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REGIOSPECIFIC AND HIGHLY STEREOSELECTIVE ALLYLATION OF ALDEHYDES WITH ALLYLTRIFLUOROSILANE ACTIVATED BY FLUORIDE IONS.[1]

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Summary: Allyltrifluorosilane/CsF systems form pentacoordinate allylsiliconates which undergo chemoselective, regiospecific and highly stereoselective allylation of aldehydes, presumably via six-membered cyclic transition states.

Previously we have reported that an allylic nucleophilic species is generated readily from trimethylallylsilane by the catalysis with fluoride ions.[2] The reaction provides a versatile method of introducing an allyl group into carbonyl compounds.[3] However, the exclusive regiospecificity of allylation, which is characteristic of the Lewis acid-catalyzed allylation with allylsilanes,[4] disappeared. Herein, we report a novel allylation of aldehydes with allyltrifluorosilanes in the presence of fluoride ions, which is not only useful as chemoselective, regiospecific and highly stereoselective allylation but affords an interesting mechanistic probe for the fluoride-catalyzed reaction of allylsilanes.[5]

$$R^1R^2C{=}CHCH_2SiF_3 \;+\; R^3CHO \xrightarrow{F^-/THF} H_2C{=}CHCR^1R^2\underset{\displaystyle OH}{CH}R^3 \qquad (1)$$

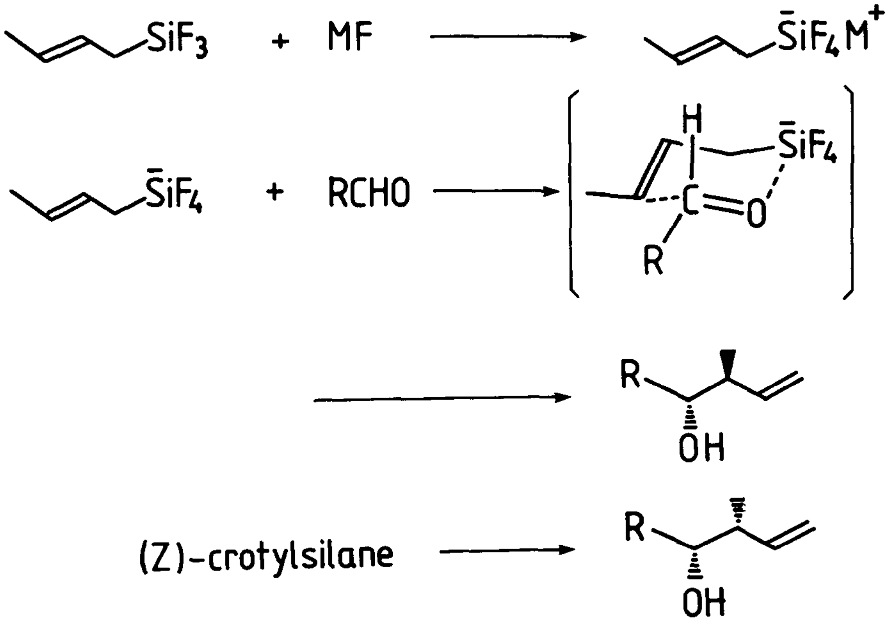
Typically, 2,2-dimethyl-1-phenylbut-3-en-1-ol was prepared by the following procedure: a mixture of benzaldehyde (1.00 mmol), prenyltrifluorosilane (2.01 mmol), and cesium fluoride (2.36 mmol) in THF (5ml) was stirred at room temperature for 16 h. After methanolysis with MeOH-HCl of the reaction mixture, the solvent was evaporated and the residue was purified by TLC affording 2,2-dimethyl-1-phenylbut-3-en-1-ol in 96 % yield.

The results of allylation of various aldehydes with allyltrifluorosilanes and cesium fluoride are shown in Table 1. The allylation was regiospecific where the carbon-carbon bond formation occurred exclusively at the γ-carbon of allylsilanes. No other regio-isomers were detected in all the cases in Table 1. Although allylation of carbonyl compounds with allylsilanes and Lewis acids has been well established as a procedure for the regiospecific preparation of homoallyl alcohols,[5] the yields are often lowered by the undesired side reactions.[6,7] Advantageously, the present allylation can be carried out under very mild and neutral conditions affording the homoallyl alcohols in excellent yields. The use of allyltrifluorosilanes[8] is essential for the successful regiospecific allylation. Thus, prenylmethyldifluorosilane reacted with benzaldehyde under more rigorous conditions to afford a mixture of the regioisomers of homoallyl alcohols, 4-methyl-1-phenylpent-3-ene-1-ol and 2,2-dimethyl-1-phenylbut-3-en-1-ol in the yields of 37 and 45 %, respectively. Prenyltrimethylsilane and prenyldimethylfluorosilane did not react with benzaldehyde in the presence of cesium fluoride even by heating for a prolong time. Tetrabutylammonium fluoride can be used similarly as a fluoride ion source, while potassium fluoride was less effective.

There has been extensively investigated the stereochemical control in addition of crotylmetals to aldehydes from both mechanistic and synthetic view points.[12] Recently, reactions of crotyltrimethylsilanes with aldehydes in the presence of Lewis acids have been found to proceed via acyclic transition states to give erythro products regardless of the stereochemistry of the starting crotylsilanes.[13] In contrast to this, (E)- and (Z)-crotyltrifluorosilane/CsF systems showed high threo- and erythro-selectivity, respectively, in the addition to aldehydes. As shown in Table 1, the ratio of diastereomers was found to be actually the same as the starting E/Z ratio of crotylsilanes. A similar selectivity was found for the crotylation of 2-ethylbutanal.[14] The allyltrifluorosilane/CsF systems are highly promising as synthetic reagents for diastereospecific allylation of aldehydes.

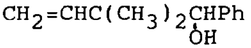
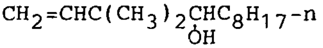
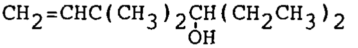
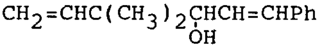
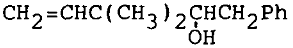
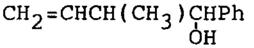
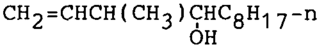
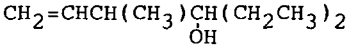
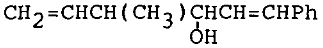
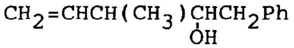
The present reaction may be rationalized by the following mechanism illustrated in Scheme 1, as suggested by the similarity of the diastereoselection to the allylboronate addition.[15] Thus, the nucleophilic attack of a

Scheme 1. Mechanism of the Crotylation



fluoride ion to an allyltrifluorosilane may afford rather stable pentacoordinate allylsiliconate which in turn reacts with an aldehyde via a six-membered cyclic transition state. This may be caused by the significant Lewis acidity of the tetrafluorosiliconate[16] and the enhanced nucleophilicity[17] of the γ-carbon of the allylsiliconate.[18]

Table 1. Reaction of Allyltrifluorosilanes with Aldehydes in the Presence of Cesium Fluoride.[a]

Allylsilane	Aldehyde	Reaction Conditions	Products (% Yield)
$(CH_3)_2C{=}CHCH_2SiF_3$ (**1a**)	PhCHO	rt, 16 h	 $CH_2{=}CHC(CH_3)_2\underset{OH}{C}HPh$ (96)
1a	$n\text{-}C_8H_{17}CHO$	rt, 24 h	 $CH_2{=}CHC(CH_3)_2\underset{OH}{C}HC_8H_{17}\text{-}n$ (93)
1a	$(CH_3CH_2)_2CHCHO$	reflux, 36 h	 $CH_2{=}CHC(CH_3)_2\underset{OH}{C}H(CH_2CH_3)_2$ (92)
1a	PhCH=CHCHO	rt, 28 h	 $CH_2{=}CHC(CH_3)_2\underset{OH}{C}HCH{=}CHPh$ (94)
1a	$PhCH_2CHO$	rt, 16 h	 $CH_2{=}CHC(CH_3)_2\underset{OH}{C}HCH_2Ph$ (90)
$CH_3CH{=}CHCH_2SiF_3$ (**1b**, E/Z= 90/10)	PhCHO	rt, 16 h	 $CH_2{=}CHCH(CH_3)\underset{OH}{C}HPh$ (93) (**2**, threo/erythro= 88/12)
1b (E/Z= 21/79)	PhCHO	rt, 20 h	**2** (93) (threo/erythro= 19/81)
1b (E/Z= 90/10)	$n\text{-}C_8H_{17}CHO$	rt, 24 h	 $CH_2{=}CHCH(CH_3)\underset{OH}{C}HC_8H_{17}\text{-}n$ (90)[e]
1b (E/Z= 90/10)	$(CH_3CH_2)_2CHCHO$	rt, 24 h	 $CH_2{=}CHCH(CH_3)\underset{OH}{C}H(CH_2CH_3)_2$ (88) (**3**, threo/erythro= 92/8)
1b (E/Z= 21/79)	$(CH_3CH_2)_2CHCHO$	rt, 20 h	**3** (84) (threo/erythro= 27/73)
1b (E/Z= 90/10)	PhCH=CHCHO	rt, 28 h	 $CH_2{=}CHCH(CH_3)\underset{OH}{C}HCH{=}CHPh$ (93)[e]
1b (E/Z= 90/10)	$PhCH_2CHO$	rt, 6 h	 $CH_2{=}CHCH(CH_3)\underset{OH}{C}HCH_2Ph$ (92)[e]

a. Following molar ratio of the starting materials was used; an aldehyde: an allyltrifluorosilane: cesium fluoride= 1: 2.0: 2.3.

b. Yield after isolation by Kugelrohr distillation or preparative TLC.

c. The ratio of diastereomers was determined by ^1H nmr analysis.

d. The ratio of diastereomers was determined by glc analysis.

e. The ratio of diastereomers was not determined.

References and Notes

1) Chemistry of Organosilicon Compounds 234.
2) A. Hosomi, A. Shirahata, and H. Sakurai, Tetrahedron Lett., 3043 (1978).
3) G. Majetich, A. Casares, D. Chapman, and M. Behnke, J. Org. Chem., **51**, 1745 (1986) and references cited therein.
4) (a) A. Hosomi and H. Sakurai, Tetrahedron Lett., 1295 (1976); (b) H. Sakurai, Pure and Appl. Chem., **54**, 1 (1982).
5) The mechanistic details of the allylation of carbonyl compounds will be reported elsewhere.
6) A. Hosomi and H. Sakurai, Tetrahedron Lett., 2589 (1978).
7) L. Coppi, A. Ricci, and M. Toddei, Tetrahedron Lett., **28**, 973 (1987).
8) Allyltrifluorosilanes used here were prepared from the corresponding allyltrichlorosilanes by the reaction with $ZnF_2 \cdot 4H_2O$[9] in acceptable yields. Prenyl- and (E)-rich crotyltrichlorosilanes were prepared by the reaction of the corresponding allyl chlorides with trichlorosilane-NEt_3 in the presence of copper(I) chloride.[10] (Z)-rich crotyltrichlorosilane was prepared by hydrosilylation of butadiene with trichlorosilane catalyzed by $Pd(II)(PhCN)_2Cl_2$.[11]
9) A. E. Newkirk, J. Am. Chem. Soc., **68**, 2736 (1946).
10) N. Furuya and T. Sukawa, J. Organomet. Chem., **96**, C1 (1975).
11) V. P. Yurev, I. M. Salimgareeva, O. Zh. Zhebarov, and G. A. Tolstikov, J. Gen. Chem. U. S. S. R., **46**, 372 (1976).
12) For reviews, see (a) P. A. Bartlett, Tetrahedron, **36**, 3 (1980); (b) Y. Yamamoto and K. Maruyama, Heterocycles, **18**, 357 (1982); (c) R. W. Hoffman, Angew. Chem. Int. Ed. Engl., **21**, 555 (1982).
13) T. Hayashi, K. Kabeta, I. Hamachi, and M. Kumada, Tetrahedron Lett., **24**, 2865 (1983).
14) Since the observed diastereomer ratio would be influenced by the lower reactivity of (Z)-crotylsilane than the (E)-isomer to 2-ethylbutanal, the erythro- and threo-selectivity of the (Z)- and (E)-isomers, respectively, may actually be much higher than that expected by the observed diastereomer ratio.
15) R. W. Hoffman and H. J. Zeiss, J. Org. Chem., **46**, 1309 (1981).
16) (a) R. Marat and A. F. Janzen, Can. J. Chem., **55**, 3845 (1977); (b) I. Wharf and M. Onyszchuk, *ibid.*, **50**, 3450 (1972).
17) ^{13}C NMR analyses of the isolated allylsiliconates[3] suggest that a pentacoordinate silicon atom may be more electron donating to a π system than a tetravalent silicon atom.
18) We have recently isolated the first pentacoordinate allylsiliconates and found that they actually react with aldehydes in the similar manner with the present allytrifluorosilane/fluoride ion systems; M. Kira, K. Sato, and H. Sakurai, to be published.

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