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OXIDATIVE CLEAVAGE OF SILICON–CARBON BONDS IN ORGANOSILICON FLUORIDES TO ALCOHOLS[1]

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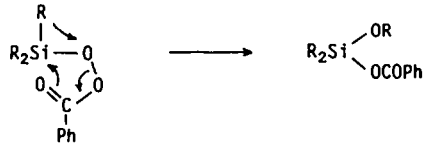
Abstract—Certain functional silyl groups have been shown to be synthetically equivalent to the OH group. All of the C–Si bonds in organosilicon fluorides, $K_2[RSiF_5]$ and R_nSiF_{4-n} ($n = 1, 2, 3$) are cleaved by *m*-chloroperbenzoic acid (MCPBA) in DMF to give the corresponding alcohols in high yields. Although the reaction with $RSiF_5^{2-}$ and $RSiF_3$ proceeds without any additive, cleavage of R_2SiF_2 and R_3SiF requires, respectively, a catalytic or excess amount of KF. A triorganoethoxysilane also undergoes similar oxidative cleavage reactions in the presence of an excess amount of KF. The MCPBA-oxidation of *exo*- and *endo*-2-norbornyl-silicate and -trifluorosilane proceeds stereospecifically with retention of configuration at carbon. A remarkable solvent effect has been observed in the oxidative cleavage of $RSiF_3$. A plausable mechanism involves a hexacoordinate silicon species in which the organic group intramolecularly migrates from Si to O of the coordinated MCPBA.

We describe herein oxidative cleavage reactions of organo-silicon compounds where the functional silyl group is synthetically equivalent to the OH group.

$$\boxed{\text{R-}si \equiv \text{R–OH}}$$

Si–C bonds are fairly resistant to oxidative cleavage.[2] There have been only a few methods for the introduction of an O functionality into an organic group via cleavage of the Si–C bond. *A priori*, two methodologies may be envisaged for such processes, as shown in Scheme 1. In those cases where the organic group attached to Si is more or less "activated" towards an oxidizing agent, the reagent interacts firstly with the organic group rather than the Si atom (Route A). A typical example is the formation of carboxylic acids from acyltrimethylsilanes via oxidation with alkaline hydrogen peroxide.[3] The following synthetically useful reactions also come into this category: the Sila-Pummerer rearrangement of α-silylsulfides,[4] conversion of vinylsilanes to enol silyl ethers by oxidation with a nitrile oxide,[5] and, albeit mechanistically somewhat different, transformation of vinylsilanes to carbonyl functionalities through α,β-epoxysilanes,[6] and allyl alcohol synthesis from allylsilanes.[7]

The oxidation of "unactivated" alkyl or aryl groups may be attained via the interaction of the oxidizing agent with the Si center (Route B). The formation of alkoxysilanes from triorganosilyl perbenzoates via intramolecular rearrangement has provided a typical example of this route.[8]



Little attention, however, has been paid to the synthetic application of this type of reaction. Our present alcohol synthesis falls under the latter category.

RESULTS AND DISCUSSION

Synthesis of alcohols from organosilicon fluorides by the action of *m*-chloroperbenzoic acid (MCPBA) is summarized in eqns (1)–(4).

$$RSiF_5^{2-} + \text{MCPBA} \xrightarrow{\text{DMF}} \text{ROH} \quad (1)$$

$$RSiF_3 + \text{MCPBA} \xrightarrow{\text{DMF}} \text{ROH} \quad (2)$$

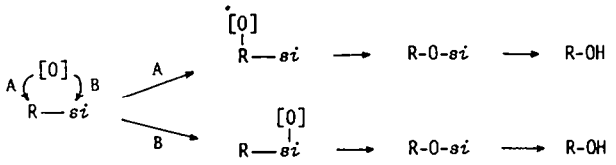
$$R_2SiF_2 + 2\,\text{MCPBA} + \text{cat. KF} \xrightarrow{\text{DMF}} 2\,\text{ROH} \quad (3)$$

$$R_3SiF + 3\,\text{MCPBA} + \text{xs. KF} \xrightarrow{\text{DMF}} 3\,\text{ROH} \quad (4)$$

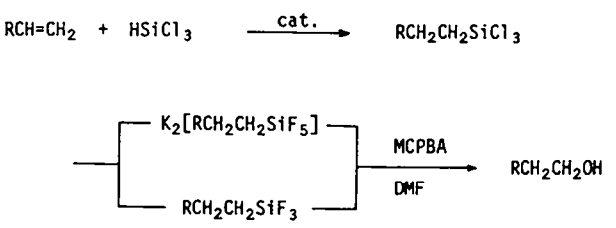
All of the organic groups are transformed into the corresponding alcohols under mild conditions. These reactions provide the first, practically useful methods for the introduction of oxygen functionality into "unactivated" alkyl groups in place of a silyl group, and open up new processes for the anti-Markownikoff hydration of olefins in conjunction with hydrosilylation (Scheme 2).

Organopentafluorosilicates (eqn 1). We have firstly observed that organopentafluorosilicates (only dipotassium salts[9] are used throughout this paper) readily react with MCPBA in DMF to afford the corresponding alcohols,[10] as shown by the data summarized in Table 1. Reactions of primary alkyl-silicates are slightly exothermic, while with secondary alkyl-silicates heating at 50° is necessary to obtain satisfactory yields. The MCPBA-cleavage of, at least, the primary alkyl–Si bond in silicates proceeds much faster than the epoxidation of double bonds as indicated by the selective formation of 4-(2-hydroxyethyl)cyclohexene from 4-vinylcyclohexene (entry 5). This opens a new route to unsaturated primary alcohols from various polyenes. The ester group tolerates the overall transformation.

Since the Pt-catalyzed hydrosilylation of internal



Scheme 1.



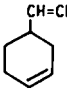
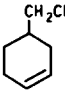
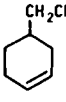
Scheme 2.

olefins forms primary alkyl-Si compounds exclusively,[11] the present procedure provides a novel route to primary alcohols from a mixture of positional isomers of olefins (entry 2).

Organotrifluorosilanes (eqn 2). Organotrifluorosilanes are more reactive than organopentafluorosilicates and react quite readily with MCPBA in DMF to form alcohols in high yields. The reaction is so vigorous that the temperature rises up to near 90° almost immediately if MCPBA is added all at once. The reaction can be controlled by dropwise addition of a solution of MCPBA in DMF. Only several representative results are given in Table 2. Of particular interest is that even the sterically crowded neophyl (2-methyl-2-phenylpropyl) alcohol is obtained in high yield from neophyltrifluorosilane (entry 12), while the corresponding silicate gives only a trace amount of the alcohol.[1] An α,ω-alkanediol is also obtained by this route, although the difunctional silicate is hard to prepare.

Diorganodifluoro- and triorganomonofluoro-silanes (eqns 3 and 4). Several representative results are summarized in Table 3. Dioctyldifluorosilane does react with MCPBA in DMF, but the reaction proceeds slowly and gives octanol only in low yields (entry 17). The reaction is dramatically improved by the addition of a catalytic amount (*ca* 1 mol%) of KF, occurring exothermically

Table 1. Oxidative cleavage of $K_2[RSiF_5]$ by MCPBA in DMF[a]

entry	olefin	R in $K_2[RSiF_5]$	product	yield (%)[b]
1	$C_6H_{13}CH{=}CH_2$	C_8H_{17}-	$C_8H_{17}OH$	82 (69)
2	C_8H_{16}[c]	C_8H_{17}-	$C_8H_{17}OH$	68 (57)
3	$C_{10}H_{21}CH{=}CH_2$	$C_{12}H_{25}$-	$C_{12}H_{25}OH$	75 (43)
4	$MeO_2C(CH_2)_8CH{=}CH_2$	$MeO_2C(CH_2)_{10}$-	$MeO_2C(CH_2)_{10}OH$	77 (64)
5				54 (35)
6	C_6H_{10}[d]	C_6H_{11}-[e]	$C_6H_{11}OH$[e]	22 (13)
7	C_7H_{10}[f]	*exo*-C_7H_{11}-[g,h]	*exo*-$C_7H_{11}OH$[g,h]	70[i] (44)
8	—	*endo*-C_7H_{11}-[g,j]	*endo*-$C_7H_{11}OH$[g,j]	74[i]
9	—	C_6H_5-	C_6H_5OH	64[k]

[a] Unless otherwise stated, a mixture of $K_2[RSiF_5]$ (3 mmol), MCPBA (3 mmol), and dry DMF was stirred at room temp for 6 hr. [b] Isolated yield based on the silicate, unless otherwise stated. The overall yield from the olefin is given in parentheses. [c] An isomeric mixture of internal and terminal olefins. [d] C_6H_{10} = cyclohexene. [e] C_6H_{11}- = cyclohexyl. [f] C_7H_{10} = 2-norbornene. [g] C_7H_{11}- = 2-norbornyl. [h] *exo* 100%. [i] At 50° for 8 hr. [j] *endo* 95%. [k] GLC yield.

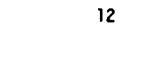
and giving octanol in almost quantitative yields (entry 20). Both of the octyl groups are transformed into octanol. An excess amount of KF does not retard the cleavage reaction (*vide infra*). Commercially available anhydrous KF or dihydrate can be used.

In the presence of about two equiv of KF, octyldimethyl- and dioctylphenyl-fluorosilane are also cleaved smoothly by MCPBA at room temperature, the latter reacting exothermically. In the presence of a catalytic amount of KF, the alcohols are formed only in poor yields (entry 23). Trioctyl-fluorosilane requires heating around 50°.

Alkoxysilanes and chlorosilanes. All the Si–C bonds in dioctylphenylethoxysilane are also transformed into alcohols (entry 25) under similar conditions to those for the corresponding fluorosilane mentioned above.

It has recently been reported[12] that organotrialkoxysilanes are oxidized by MCPBA, but in less than 50% yields. Our present findings show a marked effect of a fluoride ion in this type of oxidation.

Table 2. Oxidative cleavage of $RSiF_3$ by MCPBA in DMF[a]

entry	$RSiF_3$	conditions[b]	product	yield (%)[c]
10	$C_8H_{17}SiF_3$	r.t., 5 hr	$C_8H_{17}OH$	(95)
11	$PhCH_2CH_2SiF_3$	r.t., 4 hr	$PhCH_2CH_2OH$	81
12		r.t., 3 hr		67
13	*exo*-$C_7H_{11}SiF_3$[d,e]	r.t., 3 hr	*exo*-$C_7H_{11}OH$[d,e]	68
14	*endo*-$C_7H_{11}SiF_3$[d,f]	r.t., 3 hr	*endo*-$C_7H_{11}OH$[d,f]	62
15	$F_3Si(CH_2)_8SiF_3$	r.t.~50°, 3 hr	$HO(CH_2)_8OH$	35
16	$PhSiF_3$	r.t., 5 hr	PhOH	(77)

[a] A mixture of $RSiF_3$ (3 mmol), MCPBA (3 mmol), and dry DMF was stirred at a given temperature for a given period of time. [b] A highly exothermic reaction occurred in the initial stage. [c] Isolated yield. GLC yields are given in parentheses. [d] C_7H_{11}- = 2-norbornyl. [e] *exo* 100%. [f] *endo* 95%.

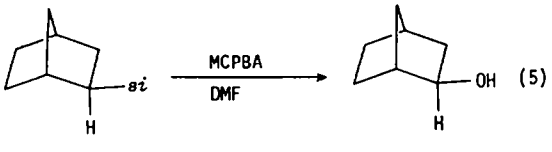
Table 3. MCPBA-oxidation of R_2SiF_2, R_3SiF, R_3SiOEt and organochlorosilanes in the presence of KF in DMF[a]

entry	compound	MCPBA (equiv)	KF (equiv)	conditions	product(s)	yield (%)[b]
17	$(C_8H_{17})_2SiF_2$	2	0	r.t., 1 day	2 $C_8H_{17}OH$	40
18		2	2.5	r.t., 5 hr		100
19		2	0.1	r.t., 5 hr		92
20		2	0.01	r.t., 5 hr		95
21	$(C_8H_{17})Me_2SiF$	3	2	r.t., 5 hr	$C_8H_{17}OH$	76
22	$(C_8H_{17})_2PhSiF$	3	2	r.t., 5 hr	2 $C_8H_{17}OH$	79
					PhOH	100
23		3	0.1	r.t., 5 hr	2 $C_8H_{17}OH$	44
					PhOH	41
24	$(C_8H_{17})_3SiF$	3	2	50°, 5 hr	3 $C_8H_{17}OH$	72
25	$(C_8H_{17})_2PhSiOEt$	4	3	r.t., 5 hr	2 $C_8H_{17}OH$	92
					PhOH	58
26	$(C_8H_{17})_2SiCl_2$	2	5	r.t., 1 day	2 $C_8H_{17}OH$	45
27	$(C_8H_{17})_2PhSiCl$	3	3	r.t., 5 hr	2 $C_8H_{17}OH$	12
					PhOH	1

[a] Carried out on a 1–3 mmol scale. [b] Determined by GLC.

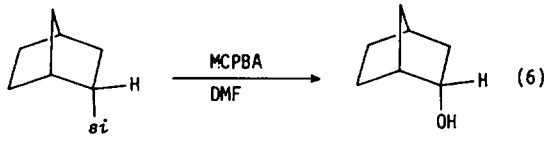
In contrast to fluorosilanes and ethoxysilanes, the MCPBA-oxidation of the corresponding chlorosilanes proceeds rather sluggishly. For example, treatment of octyltrichlorosilane with MCPBA in DMF resulted in the formation of chlorine gas, together with only a trace amount of octanol. Dioctyldichlorosilane and dioctylphenylchlorosilane also gave only low yields of the corresponding alcohols even in the presence of excess amounts of KF (entries 26, 27). These results imply that readily oxidizable negative ligands on Si such as Cl consume MCPBA, complicate the reaction and lower the yield of alcohols.

Stereochemistry. The MCPBA-oxidation of *exo*- and *endo*-2-norbornyl-pentafluorosilicate and -trifluorosilane proceeds highly stereospecifically with complete retention of configuration at carbon (eqns 5 and 6).



(5)

exo 100% *exo* 100%



(6)

endo 95% *endo* 95%

[*si* = SiF_5^{2-} or SiF_3]

This result indicates the front-side attack of the oxidizing agent, making a sharp contrast with the inversion stereochemistry observed in the bromine and NBS cleavage of the silicate.[9]

This stereospecific alcohol synthesis has already been applied to the asymmetric synthesis of optically active alcohols from olefins via catalytic asymmetric hydrosilylation[13] and the determination of the absolute configuration of optically active allylsilanes.[14]

Synthetic utility. High reactivity of the C–Si bonds in ordinary tetracoordinate organosilicon fluorides towards the MCPBA oxidation was rather a great surprise even to us, because there has been virtually no such a facile oxidative cleavage reaction of all of the C–Si bonds. From the synthetic viewpoints, organofluorsilanes may be superior to the corresponding silicates. Fluorosilanes are readily available from the corresponding chlorosilanes by treatment with stoichiometric amount of $CuF_2 \cdot 2H_2O$ (eqn 7). Thus, our new method, may be one of the most convenient laboratory methods[15]

$$R_nSiCl_{4-n} + \frac{4-n}{2}CuF_2 \rightarrow R_nSiF_{4-n} + \frac{4-n}{2}CuCl_2. \quad (7)$$

The present overall transformation should be useful as an alternative to hydroboration,[16] hydroalumination,[17] and hydrozirconation.[18] We have found that alkenyltrifluorosilanes are readily cleaved by MCPBA in DMF even at −50° to form the corresponding carbonyl compounds. These results will be reported elsewhere. Further synthetic applications are now in progress.

Mechanistic studies. Significant features are summarized as follows.

(1) The reactivity decreases qualitatively in the order $RSiF_3 > RSiF_5^{2-} \sim R_2SiF_2 > R_3SiF$. Thus, in tetracoordinate silicon derivatives, the more the fluorine atoms on silicon, the higher the reactivity. This order is a contrast to that observed in other traditional electrophilic cleavage reactions of the C–Si bond which diminished by progressive substitution on Si by electronegative groups.[19]

(2) Retention of stereochemistry at C has been observed both for tetracoordinate $RSiF_3$ and hexacoordinate $RSiF_5^{2-}$, suggesting a common mechanism.

(3) Cleavage of silicates was almost completely inhibited by extra LiF or KF in diglyme.

(4) Remarkable solvent effects have been observed. Yields of octanol produced from $K_2[C_8H_{17}SiF_5]$ varied with the reaction medium as follows: THF, trace; EtOH, MeCN, dioxane, ~30%; benzene 45%; diglyme, 60%; benzene plus 1 equiv 18-crown-6, 70%; DMF, 82%. In cleavage of $(C_8H_{17})_2SiF_2$ catalyzed by KF: benzene, 15%; THF, 61%; DMF, 95%. The most informative solvent effect has been observed for $C_8H_{17}SiF_3$ as shown in Table 4. There seems to be a notable correlation of the product yields with the donicity of the solvent (Gutman's donor number: DN)[20] rather than the dielectric constant. While in solvents of low donor number (DN ≤ 20) the alcohol is formed in only varied and lower than 50% yields, in DMF, NMP and HMPA, whose DN's are greater than 25, the reaction proceeds exothermically to give octanol in 85–100% yields. Addition of 1 or 2 equiv of donor solvent to poor solvents improved the yields of

Table 4. Solvent effects on the MCPBA cleavage of octyltrifluorosilane

$C_8H_{17}SiF_3$ + MCPBA —(r.t., 4 - 6 hr)→ $C_8H_{17}OH$

solvent	yield (%)[a]	DN[b]	ε[c]
C_6H_6	23	0.1	2.3
$PhNO_2$	48	4.4	34.8
dioxane	28	14.8	2.2
propylene carbonate	17	15.1	69.0
Et_2O	12	19.2	4.3
THF	35	20.0	7.6
DMF	95	26.6	36.1
NMP[d]	83	27.3	32.0
HMPA	100	38.8	30.0
CCl_4	14		
diglyme	32		
EtOH	69		
Et_2O + 1 equiv DMF	40		
Et_2O + 1 equiv HMPA	69		
THF + 1 equiv DMF	82		
THF + 1 equiv HMPA	82		
CCl_4 + 1 equiv HMPA	71		

[a] Determined by GLC after hydrolysis.

[b] DN: Gutmann's donor number (kcal mol^{-1}).

[c] ε: dielectric constant.

[d] NMP: *N*-methylpyrrolidone.

octanol. These solvent effects suggest that the coordination of such a donor solvent with a silicon center may play an important role in the present cleavage reaction.

(5) Interaction between an organotrifluorosilane and a donor solvent could be observed spectroscopically.

^{1}H NMR spectra are shown in Fig. 1. The methylene protons α to silicon in octyltrifluorosilane showed a down field shift from around δ 0.92 to δ 1.15 by the addition of *ca* 4 equiv of DMF. The spectra of $PhCH_2CH_2SiF_3$ show clearly disappearance of the ^{1}H-^{19}F coupling by the addition of *ca* 0.5 equiv of DMF. ^{13}C, ^{19}F and ^{29}Si NMR spectra of $C_8H_{17}SiF_3$ in $CDCl_3$ in the absence or presence of 1 equiv of HMPA are reproduced in Fig. 2. In both the ^{13}C and ^{29}Si NMR spectra, coupling with ^{19}F on silicon disappears upon addition of HMPA. Addition of HMPA causes broadening of the ^{19}F NMR (unassigned signals also appeared). These spectral behaviors indicate that a donor solvent induces the fluoride ligand exchange intermolecularly through penta- and hexa-coordinate Si species. The rate of the exchange is faster than the NMR time scale. A trace amount of a free fluoride ion present in the mixture should play an important role in this exchange processes. A very simplified exchange processes are shown in Scheme 3. It should be noted that the hexacoordinate organopentafluorosilicate can form a pentacoordinate species through dissociation of a fluoride ion. These coordinatively unsaturated pentacoordinate silicon species seem to be the common key intermediate in the oxidation, as well as the fluoride exchange.

(6) IR spectra further support the interaction between HMPA and a fluorosilane. Thus, ν(P=O) of HMPA occurring at 1220 cm^{-1} in CCl_4 shifted to 1200 cm^{-1} in the presence of 1 equiv of octyltrifluorosilane.

(7) In a control experiment, an equimolar mixture of octyltrifluorosilane, *m*-chlorobenzoic acid (MCBA) in place of MCPBA, and HMPA in CCl_4 shows neither IR absorption due to ν(Si–O) nor change on GLC analysis , indicating no formation of the Si–O covalent bond in a detectable amount.

(8) The initial oxidation product of octyltrifluorosilane seems to be an alkoxysilane species. The ^{1}H NMR spectrum of the product prior to hydrolysis showed a somewhat complex triplet at δ 3.8, together with a triplet at δ 3.6 due to octanol. Upon hydrolysis, the former disappeared and the intensity of the latter increased.

While the exact mechanism is not clear yet, a plausible general mechanism consistent with these observations is visualized in Scheme 4. Thus, a coordinatively unsaturated pentacoordinate Si species may well be susceptible to the further coordination of MCPBA to form a

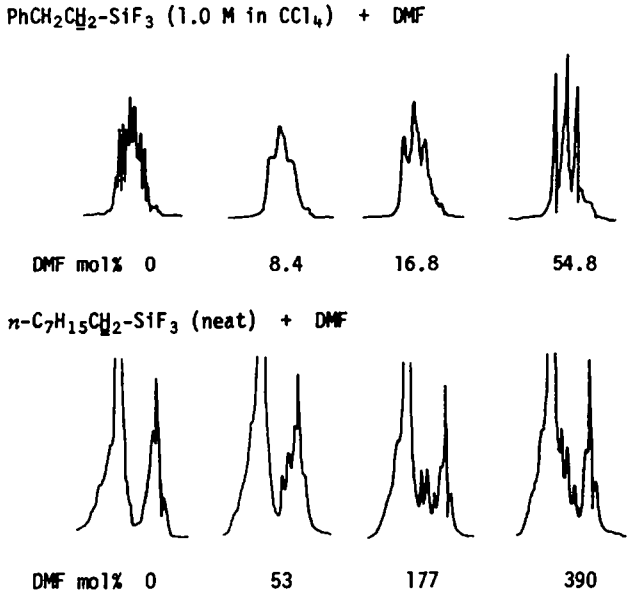
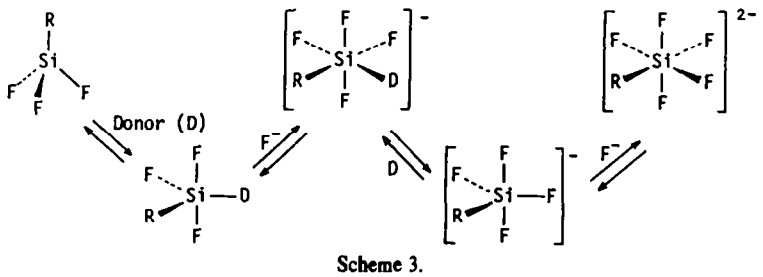


Fig. 1. ^{1}H NMR spectral behavior of the methylene protons α to silicon in RCH_2SiF_3 in the presence of DMF as a donor solvent.



Scheme 3.

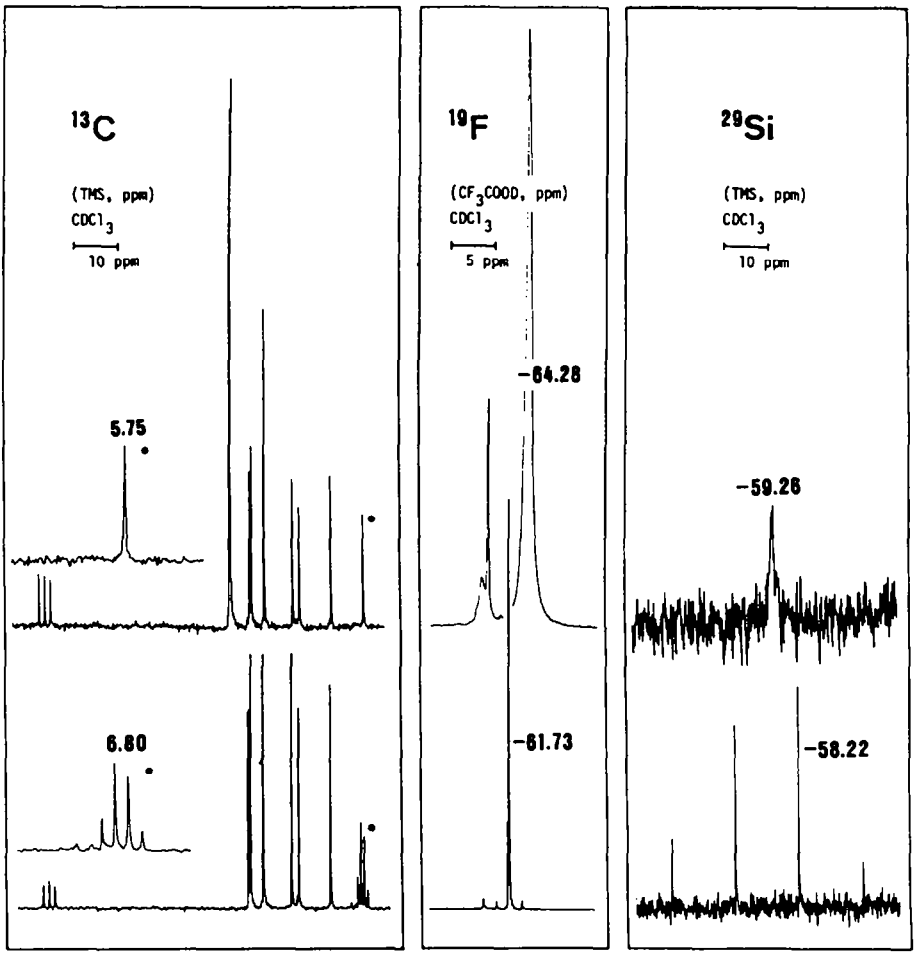
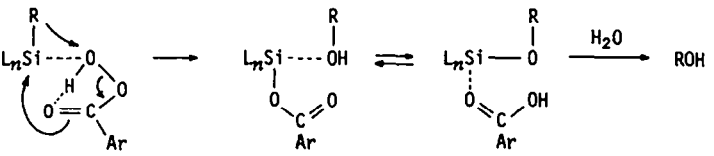


Fig. 2. ^{13}C, ^{19}F and ^{29}Si NMR spectra of $C_8H_{17}SiF_3$ in the absence of HMPA (lower) and in the presence of 1 equiv of HMPA (upper).



L = F, R, and/or donor solvent

Scheme 4.

coordinatively saturated hexacoordinate intermediate where the C–Si bond is highly polarized and the organic group readily migrates intramolecularly to the oxygen atom of the coordinated MCPBA. Less acidic[22] R_2SiF_2 requires a catalytic amount of KF to accelerate the formation of a pentacoordinate species.[23] In the case of R_3SiF the initially formed alkoxysilane species should be converted to fluorosilane species for the further efficient oxidative cleavage to occur; the reaction therefore requiring more than the stoichiometric amount of KF.

This mode of activation of organosilicon compounds by a donor solvent and/or a fluoride ion is reminiscent of Corriu's observation on the donor solvent acceleration of the nucleophilic substitution at Si.[24] Intramolecular interaction of the trifluorosilyl group and an acyl oxygen has recently been shown by X-ray structure determination of aroyloxymethyltrifluorosilane.[25]

EXPERIMENTAL

General. ^1H NMR, IR, MS and GLC facilities have been described in our previous paper.[9] ^{13}C, ^{19}F and ^{29}Si NMR spectra were recorded on a JEOL FX-100 spectrometer.

Materials. Organopentafluorosilicates have been reported previously.[9] Dioctyldichlorosilane and trioctylchlorosilane were prepared by the reaction of $SiCl_4$ with octylmagnesium chloride in ether.[26] Dioctylphenylchlorosilane (b.p. 218–230°/8 torr., ^1H

NMR: 0.74–1.60 (m, 34H, including 0.90, t, $J = 6$ Hz, 6H), 7.20–7.72 (m, 5H)) was prepared similarly from phenyltrichlorosilane and converted to the ethoxysilane by treatment with EtOH and Et_3N in ether: b.p. 215–240°/3 torr. ^{1}H NMR: 0.62–1.68 (m, 37H, including 0.88, t, $J = 6$ Hz, 6H), 1.19 (t, $J = 8$ Hz, 3H), 3.64 (q, $J = 8$ Hz, 2H), 7.12–7.56 (m, 5H).

Preparation of fluorosilanes. All fluorosilanes were prepared from the corresponding chlorosilanes by treatment with stoichiometric amount (*cf* eqn 7) of $CuF_2 \cdot 2H_2O$ in ether, and gave satisfactory fluorine analysis by titration ($F \pm 0.40$). A typical procedure is given below.

Octyltrifluorosilane. To a suspension of $CuF_2 \cdot 2H_2O$ (20.7 g; 150 mmol) in ether was added octyltrichlorosilane (24.8 g; 100 mmol) dropwise at 0° with stirring. The light blue mixture changed to brown and then gradually to greenish. After 12 hr-stirring at room temp, pentane (30 ml) was added to ensure precipitation of Cu(II) salts. Filtration of the mixture gave a colorless filtrate which was dried over Na_2SO_4. Filtration, evaporation, and distillation gave 16.3 g (82% yield) of pure octyltrifluorosilane boiling at 54°/23 torr. ^{1}H NMR 0.8–1.1 (m, 5H, CH_3 and CH_2Si), 1.2–1.8 (m, 12H).

(2-Phenylethyl)trifluorosilane. 61–73%; b.p. 60–61°/18 torr. (bath). ^{1}H NMR: 1.0–1.5 (m, 2H), 2.6–3.0 (m, 2H), 6.8–7.6 (m, 5H). *(2-Methyl-2-phenylpropyl)trifluorosilane.* 41%; b.p. 86°/24 torr. ^{1}H NMR: 1.49 (s, 8H), 7.05–7.45 (m, 5H). *exo-2-Norbornyltrifluorosilane.* 71%; b.p. 65–75°/95 torr. (bath). ^{1}H NMR: 0.9–1.9 (m, 9H), 2.3–2.6 (m, 2H).

1,8-Bis(trifluorosilyl)octane. 49%; b.p. 95°/30 torr. (bath). ^{1}H NMR: 0.70–1.15 (m, 4H), 1.15–1.80 (m, 12H).

Dioctyldifluorosilane. 85%; b.p. 150°/12 torr. (bath). ^{1}H NMR: 0.45–1.1 (m, 10H), 1.35 (br. s, 24H).

Octyldimethylfluorosilane. 88%; b.p. 80–100°/15 torr. (bath). ^{1}H NMR: 0.18 (d, $J = 9$ Hz, 6H), 0.48–1.77 (m, 17H, including 0.89, t, $J = 6$ Hz, 3H).

Dioctylphenylfluorosilane. 89%; b.p. ~210°/3 torr. (bath). ^{1}H NMR: 0.86 (t, $J = 5$ Hz, 6H), 1.04–1.68 (m, 28H), 7.20–7.64 (m, 5H).

Trioctylfluorosilane. 85%; b.p. ~250°/12 torr. (bath) (lit.[27] b.p. 190°/1 torr.).

Oxidative cleavage with MCPBA

Typical experimental procedures for organopentafluorosilicates have been given in our previous papers.[1,10]

Organotrifluorosilanes. Typical procedures are given for the oxidation of *exo*- and *endo*-2-norbornyltrifluorosilane.

exo-2-*Norbornyl alcohol.* To a soln of *exo*-norbornyltrifluorosilane (920 mg; 5.1 mmol) in DMF (7 ml) was added dropwise a soln of MCPBA (purity 80%, 2.20 g; 10.2 mmol) in DMF (8 ml) at room temp with stirring. Immediately an exothermic reaction started and the mixture turned cloudy. The mixture was stirred at room temp for 3 hr, poured into 70 ml water and extracted with ether (15 ml × 5). The ether extracts were combined, washed successively once with $NaHSO_3$ aq, three times with $NaHCO_3$ aq, and once with water, and dried over Na_2SO_4. After evaporation of solvents the viscous residue was sublimed at 65°/14 torr. to give 387 mg (68% yield) of *exo*-2-norbornyl alcohol, essentially pure by GLC and ^{1}H NMR which showed a broad doublet-like signal at δ 3.62 owing to the OH-bearing methine proton. No signals due to the *endo* isomer were detected. A sample sublimed again under atmospheric pressure at 140° melted at 124–128° in a sealed tube (lit.,[28] m.p. 124–128°).

endo-2-*Norbornyl alcohol.* A similar reaction of *endo*-2-norbornyltrifluorosilane[9] (490 mg; 2.7 mmol; *endo*/*exo* = 95/5) with MCPBA (885 mg of 80% purity; 4.1 mmol) in 10 ml of DMF gave, after usual work-up and sublimation, 188 mg (62% yield) of *endo*-2-norbornyl alcohol. The *endo*/*exo* ratio was determined to be 95/5 by ^{1}H NMR, the OH-bearing methine proton occurring at δ 4.11 (dt, $J = 4$ and 10 Hz). A small amount (several per cent) of norbornanone was formed as a by-product. Recrystallization from pentane and sublimation at 140° under atmospheric pressure gave a pure sample which melted at 143–145° in a sealed tube (lit.,[28] m.p. 148–150°).

Oxidation of dioctyldifluorosilane. To a stirred mixture of dioctyldifluorosilane (295 mg; 0.92 mmol), commercial anhyd KF (0.8 mg), and dry DMF (5 ml) was added MCPBA (439 mg of 80% purity; 2.03 mmol). A mildly exothermic reaction started after about 10 min, resulting in a cloudy mixture. After 5 hr-stirring at room temp the mixture was worked up in essentially the same manner as described for organotrifluorosilanes.

Oxidation of triorgano-fluorosilanes and -ethoxysilanes. Essentially the same procedure as above was employed, except 3–4 equiv of MCPBA and 2–3 equiv of KF were used.

The following alcohols were characterized fully, while other products were identified by comparison with authentic samples.

Methyl 11-hydroxyundecanoate. m.p. 25.5–26.5° (lit.,[29] m.p. 26–27°). ^{1}H NMR: 1.2–1.8 (m, including br. s at 1.31, 16H), 2.16 (s, 1H), 2.34 (t, $J = 7$ Hz, 2H), 3.65 (t, $J = 7$ Hz, 2H), 3.69 (s, 3H).

4-(2-Hydroxyethyl)cyclohexene. n_D^{20} 1.4838 (lit.,[30] n_D^{20} 1.4834). ^{1}H NMR: 1.1–2.25 (m, 9H), 3.73 (t, $J = 7$ Hz, 2H), 5.55–5.8 (m, 2H).

2-Methyl-2-phenylpropanol. b.p. 145–155°/19 torr. (lit.,[31] b.p. 113°/14 torr.). ^{1}H NMR 1.27 (s, 6H), 1.98 (s, 1H), 3.44 (s, 2H), 7.05–7.30 (m, 5H). MS; 150 (M^+, 11), 119 (100).

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