

CLEAVAGE OF THE SILICON-VINYL CARBON BOND BY FLUORIDE ION:

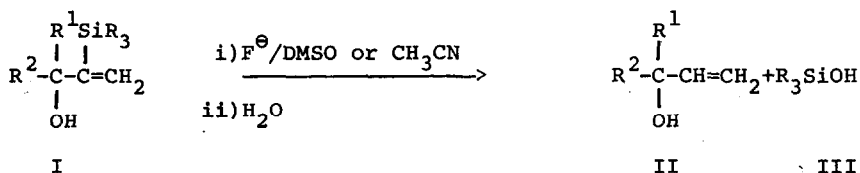
AN UNEXPECTED β -HYDROXY EFFECT

T.H. Chan* and W. Mychajlowski
 Department of Chemistry, McGill University
 Montreal, Quebec, Canada

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While the cleavage of silicon-alkynyl carbon bond can be accomplished by a host of nucleophiles including hydroxide¹ and fluoride ions², the corresponding cleavage of silicon-vinyl carbon bond by nucleophilic displacement at silicon is extremely rare³. Thus, vinyltrimethylsilane is stable towards potassium fluoride in refluxing ethanol² and the compound $\text{CH}_3\text{CH}=\text{CHSiH}_3$ is not cleaved by hot aqueous alkali⁴.

In the course of our investigation on the synthetic utility of vinylsilanes^{5,6}, we have prepared a number of compounds of general structure I. We were surprised to find that, when compounds I were treated with fluoride ion in a dipolar solvent followed by quenching with water, cleavage of the silicon-vinyl carbon bonds occurred with the formation of the corresponding allyl alcohols II and the triorganosilanol III. (See Table).



The fluoride ion used can be tetraethyl or tetramethylammonium fluoride or some inorganic salts such as potassium or cesium fluoride. The solvent can be dimethylsulfoxide or acetonitrile. That the cleavage reaction is unique to the fluoride ion can be demonstrated by the resistance of Ia towards tetraalkyl-

ammonium bromide, iodide or chloride under identical conditions.

The other substituents (R) on the silicon seem to influence the reaction to some extent. The triphenylsilyl group was cleaved at a faster rate than the trimethylsilyl group.

The presence of the hydroxy group at the β -carbon is however essential for the reaction to occur. Neither vinyltriphenylsilane nor vinyltrimethylsilane were cleaved under similar or more forcing conditions. When the β -hydroxy group of Ia was acetylated by acetic anhydride, compound IV could be obtained. IV was stable towards potassium fluoride in dimethylsulfoxide up to 100°. On the other hand, when the hydroxy group was converted to a better leaving group, e.g. the trifluoroacetate V or the chloride VI, fluoride ion promoted an elimination reaction to occur with the formation of the corresponding allene⁵.

The specific role of the β -hydroxy group in this cleavage reaction can be further demonstrated by comparing compound Ie with VII. While Ie could be cleaved by fluoride ion to allyl alcohol, VII, which has a γ -hydroxy group, was completely stable under those reaction conditions.

The cleavage reaction cannot be extended to silicon-carbon bond where the carbon is saturated (See Table, entries VIII and IX).

In the absence of quantitative studies, it is difficult to be definite about the mechanism of this cleavage reaction. At the moment, we favor the cyclic transition state X to account for the course of the reaction. The occurrence of the cleavage reaction depends then on the cooperative effect of the following factors: (1) the strong hydrogen bond between hydroxy groups and the fluoride ion, (2) the favorable entropy of a six-membered ring, (3) the affinity of fluoride ion for silicon and (4) the vinyl carbanion as the leaving group.

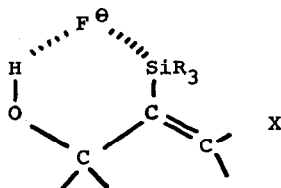
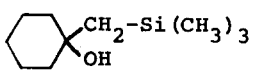


Table: Reaction of Organosilicon Compounds with Fluoride Ion

Starting Material	Reaction Conditions reagent/solvent/temp./time	Products (% isolated yield)
I. $\begin{array}{c} \text{R}^2 \\ \\ \text{R}^1-\text{C}-\text{C}=\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{SiR}_3 \end{array}$		II. $\begin{array}{c} \text{R}^2 \\ \\ \text{R}^1-\text{C}-\text{CH}=\text{CH}_2 \\ \\ \text{OH} \end{array}$
Ia: $\text{R}=\text{R}^1=\text{C}_6\text{H}_5, \text{R}^2=\text{H}$	$\text{Me}_4\text{NF}/\text{CH}_3\text{CN}/\text{r.t.}/2\text{h}$	IIa: $\text{R}^1=\text{C}_6\text{H}_5, \text{R}^2=\text{H}$ (80)
Ib: $\text{R}=\text{R}^1=\text{R}^2=\text{C}_6\text{H}_5$	$\text{Et}_4\text{NF}/\text{DMSO}/\text{r.t.}/2\text{h}$	IIb: $\text{R}^1=\text{R}^2=\text{C}_6\text{H}_5$ (65)
Ic: $\text{R}=\text{C}_6\text{H}_5, \text{R}^1=\text{n}-\text{C}_{10}\text{H}_{21}, \text{R}^2=\text{H}$	$\text{Et}_4\text{NF}/\text{DMSO}/\text{r.t.}/2\text{h}$	IIc: $\text{R}^1=\text{n}-\text{C}_{10}\text{H}_{21}, \text{R}^2=\text{H}$ (68)
Id: $\text{R}=\text{CH}_3, \text{R}^1=\text{C}_6\text{H}_5, \text{R}^2=\text{H}$	$\text{Me}_4\text{NF}/\text{CH}_3\text{CN}/80^\circ/3\text{h}$	IIId: $\text{R}^1=\text{C}_6\text{H}_5, \text{R}^2=\text{H}$ (65)
Ie: $\text{R}=\text{CH}_3, \text{R}^1=\text{R}^2=\text{H}$	$\text{KF}/\text{DMSO}/150^\circ/2\text{h}$	IIe: $\text{R}^1=\text{R}^2=\text{H}$ (>90a)
If: $\text{R}=\text{CH}_3, \text{R}^1=\text{CH}_3,$ $\text{R}^2=(\text{CH}_2)_2-\text{CH}=\text{C} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$	$\text{Et}_4\text{NF}/\text{CH}_3\text{CN}/80^\circ/2\text{h}$	IIIf: $\text{R}^1=\text{CH}_3,$ $\text{R}^2=(\text{CH}_2)_2-\text{CH}=\text{C} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$ (52)
Ig: $\text{R}=\text{CH}_3, \text{R}^1, \text{R}^2=(\text{CH}_2)_5$	$\text{Et}_4\text{NF}/\text{CH}_3\text{CN}/80^\circ/2\text{h}$	IIIg: $\text{R}^1, \text{R}^2=(\text{CH}_2)_5$ (64)
IV. $\begin{array}{c} \text{C}_6\text{H}_5\text{CH}-\text{C}=\text{CH}_2 \\ \quad \\ \text{OAc} \quad \text{Si}(\text{C}_6\text{H}_5)_3 \end{array}$	$\text{KF}/\text{DMSO}/100/2\text{h}$	No reaction
V. $\begin{array}{c} \text{C}_6\text{H}_5\text{CH}-\text{C}=\text{CH}_2 \\ \quad \\ \text{CF}_3\text{C}=\text{O} \quad \text{Si}(\text{C}_6\text{H}_5)_3 \end{array}$	$\text{Et}_4\text{NF}/\text{CH}_3\text{CN}/\text{r.t.}/2\text{h}$	$\text{C}_6\text{H}_5\text{CH}=\text{C}=\text{CH}_2$ (60)
VI. $\begin{array}{c} \text{C}_6\text{H}_5\text{CH}-\text{C}=\text{CH}_2^b \\ \quad \\ \text{Cl} \quad \text{Si}(\text{CH}_3)_3 \end{array}$	$\text{KF}/\text{DMSO}/\text{r.t.}/10\text{h}$	$\text{C}_6\text{H}_5\text{CH}=\text{C}=\text{CH}_2$ (60)
VII. $\begin{array}{c} \text{HOCH}_2\text{CH}_2-\text{C}=\text{CH}_2 \\ \\ \text{Si}(\text{C}_6\text{H}_5)_3 \end{array}$	$\text{KF}/\text{DMSO}/150^\circ/2\text{h}$	No reaction
VIII. 	$\text{KF}/\text{DMSO}/120^\circ/2\text{h}$	No reaction
IX. $\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{CHCH}-\text{CH}_2\text{Si}(\text{CH}_3)_3 \\ \\ \text{OH} \end{array}$	$\text{KF}/\text{DMSO}/150^\circ/2\text{h}$	No reaction

a. Determined by nmr with internal standard.

b. A mixture of double bond isomers. See reference (5).

In view of the increasing importance of organosilicon compounds in organic synthesis and the pivotal role that fluoride ion is to play⁵⁻⁹; it is important to recognize the subtle effect of the kind described here. We hope to explore further the origin of this unexpected β -hydroxy effect.

References

- (1) C. Eaborn and D.R.M. Walton, *J. Organometal Chem.*, 4, 217 (1965).
- (2) C.S. Kraihanzel and J.E. Poist, *J. Organometal. Chem.*, 8, 239 (1967).
- (3) See C. Eaborn and R.W. Bott in "Organometallic Compounds of the Group IV elements" ed. A.G. MacDiarmid, Vol. 1, part 1, p. 392. Marcel Dekka, New York, 1968.
- (4) D.L. Bailey and A.N. Pines, *Ind. Eng. Chem.*, 46, 2363 (1954).
- (5) T.H. Chan and W. Mychajlowskij, *Tetrahedron Letters*, 171 (1974).
- (6) T.H. Chan, M. Li, W. Mychajlowskij and D.N. Harpp, to be published.
- (7) E.J. Corey and A. Venkateswarlu, *J. Amer. Chem. Soc.*, 94, 6190 (1972).
- (8) R.F. Cunico and E.M. Dexheimer, *J. Amer. Chem. Soc.*, 94, 2868 (1972).
- (9) R.B. Miller and T. Reichenbach, *Tetrahedron Letters*, 543 (1974).

Acknowledgement

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