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FLUORIDE ION-PROMOTED ISOMERIZATION OF METHYL-SUBSTITUTED ALLYLSILANES. REGIOSELECTIVE SYNTHESES OF ALLYLSILANES

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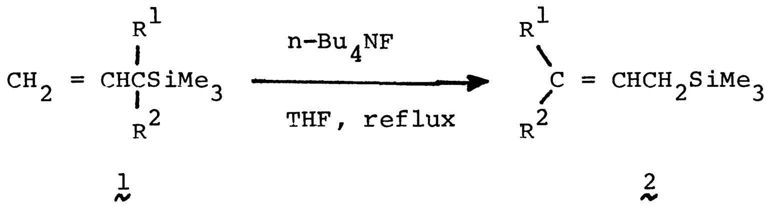
Fluoride ion-catalyzed isomerization of methyl-substituted allylsilanes is reported. In the reaction, a regioisomer of allylsilanes, in which the silicon atom binds to the less substituted carbon atom of the allylic group, is obtained. Accordingly, the reaction is useful as a new route to regioselective synthesis of allylsilanes.

Recently much attention has been focused on the application of allylsilanes to organic synthesis.[1)] Among various synthetic applications reported hitherto, the most interesting one involves the allyl transfer reaction promoted by Lewis acid to an electrophilic carbon center, with regiospecific transposition of the allylic part.[1a-g)] However, to date, regioselective synthesis of alkyl-substituted allylsilanes, neccessary for this purpose, has not been fully developed.[2)] We report in this paper a convenient procedure for the preparation of a regioisomer of methyl-substituted allylsilanes, in which the silicon atom is bonded to the less substituted carbon atom of the allylic group.

During the course of the investigation of the allyl anion generated by the fluoride ion-catalyzed reaction of allylsilanes,[3)] it has been found that 1-methyl-2-propenyltrimethylsilane (1a : $R^1 = H$, $R^2 = Me$) can be converted quantitatively to 2-butenyltrimethylsilane (2a : $R^1 = H$, $R^2 = Me$; E : Z = 34 : 66) by heating at reflux in the presence of a catalytic amount of tetra-n-butylammonium fluoride (TBAF) in tetrahydrofuran. (ep. 1) Similarly, 1,1-dimethyl-2-propenyltrimethylsilane (1b : $R^1 = R^2 = Me$)[2a)] isomerized completely to a sterically less hindered regioisomer (2b : $R^1 = R^2 = Me$).

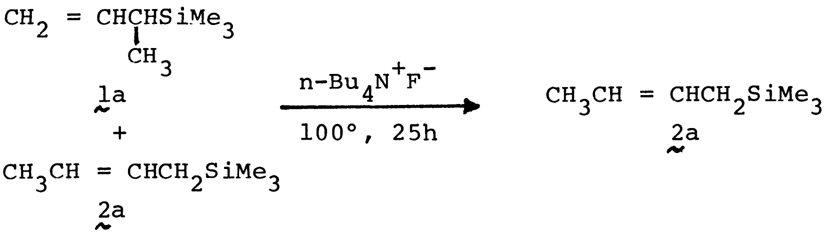


$$CH_2=CH\overset{R^1}{\underset{R^2}{C}}SiMe_3 \xrightarrow[\text{THF, reflux}]{n\text{-}Bu_4NF} \overset{R^1}{\underset{R^2}{\;}}C=CHCH_2SiMe_3 \qquad (1)$$

1 2

These results, therefore, open a new route to practical preparation of one regioisomer of alkyl-substituted allylsilanes. In these reactions, a thermodynamically more stable isomer is obtained, where the silicon atom binds to the less substituted carbon atom in the allylic part. Recently, we have reported regioselective preparation of allylsilanes of the type 1 such as 1,1-dimethyl-2-propenyltrimethylsilane (1b), a useful reagent of prenylation.[2a)] Therefore, it is now possible to prepare each isomer selectively by a combination of these two methods.

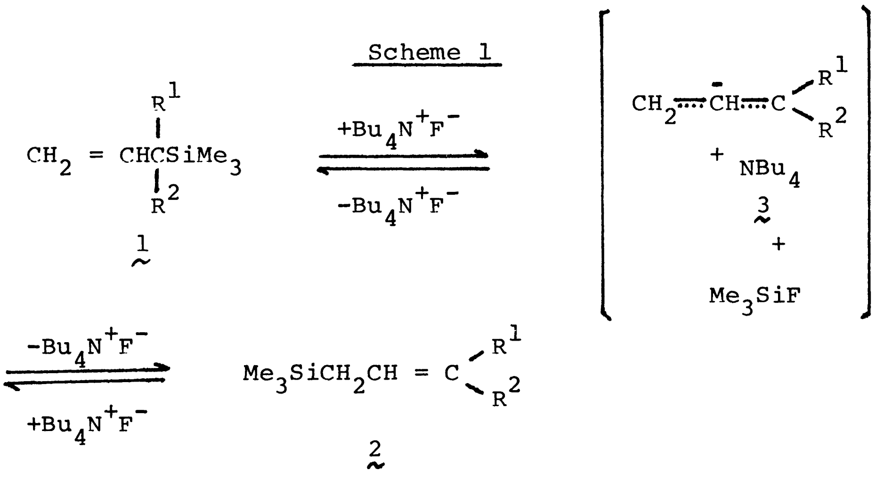
In general, two regioisomers with respect to the allylic group are obtained as a mixture from the reaction of an allylic Grignard reagent with chlorosilanes. Usually separation of these isomers is tedious and laborious distillation or glc collection through a column packed with benzyl cyanide-silver nitrate on a support is required for isolation of each isomer.[4)] However, isolation of one regioisomer was indeed realized without such operations by the present procedure. Thus, a 48 : 52 mixture of two regioisomers, 1a and 2a (E : Z = 58 : 42), which was prepared readily from the reaction of trimethylchlorosilane with the Grignard reagent of 2-butenylchloride, was converted quantitatively to one regioisomer 2a (E : Z = 36 : 64) by the reaction catalyzed by TBAF at 100°C for 25 h. (eq. 2)[5)]



$$\begin{array}{c} CH_2=CH\underset{CH_3}{C}HSiMe_3 \\ \text{1a} \\ + \\ CH_3CH=CHCH_2SiMe_3 \\ \text{2a} \end{array} \xrightarrow[100°,\ 25h]{n\text{-}Bu_4N^+F^-} \begin{array}{c} CH_3CH=CHCH_2SiMe_3 \\ \text{2a} \end{array} \qquad (2)$$

It appears reasonable that an allyl anionic species 3 (Scheme 1) plays an important role in the isomerization reaction, from the facts described above, and, in addition, from the result of a crossover experiment between 2-butenyltrimethylsilane and allylethyldimethylsilane, in which two corresponding crossover products are obtained by heating an equimolar mixture of these allylsilanes in the presence of TBAF under a similar condition. A recent finding in our laboratory on the fluoride ion-catalyzed allyl transfer reaction to the carbonyl compounds also supports the intermediacy of the allyl anion.[3)]

Scheme 1



Synthesis of 2-butenyltrimethylsilane (**2a**) is an illustrative operation of these reactions. A 48 : 52 mixture (3.65 g) of 1-methyl-2-propenyltrimethylsilane (**1a**) and 2-butenyltrimethylsilane (**2a**) prepared from the reaction of trimethylchlorosilane and the Grignard reagent of 1-chloro-2-butene according to our previous paper,[4b)] was heated to 100°C for 25 h in a sealed tube in the presence of TBAF (100 mg, 0.38 mmol). Flash distillation of the reaction mixture gave 3.42 g (26.7 mmol) of **2a** (E : Z = 36 : 64) in 94 % yield.

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References and Notes

1) Recent studies in this area can be traced through the following references: a) A. Hosomi and H. Sakurai, J. Am. Chem. Soc., 99, 1673 (1977); b) idem, Tetrahedron Lett., 1295 (1976); c) A. Hosomi, H. Hashimoto, and H. Sakurai, J. Org. Chem., 43, in press (1978); d) P. -J. Pillot, J. Dunogues, and R. Calas, Tetrahedron Lett., 1871 (1976); e) G. Deleris, J. Dunogues, and R. Calas, ibid., 2449 (1976); f) B. -W. Au-Yueng and I. Fleming, Chem. Commun., 79 (1977); g) idem, ibid., 81 (1977); h) I. Ojima, Y. Miyazawa, and M. Kumagai, Tetrahedron Lett., 1375 (1977); i) K. Itoh, M. Fukui, and Y. Kurachi, Chem. Commun., 500 (1977); j) D. Ayalo-Chass, E. Ehlinger, and P. Magnus., ibid., 772 (1977).

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3) A. Hosomi, A. Shirahata, and H. Sakurai, Tetrahedron Lett., in press (1978).

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5) The E/Z isomer ratio depends strongly on the course of the reaction. It has been reported that the reaction of 2-butenyllithium, prepared by transmetalation from the corresponding stannane, with trimethylchlorosilane gave **2**a (E : Z = 3 : 2).[2c]

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