

OXIDATIVE SI-C BOND CLEAVAGE OF ORGANOTRIFLUOROSILANES INVOLVING  
ORGANIC-GROUP MIGRATION FROM HYPERCOORDINATE SILICON TO OXYGEN<sup>1)</sup>

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Summary: Various organotrifluorosilanes react with trimethylamine-N-oxide without catalyst to give the corresponding alcohols in high yields under mild conditions. Stereospecific nature of the reaction is suggestive of the involvement of intramolecular 1,2-organic-group migration from hypercoordinate silicon to oxygen.

Cleavage of Si-C bonds of organosilicon compounds is continually receiving much attention in view of the versatile utility in organic synthesis.<sup>2)</sup> The oxidative cleavage of Si-C bond giving alcohols is one of the particularly interesting processes, because of the wide presence of hydroxy groups in natural products. Peracids and peroxides are often used as oxidizing reagents<sup>3)</sup> but the use is limited to the substrates without functional groups sensitive to such reagents. We have recently reported<sup>4)</sup> an alternative method for the oxidative cleavage of Si-C bond of organodialkoxymethylsilanes with trimethylamine-N-oxide in the presence of an additive such as  $\text{KHF}_2$ .<sup>5)</sup> Whereas the amine-N-oxide is promising as an useful reagent for selective Si-C bond cleavage method involving functional groups in the molecules, rather drastic reaction conditions are required when the alkoxysilanes are used as substrates (70 - 140 °C in DMF, in the presence of 3- 4 eq of  $\text{KHF}_2$ ).

In this paper we describe that the Si-C bond cleavage with trimethylamine-N-oxide is achieved under much milder conditions without any other additives when organotrifluorosilanes<sup>6)</sup> are used as organosilanes. The present reaction has very high synthetic utility, since organotrifluorosilanes can easily be prepared by fluorination with antimony trifluoride<sup>7)</sup> of the corresponding trichlorosilanes, which are obtained by known methods such as hydrosilylation of olefins with trichlorosilanes in the presence of  $\text{H}_2\text{PtCl}_6$ <sup>8)</sup> and Benkeser's reaction.<sup>9)</sup> The high reactivity of organotrifluorosilanes may be attributed to the well-known effect of electronegative and small fluorine substituents, which stabilize highly coordinate silicon atom. Mechanistically the present reaction may involve the concerted 1,2-alkyl and aryl migration from pentacoordinate silicon to oxygen.

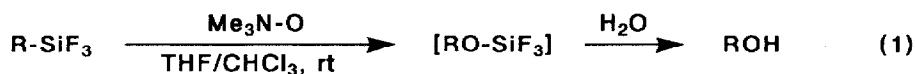


Table 1. Reaction of Organotrifluorosilanes with Trimethylamine-N-oxide in THF/CHCl<sub>3</sub>

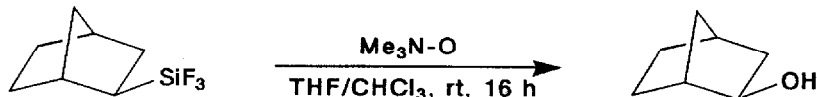
Entry	Trifluorosilane	Conditions	Yield (%) of Alcohol
1	PhSiF <sub>3</sub>	rt, 12 h	80
2	PhCH <sub>2</sub> SiF <sub>3</sub>	rt, 12 h	98
3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> SiF <sub>3</sub>	rt, 50 h	94
4	exo-norbornyl-SiF <sub>3</sub> <sup>a)</sup>	rt, 16 h	89 <sup>b)</sup>
5	(E)-crotyl-SiF <sub>3</sub> <sup>c)</sup>	rt, 20 h	83 <sup>d)</sup>
6	(Z)-crotyl-SiF <sub>3</sub> <sup>e)</sup>	rt, 20 h	85 <sup>f)</sup>

a) Exo/endo = 100/0. b) Exo/endo = 100/0. c) E/Z = 97/3.

d) E/Z = 96/4. e) E/Z = 5/95. f) E/Z = 6/94.

A typical experimental procedure is as follows: To a THF (2 ml) solution of benzyltrifluorosilane (2.0 mmol) was added dropwise anhydrous trimethylamine-N-oxide (1.5 N CHCl<sub>3</sub> solution,<sup>10</sup>) 2.0 mmol) at 0 °C under argon. The mixture was stirred at ambient temperature for 12 h, diluted with ether, and then chromatographed on a short silica-gel column. Evaporation of solvents gave pure benzyl alcohol in 98% yield. The representative results are summarized in Table 1.

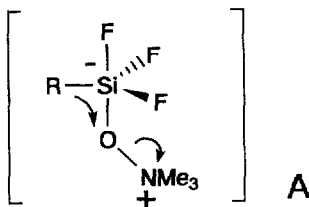
Various alkyl- and aryltrifluorosilanes react smoothly with trimethylamine-N-oxide at room temperature without catalyst to give the corresponding alcohol in high yields, while organotrifluorosilanes such as phenyltrichlorosilane were inert to the amine-N-oxide under the similar conditions. The oxygens of dimethyl sulfoxide and triphenylphosphine oxide were not transferred to organotrifluorosilanes even under more rigorous reaction conditions. Exo-norbornyl alcohol<sup>3a)</sup> (exo/endo = 100/0)<sup>11)</sup> was obtained in 89% yield from exo-norbornyltrifluorosilane<sup>12)</sup> (exo/endo = 100/0)<sup>11)</sup> with retention of configuration at the carbon atom bearing SiF<sub>3</sub> group. (E)- and (Z)-Crotyltrifluoro-



silanes were converted to the corresponding alcohols without further oxidation of the C-C double bond. The stereochemistry of the alkenyl group was retained throughout the reaction. Thus, the reaction of (E)-crotyltrifluorosilane (E/Z = 97/3)<sup>11)</sup> with trimethylamine-N-oxide gave (E)-crotyl alcohol (E/Z = 96/4)<sup>11)</sup> in 83% yield, while (Z)-crotyltrifluorosilane (E/Z = 5/95)<sup>11)</sup> afforded (Z)-

crotyl alcohol (E/Z = 6/94)<sup>11)</sup> in 85% yield. It is interesting to note that pentafluorosilicate strategy<sup>3a)</sup> is not applicable to the synthesis of allyl alcohols because the prerequisite allylpentafluorosilicates cannot be prepared by usual methods.<sup>14)</sup>

Whereas detailed mechanistic studies are now under way, following particular points suggest that the oxidative cleavage proceeds through the rate-determining formation of a pentacoordinate silicon intermediate A as a consequence of the 1:1 complexation of trimethylamine-N-oxide to an organotrifluorosilane, followed by the concerted 1,2-migration of an organic group from silicon to oxygen.<sup>15)</sup> (1) Organotrifluorosilanes, which can form pentacoordinate silicon intermediates stabilized by three electronegative fluorine atoms,<sup>16)</sup> react more smoothly than organotrichlorosilanes and alkoxysilanes. (2) The (E)- and (Z)-crotylsilanes give the corresponding alcohols in stereospecific and regiospecific manner. No positional nor stereo isomerization occurs during the reaction. (3) Oxidation of exo-norbornyltrifluorosilane produces stereospecifically exo-norbornyl alcohol.



The migration mode would be similar to the amine-N-oxide oxidation of organoboranes through "ate" complexes as reported by Soderquist et al.<sup>10)</sup> Whereas a number of 1,2-migrations of organic groups have been reported to occur from a hypercoordinate silicon atom to adjacent sites, the coordination number at the silicon atom has often been discounted.<sup>3,15)</sup> In this context, it will be very interesting to determine whether the present migration occurs at a pentacoordinate or a hexacoordinate silicon atom. Further works are now in progress.

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