride ions. The mechanism of the reaction was discussed.

Recently, we have reported that allyltrifluorosilanes react with various aldehydes chemoselectively in the presence of fluoride ions to give the corresponding homoallyl alcohols in high yields.[2] The regiospecificity and the high diastereoselectivity in the reaction with prenyl- and crotylsilanes have suggested that the allylation proceeds through a six-membered cyclic transition state including the complexation of carbonyl oxygen to the silicon of pentacoordinate allyltetrafluorosilicate generated in advance, on the analogy of the allylation with isolated pentacoordinate allylsilicates[3] as well as with allylboronates.[4]

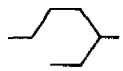
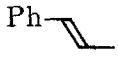
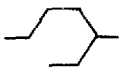
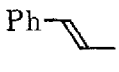
Stereohomogeneous synthesis of (E)- and (Z)-crotyltrifluorosilanes is highly desired in view of the importance of the stereocontrolled synthesis of β-methylhomoallyl alcohols[5] as well as elucidation of the detailed mechanism. We wish herein to report the satisfactory synthesis of each isomer of crotyltrifluorosilanes with rather convenient procedure together with the stereochemistry of the reaction with various aldehydes in the presence of fluoride ions. The crotyltrifluorosilanes are configurationally very stable and storable for a couple of months at 0 °C without any change of the purity as expected from the low tendency to the metallotropic rearrangement.[6] The present reagent system would thus fulfill almost all conditions for stereoselective crotylation.[4] (E)- and (Z)-crotyltrifluorosilanes (**1E**, **1Z**) were prepared with more than 99% purity through the following synthetic scheme.



(E)-Crotyltrichlorosilane (**2E**) was prepared by a similar procedure to the reported by Furuya and Sukawa:[7] a mixture of (E)-crotyl chloride[8] (5.44 g, 60.0 mmol), trichlorosilane (11.68 g, 86.2 mmol), and ether (10 ml) was added to an ether suspension (30 ml) of

copper(I) chloride (200 mg, 2.0 mmol) and triethylamine (7.20 g, 71.1 mmol) at room temperature. After being stirred for 1.5 h, the reaction mixture was filtered. Distillation of the filtrate gave **2E** in 76%. The ratio of (E)- to (Z)-isomers was determined to be 99/1 by glc analysis. (Z)-Crotyltrichlorosilane (**2Z**) was prepared by using the method of Tsuji et al.[12] with modifications. Thus, in an argon purged autoclave (100 ml) were placed trichlorosilane (56 g, 0.413 mol) and $Pd(PPh_3)_4$ (0.930 g, 1.04 mmol). After introducing butadiene (34 ml, 0.40 mol) to the vessel at −78 °C, stirring for 6 h and then usual work-up gave **2Z** in 84% yield. Glc analysis showed the E/Z ratio to be 0.9/99.1. The reaction temperature was of key importance to obtain the high stereoselectivity; the E/Z ratio of the products was found to be 9/91 at 100 °C. Both (E)- and (Z)-crotyltrifluorosilanes were prepared by the Sharpe's procedure[13] in 94 and 89% yields, respectively: the chlorosilanes were treated with anhydrous antimony trifluoride and then distilled directly from the reaction flask. The isomeric purity was transferred intact during the fluorination, while the use of di-n-butyl ether as a solvent was important for the preparation of the pure (Z)-isomer. Fluorination using zinc fluoride[14] gave less satisfactory results; the yields of the trifluorosilanes were usually 30-40%.

Table 1. Diastereoselective Addition of Crotyltrifluorosilanes to Aldehydes in the presence of Cesium Fluoride.

Aldehyde	Allylsilane	Reaction Conditions	Yield/%[a]	**3t**/**3e**[b]
PhCHO	**1E**	0 °C, 1 h	92	99/1
n-C_8H_{17}CHO	**1E**	rt, 4 h	96	99/1
	**1E**	rt, 8 h	68	99/1
	**1E**	rt, 8 h	77	98/2
PhMeCHCHO	**1E**	0 °C, 1.5 h	91	99/1[c]
PhCHO	**1Z**	0 °C, 1 h	96	1/99
n-C_8H_{17}CHO	**1Z**	rt, 5 h	89	2/98
	**1Z**	rt, 12 h	90	10/90
	**1Z**	rt, 14 h	77	3/97
PhMeCHCHO	**1Z**	rt, 2 h	92	10/90[d]

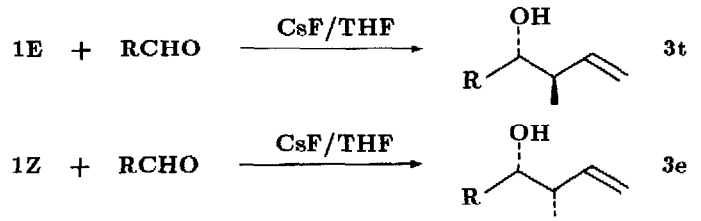
a. The yield was determined after isolation with TLC or Kugel-rohr distillation.

b. The diastereomer ratio was determined by means of capillary glc.

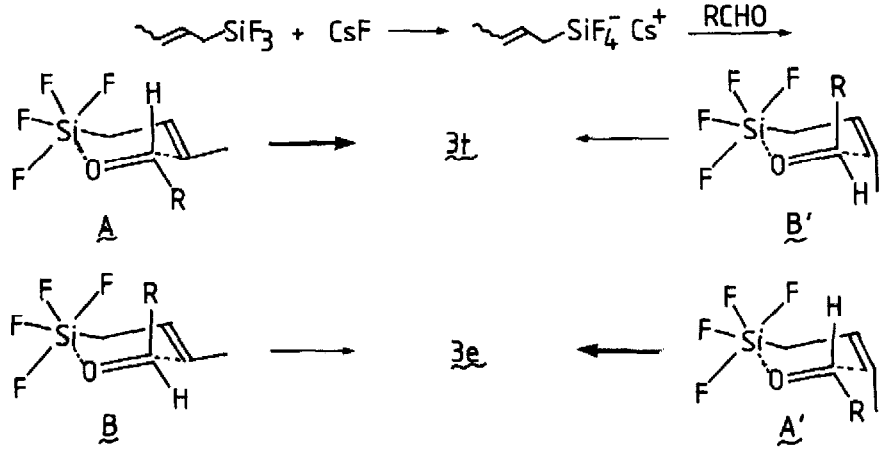
c. The Cram/anti-Cram isomer ratio was 81/19 for **3e**.

d. The Cram/anti-Cram isomer ratio was 80/20 for **3t**.

As shown in Table 1, crotylation of aldehydes was achieved in high diastereoselectivity as well as in high isolated yields by using the similar reaction conditions as previously reported.[2]



As previously suggested,[2,3] the present allylation is best explained to occur via cyclic six-membered transition states having chair conformations The product stereochemistry is properly related if the residue R of the aldehyde occupies exclusively an equatorial position (**A** and **A'**). This would be caused mainly by 1,3-interaction with an apical fluorine atom on the hexacoordinate silicon. The excellent diastereoselectivity observed in the E-series may be explained additionally by taking the difference of the number of gauche interactions between R-equatorial (**A**) and R-axial (**B**) conformations into consideration: **A** has an R/Me gauche interaction while **B** has two gauche interactions, R/Me and R/vinyl. On the other hand, the stereoselectivity was slightly diminished in the Z-series, especially when a sterically hindered aldehyde like 2-ethylhexanal and 2-phenylpropanal was used. The diminished selectivity has also been observed in the case of crotylation with (Z)-crotylboronate and the origin was attributed to the higher reactivity of the contaminated E-isomer.[4]



However, this is not the case at least in the present reaction where the sterically pure (Z)-crotyl reagent was used. The decreased selectivity in the Z-series may be originated from the following reasons. Two gauche interactions are involved in both **A'** and **B'** : R/Me and Me/O in the former and R/vinyl and Me/O in the latter. Thus, the energy difference

between the two transition-state conformations may be intrinsically smaller in the Z-series than in the E-series. The sum of the gauche energies may be even smaller in **B'** than in **A'** when the R group is bulky, lowering the diastereoselectivity. The possibility that the boat-like transition state can also contribute in the Z-series may not be precluded, though.[5c] The Cram/anti-Cram selectivity was observed to be rather normal in the reactions with 2-phenylpropanal (Table 1).[5]

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8. (E)-Crotyl chloride was prepared by the reduction of crotonaldehyde with $LiAlH_4$ in ether,[9] followed by the reaction with PCl_3-pyridine.[10] (E)-Crotyl chloride thus obtained was separated by fractional distillation from the concomitant 3-chloro-1-butene (about 10%); the yield of (E)-crotyl chloride was 49% from the purified (E)-crotyl alcohol. Because commercially available crotonaldehyde contains usually 2-5% of the (Z)-isomer, the alcohol obtained by the reduction should be purified isomerically by treating with 3,5-dinitrobenzoyl chloride[11] followed by recrystallization of the benzoate in acetone and/or ethanol, and then alkaline hydrolysis: by this procedure, the (E)-crotyl alcohol was obtained in more than 99% purity.
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