

Cleavage of siloxanes with organyltrifluoro- and diorganyldifluorosilanes

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Abstract

Hexamethyldisiloxane is cleaved with organyltrifluoro- or diorganyldifluorosilanes as low as 20°C in the absence of catalysts to form earlier unknown 1,1,1-trimethyl-, 3-organyl-3,3-difluoro- or 1,1,1-trimethyl-, 3,3-diorganyl-3-difluorodisiloxanes with the general formula $R_{4-n}SiF_{n-1}OSi(CH_3)_3$ ($n = 2-3$) in 57–97% yield. The Si–O bond in 1,1,3,3-tetramethyldisiloxane is broken with organyltrifluoro- or diorganyldifluorosilanes in a similar manner but more slowly to give 1,1-dimethyl-, 3-organyl-, 3,3-difluoro- or 1,1-dimethyl-, 3,3-diorganyl-, 3-fluorodisiloxanes with the general formula $R_{4-n}SiF_{n-1}OSiH(CH_3)_2$ ($n = 2-3$) in 50–70% yield. The reaction of phenyltrifluorosilane with 1,1,1,3,3,5,5,5-octamethyltrifluorosiloxane leads to 1,1,1,3,3-pentamethyl-, 5,5-difluoro-, 5-phenyltrisiloxane, whereas the reaction with tetrakis (trimethylsiloxy)siloxane gives tri(trimethylsiloxy)difluoro(phenyl)silane. Even under normal conditions of storage, the cleavage products disproportionate readily in different directions. The ability of these compounds to disproportionation depends on the nature of the substituents attached to the silicon atom and the number of fluorine atoms in the molecule.

Results and discussion

As early as 1957 one of the present authors described the catalytic cleavage of the disiloxane Si–O–Si groups in perorganylsiloxanes with organylchloro- and organylbromosilanes [1–6]. An easy cleavage of this group with 1-iodosilatrane has also been reported [7].

An attempt to introduce tributylfluorosilane into this reaction was unsuccessful [3]. Nevertheless, tetrafluorosilane cleaves hexamethyldisiloxane although under drastic conditions (3000 atm) [8].

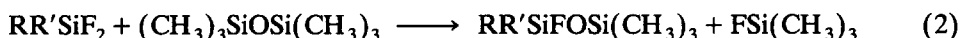
At the same time, some organyltrifluorosilanes break hexamethyldisiloxane readily enough [9]. We have found that the reaction of hexamethyldisiloxane with organyltrifluoro- or diorganyldifluorosilanes (1:1 ratio, 20°C, 24–48 h) gives 1,1,1-

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trimethyl-, 3-organyl-, 3,3-difluoro- and 1,1,1-trimethyl-3,3-diorganyl-, 3-fluorodisiloxanes, respectively, in 57–97% yield according to the following scheme:



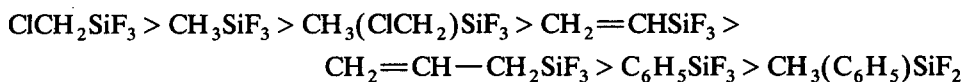
$\text{R} = \text{CH}_3, \text{ClCH}_2, \text{CH}_2=\text{CH}, \text{CH}_2=\text{CH}-\text{CH}_2, \text{C}_6\text{H}_5$



$\text{R}, \text{R}' = \text{CH}_3, \text{ClCH}_2, \text{C}_6\text{H}_5$

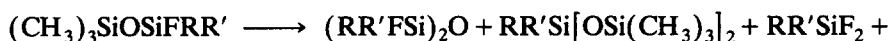
Reactions 1 and 2 occur without any catalysts. All attempts to introduce fluorides $[\text{Me}_3(\text{PhCH}_2)\text{NF}, \text{CsF}, \text{AlF}_3, \text{SbF}_3]$ or to carry out the reaction in a solvent of different dielectric constant were not a success.

Analytical gas chromatography (GLC) shows the reactivity of organylfluorosilanes increases in the following order:



The compounds synthesized in this way (I–VII, Table 1) are colorless liquids, well soluble in organic solvents.

1,1,1-Trimethyl-3,3-diorganyl-3-fluoro- and 1,1,1-trimethyl-3-organyl-3,3-difluorosiloxanes of general formula $(\text{CH}_3)_3\text{SiOSiRR}'$ (I–VII, Table 1) are unstable compounds which disproportionate slowly at 20°C (GLC) according to [10]:



(I–VII)

(A)

(B)



(C)

(D)

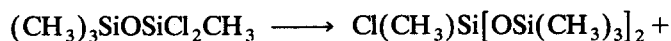
$\text{R}, \text{R}' = \text{CH}_3, \text{F}$ (I); ClCH_2, F (II); $\text{CH}_2=\text{CH}, \text{F}$ (III); $\text{C}_6\text{H}_5, \text{F}$ (IV);

$\text{CH}_3, \text{ClCH}_2$ (V); $\text{CH}_3, \text{C}_6\text{H}_5$ (VI); $\text{CH}_2=\text{CHCH}_2, \text{F}$ (VII) (3)

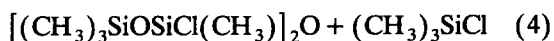
In this connection it should be borne in mind that, at room temperature, hexafluorodisiloxane disproportionates very readily to SiF_4 and SiO_2 [11].

The ease with which compounds I–VII undergo disproportionation is determined by the nature of the substituents R and R' and enhances in the following sequence: II > I > III > IV. Thus, I and II decompose by 40% during distillation under atmospheric pressure whereas IV does not change even when heated to 200°C. 1,1,1-Trimethyl-3,3-diorganyl, 3-fluorodisiloxanes are less prone to disproportionation than 1,1,1-trimethyl, 3-organyl-, 3,3-difluorodisiloxanes.

We have found that 1,1,1,3-tetramethyldichlorodisiloxane (VIII) is subject to disproportionation, but this occurs much more slowly. The yield of disproportionation products is about 10% (20°C, 10 days).

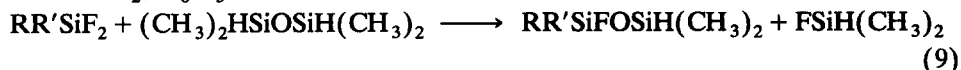


(B)



(D)

$R = \text{ClCH}_2, \text{C}_6\text{H}_5$

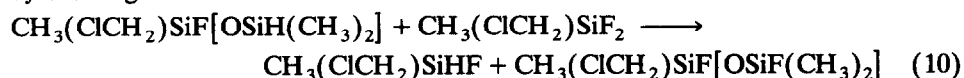


$R, R' = \text{CH}_3, \text{ClCH}_2, \text{CH}_2=\text{CH}, \text{C}_6\text{H}_5$

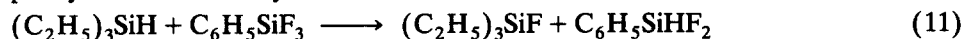
According to GLC, the reactivity of organylfluorosilanes increases in the following order: $\text{ClCH}_2\text{SiF}_3 > \text{CH}_3(\text{ClCH}_2)\text{SiF}_2 > \text{C}_6\text{H}_5\text{SiF}_3 > \text{CH}_3(\text{CH}_2=\text{CH})\text{SiF}_2 > \text{CH}_3(\text{C}_6\text{H}_5)\text{SiF}_2$.

The compounds synthesized in this manner (XI–XV, Table 1) are colorless mobile fluids, well soluble in organic solvents.

According to GLC–MS data, the reaction mixture formed in the reaction of methyl(chloromethyl)difluorosilane with 1,1,3,3-tetramethyldisiloxane also contains a small amount (6%) of 1,1,3-trimethyl-, 1,3-difluorodisiloxane formed, evidently, by exchange reaction



However, it was not possible to carry out a model reaction of triethylsilane with phenyltrifluorosilane by



Up to 10% of benzene is formed when reaction 4 ($\sim 20^\circ\text{C}$, 30 days) is employed.

According to GLC–MS, reactions 8 and 9 also give 1,1,3,3,5,5-hexamethyltrisiloxane (3–7% yield) seemingly due to the disproportionation of 1,1,3,3-tetramethyldisiloxane.

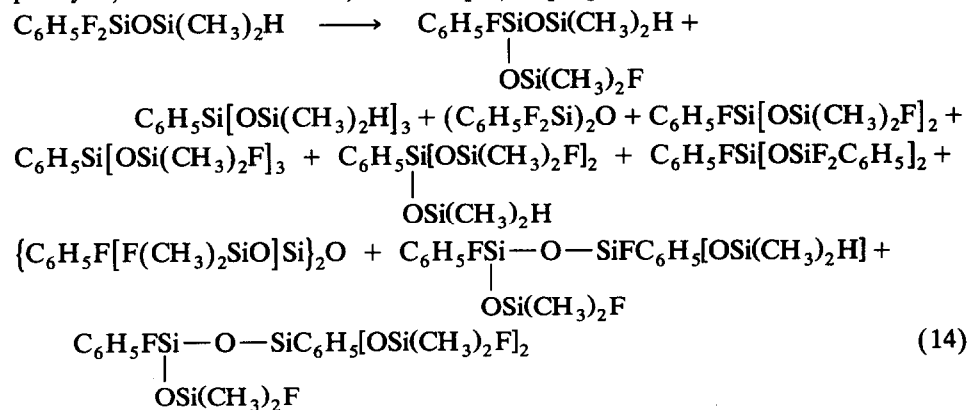


An analogous rearrangement of organosilicon compounds R_2SiHX ($\text{R} = \text{alkyl}, \text{X-alkyl}, \text{F}, \text{Cl}$) is also known [13–15].



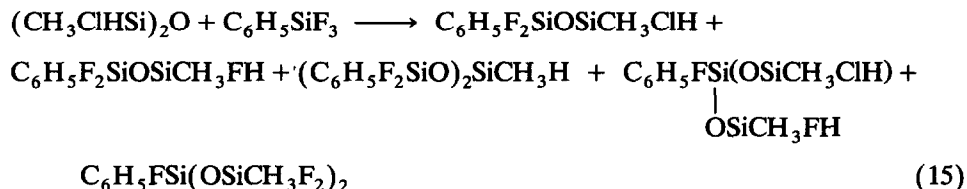
The substitution of the second and third fluorines in organylfluorosiloxanes by a dimethylsiloxy group occurs with great difficulty and gives low yields even with a 2–3-fold excess of tetramethyldisiloxane. In addition, the reaction is complicated by disproportionation which accelerates with heating.

The 1,1-dimethyl-3,3-diorganyl-3-fluoro- and 1,1-dimethyl-3-organyl-3,3-difluorosilanes synthesized (XI–XV, Table 1) are unstable in storage and undergo disproportionation in different directions as low as 20°C . Thus, 1,1-dimethyl-3-phenyl-3,3-difluorodisiloxane, for example, disproportionates as



The composition of the disproportionation products varies depending on the reaction time. Unlike the disproportionation of 1,1,1-trimethyl-3,3-diorganyl-3-fluoro- and 1,1,1-trimethyl-3-organyl-3,3-difluorosiloxanes, that of 1,1-dimethyl-3,3-diorganyl-3-fluoro- and 1,1-dimethyl-3-organyl-3,3-difluorosiloxanes is complicated by exchange of the Si-H bonds for Si-F bonds and by the formation of more branching siloxane structures.

In contrast to tetra- and hexamethyldisiloxane, the reaction of phenyltrifluorosilane with 1,3-dimethyl-, 1,3-dichlorodisiloxane proceeds considerably more slowly and is accompanied by disproportionation and exchange of the Si-H bonds for Si-F bonds. As shown by GLC-MS data the reaction follows the scheme



GLC-MS analysis of the disproportionation products **A-D** shows that the electron-impact induced decomposition of these compounds proceeds analogously to that of hexaorganysiloxanes and -silazanes [17,18]. The molecular ion peak is absent in the spectra of almost all compounds except for **IV** and **VI** in which the molecular ion is stabilized by the phenyl group.

The $[M - CH_3]^+$ ion peak is maximal or rather intense in all spectra. Subsequent fragmentation of these ions follows different directions depending on the nature of substitution. Thus, in the spectra of disproportionation products **XV**, as their structure becomes more complicated, a gradual shift of the full ion current fraction towards lower masses is observed, a significant ion current portion being concentrated on fragments containing a silicon atom. In this case, the most intense peak is mainly that of the rearrangement ion with m/z 135 ($C_6H_5Si(CH_3)_2^+$).

Unlike the spectra of the previously studied siloxanes, in those of **I-VII**, the $\text{Si}(\text{CH}_3)_3^+$ peak is of low intensity or absent. This indicates that the $(M - \text{CH}_3)^+$ ion is formed mainly at the expense of the $\text{Si}(\text{CH}_3)_3$ group.

In some spectra (compounds **I**, **XVI** and, especially, **II**, **V**), there are $(M - C_3H_7)^+$ ion peaks (exact ion masses were measured in **II** and **V**) which can be formed only by rearrangement followed by fragmentation of the $(M - CH_3)^+$ ion.

The spectra of compounds **I**, **II**, **III**, **VIII**, **IV**, **VI** (m/e 77, 81, 77.87, 93, 139, 135, respectively) show some ion peaks formed due to mutual migrations of terminal CH_3 and R groups (where $\text{R} = \text{F}$, Cl , CH_3 and ClCH_2).

In the spectra of tri- and tetrasiloxanes (compounds **B**, **C**), the $\text{Si}(\text{CH}_3)_3^+$ intensity is significantly increased and the above regularity is the case. Moreover, for tetrasiloxanes (compounds **IB**, **IIIC**) the maximal ion peak in the spectra is that with m/e 207, which seems to be formed by abstraction of $\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}$ and **R** groups ($\text{R} = \text{CH}_3, \text{CH}_2\text{CH}$).

In the mass spectra of the disproportionation products (XIV) if there are at least two C_6H_5 groups in the molecule, a rearrangement peak (m/z 197), $[(\text{C}_6\text{H}_5)_2\text{SiCH}_3]^+$ is most common.

The IR spectra of compounds I–XV display deformational vibrations at 1260 cm^{-1} , characteristic of Si–OSi antisymmetrical stretching vibrations, Si–H stretch-

ing vibrations, 2120–2130 cm^{-1} , bands at 895 and 930 cm^{-1} corresponding to SiF_2 and SiF fragments as well as bands at 1120, 1430, 1560 cm^{-1} ($\text{Si}-\text{C}_6\text{H}_5$), 1410, 1600 cm^{-1} ($\text{Si}-\text{CH}=\text{CH}_2$) and 610, 750–800 cm^{-1} ($\text{Si}-\text{CH}_2\text{Cl}$). The increase in the number of fluorine atoms in the molecule in all compounds leads to a slight (10–20 cm^{-1}) increase in $\nu_{\text{as}}(\text{SiOSi})$ and $\nu(\text{Si}-\text{H})$. A similar effect is observed when the phenyl group is replaced by a chloromethyl group.

Experimental

1,1-Dimethyl-3-chloromethyl-3,3-difluorodisiloxane (XI)

A mixture of 13.4 g (0.1 mol) of 1,1,3,3-tetramethyldisiloxane and 13.5 g (0.1 mol) of chloromethyl(trifluoro)silane was kept at room temperature over 3 days. After distillation, 7.4 g (95%) of dimethylfluorosilane was isolated into a cooled trap. Distillation of the residue gave 12.29 g (64%) of 1,1-dimethyl-3-chloromethyl-3,3-difluorodisiloxane (XI). Compounds I–XV were prepared in an analogous manner. Physico-chemical constants are presented in Table 1. Analytical chromatography of freshly prepared samples of organylfluorosiloxanes showed no traces of decomposed products. i.e., disproportionation does not occur in contact with the chromatographic phase.

Mass Spectral analyses were performed on a Varian MAT-212 spectrometer. Infrared spectra were recorded on a Specord 75 infrared spectrometer.

Mass spectra of products of disproportionation of I. I: 155 (100) $(M - \text{CH}_3)^+$, 141 (2) $(M - \text{C}_2\text{H}_5)^+$, 139(3) $(M - \text{CH}_3 - \text{CH}_4)^+$, 127(4) $(M - \text{C}_3\text{H}_7)^+$, 125(4), 81(2) $\text{CH}_3\text{SiF}_2^+$, 77(3) $(\text{CH}_3)_2\text{SiF}^+$, 73(9) $(\text{CH}_3)_3\text{Si}^+$. $(\text{CH}_3\text{F}_2\text{Si})_2\text{O}$ (IA): 163(100) $(M - \text{CH}_3)^+$, 159(3) $(M - \text{F})^+$, 149(2) $(M - \text{C}_2\text{H}_5)^+$, 134(2), 129(10), 81(14) $\text{CH}_3\text{SiF}_2^+$. $\text{CH}_3(\text{F})\text{Si}[\text{OSi}(\text{CH}_3)_2]_2$ (IB): 225(100) $(M - \text{CH}_3)^+$, 209(5) $(M - \text{CH}_3 - \text{CH}_4)^+$, 195(1), 193(2), 189(1), 151(3) $[M - (\text{CH}_3)_3\text{SiO}]^+$, 135(2), 133(2), 121(1), 73(64) $(\text{CH}_3)_3\text{Si}^+$. $\text{CH}_3\text{Si}[\text{OSi}(\text{CH}_3)_2]_3$ (IC): 295 (42) $(M - \text{CH}_3)^+$, 279(4) $(M - \text{CH}_3 - \text{CH}_4)^+$, 265(1), 263(1), 242(1), 207(100) $[M - (\text{CH}_3)_3\text{SiO} - \text{CH}_2]^+$, 191(4), 73(64) $(\text{CH}_3)_3\text{Si}^+$.

Mass spectra of products of disproportionation of II. II: 189(81) $(M - \text{CH}_3)^+$, 175(1), 161(100), 155(2) $(M - \text{ClCH}_2)^+$, 147(4), 145(8), 125(19), 81(5) $\text{CH}_3\text{SiF}_2^+$. $\text{ClCH}_2(\text{F})\text{Si}[\text{OSi}(\text{CH}_3)_2]_2$ (IIC): 259(100) $(M - \text{CH}_3)^+$, 231(44), 225 (12) $(M - \text{ClCH}_2)^+$, 216(5), 219(3) $(M - \text{ClCH}_2 - \text{CH}_2)^+$, 193(7), 87(53) $(\text{CH}_3)_2\text{SiOH}^+$, 73(100) $(\text{CH}_3)_3\text{Si}^+$. $[(\text{CH}_3)_3\text{SiO}(\text{ClCH}_2)(\text{F})\text{Si}]_2\text{O}$ (IID): 371(6), $(M - \text{CH}_3)^+$, 337(4) $(M - \text{ClCH}_2)^+$, 291 (1) $[M - (\text{CH}_3)_2\text{SiCl}]^+$, 263(4), 271(8), 197(4), 107(7) $(\text{CH}_3)_2\text{SiCH}_2\text{Cl}^+$, 93(10) $(\text{CH}_3)_2\text{SiCl}^+$, 77(5) $(\text{CH}_3)_2\text{SiF}^+$, 73(100) $(\text{CH}_3)_3\text{Si}^+$.

Mass spectra of products of disproportionation of III. III: 167(100) $(M - \text{CH}_3)^+$, 155(2) $(M - \text{CH}_2=\text{CH})^+$, 151(2) $(M - \text{C}_2\text{H}_5)^+$, 141(69) $(M - \text{CH}_3 - \text{C}_2\text{H}_5)^+$, 139(2), 137(3), 127(6), 125(17) $(M - 2\text{CH}_3 - \text{CH}_2=\text{CH})^+$, 113(2), 111(4), 93(2), 86(3), 84(6), 81(4) $\text{CH}_3\text{SiF}_2^+$, 77(5) $(\text{CH}_3)_2\text{SiF}^+$, 73(1) $(\text{CH}_3)_3\text{Si}^+$. $\text{CH}_2=\text{CH}(\text{F})\text{Si}[\text{OSi}(\text{CH}_3)_2]_2$ (IIIB): 237(100) $(M - \text{CH}_3)^+$, 221(2) $(M - \text{CH}_3 - \text{CH}_4)^+$, 209(51), 196(18), 195(10), 193(3), 151(3), 137(4), 85(31) $(\text{CH}_3)_2\text{SiCH}=\text{CH}_2^+$, 73(29) $(\text{CH}_3)_3\text{Si}^+$. $\text{CH}_2=\text{CHSi}[\text{OSi}(\text{CH}_3)_2]_3$ (IIIC): 307(28) $(M - \text{CH}_3)^+$, 291(1) $(M - \text{CH}_3 - \text{CH}_4)^+$, 263(1), 219(56) $[M - (\text{CH}_3)_2\text{SiO} - \text{CH}_2]^+$, 207(100) $[M - (\text{CH}_3)_3\text{SiO} - \text{C}_2\text{H}_5]^+$, 193(6), 191(4), 133(3), 85(49) $\text{CH}_2=\text{CHSi}(\text{CH}_3)_2^+$, 73(80) $\text{Si}(\text{CH}_3)_3^+$.

Mass-spectrum of IV. IV: 232(8) M^+ , 217(100) $(M - \text{CH}_3)^+$, 201(10) $(M - \text{CH}_3$

$-\text{CH}_4)^+$, 197(13) $(M - \text{CH}_3 - \text{HF})^+$, 187(3), 143(3) $[M - (\text{CH}_3)_3\text{SiO}]^+$, 139(2) $\text{C}_6\text{H}_5\text{Si}(\text{F})\text{CH}_3^+$, 124(5) $\text{C}_6\text{H}_5\text{SiF}^+$, 91(6), 77(3) C_6H_5^+ .

Mass-spectrum of V. V: 185(55) $(M - \text{CH}_3)^+$, 157(100), 151(46) $(M - \text{ClCH}_2)^+$, 143(3), 141(5), 136(3), 135(4) $(M - \text{ClCH}_2 - \text{CH}_4)^+$, 121(10), 73(4) $(\text{CH}_3)_3\text{Si}^+$.

Mass spectra of products of disproportionation of VI. VI: 228(5) M^+ , 213(100) $(M - \text{CH}_3)^+$, 197(20) $(M - \text{CH}_3 - \text{CH}_4)^+$, 193(5) $(M - \text{CH}_3 - \text{HF})^+$, 183(3), 139(4) $[M - (\text{CH}_3)_3\text{SiO}]^+$, 135(5) $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2^+$, 91(5), 77(4) C_6H_5^+ . $\text{C}_6\text{H}_5(\text{CH}_3)\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$ (VIB): 283(100) $(M - \text{CH}_3)^+$, 267(8) $(M - \text{CH}_3 - \text{CH}_4)^+$, 253(2), 251(4), 205(2), 193(4), 135(48) $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2^+$, 73(12) $(\text{CH}_3)_3\text{Si}^+$.

Mass spectra of products of disproportionation of VII. VII: 181(10) $(M - \text{CH}_3)^+$, 155(53) $(M - \text{CH}_2\text{CH}=\text{CH}_2)^+$, 141(63) $(M - \text{CH}_2 - \text{CH}_2\text{CH}=\text{CH}_2)^+$, 127(14), 125(38) $(M - \text{CH}_2\text{CH}=\text{CH}_2 - 2\text{CH}_3)^+$, 111(11), 81(14) $\text{CH}_3\text{SiF}_2^+$, 77(11) $(\text{CH}_3)_2\text{SiF}^+$, 73(6) $(\text{CH}_3)_3\text{Si}^+$. $\text{CH}_2=\text{CHCH}_2(\text{F})\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$ (VIIB): 251(100) $(M - \text{CH}_3)^+$, 225(41) $(M - \text{CH}_2\text{CH}=\text{CH}_2)^+$, 211(16) $(M - \text{CH}_2\text{CH}=\text{CH}_2 - \text{CH}_3)^+$, 209(34), 195(12) $(M - 2\text{CH}_3 - \text{CH}_2\text{CH}=\text{CH}_2)^+$, 193(10), 151(20), 137(16), 135(11), 121(12), 118(14), 105(21), 99(62) $(\text{CH}_3)_2\text{SiCH}_2\text{CH}=\text{CH}_2^+$, 98(17), 77(19) $(\text{CH}_3)_2\text{SiF}^+$, 73(91) $(\text{CH}_3)_3\text{Si}^+$.

Mass spectra of products of disproportionation of VIII. VIII: 187(100) $(M - \text{CH}_3)^+$, 172(22) $(M - 2\text{CH}_3)^+$, 171(3) $(M - \text{CH}_3 - \text{CH}_4)^+$, 167(3) $(M - \text{Cl})^+$, 151(5) $(M - \text{CH}_3 - \text{HCl})^+$, 113(8) $\text{CH}_3\text{SiCl}_2^+$, 93(25) $(\text{CH}_3)_2\text{SiCl}^+$, 73(10) $(\text{CH}_3)_3\text{Si}^+$. $\text{CH}_3(\text{Cl})\text{Si}[\text{Si}(\text{CH}_3)_3]_2$ (VIIIIB): 241(96) $(M - \text{CH}_3)^+$, 226(12) $(M - 2\text{CH}_3)^+$, 225(4) $(M - \text{CH}_3 - \text{CH}_4)^+$, 221(4) $(M - \text{Cl})^+$, 189(6), 167(5) $[M - (\text{CH}_3)_3\text{SiO}]^+$, 133(7), 73(100) $(\text{CH}_3)_3\text{Si}^+$. $[(\text{CH}_3)_3\text{SiO}(\text{CH}_3\text{XCl})\text{Si}]_2\text{O}$ (VIIIID): 335(1) $(M - \text{CH}_3)^+$, 227(11) $[M - \text{Cl}(\text{CH}_3)_2\text{SiOCH}_2]^+$, 207(2), 192(1), 93(3) $(\text{CH}_3)_2\text{SiCl}^+$, 73(100) $(\text{CH}_3)_3\text{Si}^+$.

Mass spectra of products of disproportionation of XI. XI: 189(8) $(M - \text{H})^+$, 175(100) $(M - \text{CH}_3)^+$, 161(33) $(M - 2\text{CH}_3 + \text{H})^+$, 146(53), 123(17) $(M - \text{ClCH}_2 - \text{F} + \text{H})^+$, 93(8) $(\text{CH}_3)_2\text{FSiO}^+$, 81(8), 77(17) $(\text{CH}_3)_2\text{SiF}$. $\text{ClCH}_2\text{SiF}[\text{OSi}(\text{CH}_3)_2\text{H}]_2$: 246(1) M^+ , 231(7) $(M - \text{CH}_3)^+$, 197(2) $(M - \text{ClCH}_2)^+$, 133(3) $\{[(\text{CH}_3)_2\text{SiH}]_2\text{O} - \text{H}\}^+$, 93(11) $(\text{CH}_3)_2\text{FSiO}^+$, 73(100) $(\text{CH}_3)_3\text{Si}^+$.

Mass spectra of products of disproportionation of XII. XII: 185(7) $(M - \text{H})^+$, 171(82) $(M - \text{CH}_3)^+$, 157(24), 145(13), 143(45), 137(100) $(M - \text{ClCH}_2)^+$, 121(8), 107(11) $(M - \text{OSiMeFH})^+$, 93(8) $(M - \text{OSi}(\text{CH}_3)_2\text{F})^+$, 91(6), 77(13) $(M - \text{OSi}(\text{ClCH}_2)\text{CH}_3\text{H})^+$, 73(8) $(M - \text{OSi}(\text{ClCH}_2)\text{FH})^+$, 53(7). $\text{ClCH}_2\text{SiCH}_3\text{[OSi}(\text{CH}_3)_2\text{H]}_2$: 242(1) M^+ , 227(3) $(M - \text{CH}_3)^+$, 193(14) $(M - \text{ClCH}_2)$, 189(33), 161(100), 145(13), 125(23), 81(9), 73(23). $\text{ClCH}_2\text{SiCH}_3[\text{OSi}(\text{CH}_3)_2\text{H}][\text{OSi}(\text{CH}_3)_2\text{F}]$: 245(4) $(M - \text{CH}_3)^+$, 211(4) $(M - \text{ClCH}_2)^+$, 195(8), 191(28), 189(72), 163(39), 161(100), 145(13), 125(21), 110(3), 81(8), 77(1), 73(12). $\text{ClCH}_2(\text{CH}_3)\text{FSiOSi}[\text{OSi}(\text{CH}_3)_2\text{H}](\text{CH}_3)\text{CH}_2\text{Cl}$: 293(5) $(M - \text{H})^+$, 255(43) $(M - \text{ClCH}_2)^+$, 249(71), 222(21), 197(7), 175(6), 161(9), 137(10), 125(9), 107(16), 93(100), 77(39), 73(68), 63(10), 58(21).

Mass spectra of products of disproportionation of XIII. XIII: 164(38) M^+ , 149(100) $(M - \text{CH}_3)^+$, 137(32) $(M - \text{CH}_2=\text{CH}_2)^+$, 136(20), 123(60), 121(58), 107(20), 91(12), 77(20), 63(20). $[\text{CH}_3(\text{CH}_2=\text{CH})\text{FSi}]_2\text{O}$: 194(10) M^+ , 179(100) $(M - \text{CH}_3)^+$, 167(13) $(M - \text{CH}=\text{CH}_2)^+$, 153(23) $(M - \text{CH}_3 - \text{CH}=\text{CH}_2 + \text{H})^+$, 141(44), 125(100), 111(9), 96(14), 81(14). $[(\text{CH}_3)_2\text{HSiO}]_2\text{Si}(\text{CH}_3)_2$: 208(15) M^+ , 193(100) $(M - \text{CH}_3)^+$, 133(14) $(M - \text{OSi}(\text{CH}_3)_2\text{H})^+$, 199(5), 73(86). $[(\text{CH}_3)_2\text{HSiO}]_2\text{CH}_3\text{Si}$

$\text{CH}=\text{CH}_2$: 220(11) M^+ , 205(100) $(M - \text{CH}_3)^+$, 193(13) $(M - \text{CH}=\text{CH}_2)^+$, 191(19), 167(53), 145(3) $(M - \text{OSi}(\text{CH}_3)_2\text{H})^+$, 133(15), 119(9), 73(67), 59(27).

Mass spectra of products of disproportionation of XIV. XIV: 214(40) M^+ , 213(32) $(M - \text{H})^+$, 199(100) $(M - \text{CH}_3)^+$, 197(24), 182(15), 178(5), 137(92) $(M - \text{C}_6\text{H}_5)^+$, 121(50) $(M - \text{OSi}(\text{CH}_3)_2\text{F})^+$, 107(6), 99(5), 91(13), 77(16), 73(2). $(\text{C}_6\text{H}_5(\text{CH}_3)\text{-FSi})_2\text{O}$: 294(5) M^+ , 279(34) $(M - \text{CH}_3)^+$, 217(7) $(M - \text{C}_6\text{H}_5)^+$, 201(100), 187(6), 143(9), 140(8), 125(17), 91(33), 81(5), 77(10). $\text{C}_6\text{H}_5(\text{CH}_3)\text{Si}[\text{OSi}(\text{CH}_3)_2\text{F}]_2$: 291(67) $(M - \text{CH}_3)^+$, 287(10) $(M - \text{F})^+$, 273(53) $(M - \text{CH}_3 - \text{F} + \text{H})^+$, 210(15), 195(15), 146(2), 143(1), 139(4), 135(100), 129(7), 121(9), 107(3), 91(4), 77(3), 73(13). $\text{C}_6\text{H}_5(\text{CH}_3)\text{FSiOSi}[\text{OSi}(\text{CH}_3)_2\text{H}](\text{CH}_3)\text{C}_6\text{H}_5$: 350(13) M^+ , 335(77) $(M - \text{CH}_3)^+$, 273(73) $(M - \text{C}_6\text{H}_5)^+$, 258(36), 197(100) $(M - \text{OSi}(\text{CH}_3)_2\text{H} - \text{C}_6\text{H}_5 + \text{H})^+$, 136(20), 135(77), 121(25), 91(9), 77(5), 73(7). $\text{C}_6\text{H}_5(\text{CH}_3)\text{FSiOSi}[\text{OSi}(\text{CH}_3)_2\text{F}](\text{CH}_3)\text{C}_6\text{H}_5$: 368(12) M^+ , 353(20) $(M - \text{CH}_3)^+$, 291(17), 276(30), 197(100), 176(6), 169(20), 135(61), 130(26) $(M - \text{OSi}(\text{CH}_3)_2\text{F} - \text{CH}_3)^+$, 91(13), 77(5), 73(6). $[\text{C}_6\text{H}_5(\text{CH}_3)\text{FSiO}]_2\text{Si}(\text{CH}_3)\text{C}_6\text{H}_5$: 430(8) M^+ , 415(35) $(M - \text{CH}_3)^+$, 352(6), 337(24), 277(17), 260(33), 197(100), 161,5(37), 135(51), 91(10), 77(6), 73(8).

Mass spectra of products of disproportionation of XV. XV: 218(100) M^+ , 217(92) $(M - \text{H})^+$, 203(78) $(M - \text{CH}_3)^+$, 197(19) $[(\text{C}_6\text{H}_5)_2\text{SiCH}_3]^+$, 187(42), 183(23), 143(36) $(M - \text{OSi}(\text{CH}_3)_2\text{H})^+$, 139(91), 125(40), 111(21), 107(16), 101(19), 91(31), 81(21), 78(48), 77(43), 73(13). $\text{C}_6\text{H}_5\text{F}_2\text{SiOSi}(\text{CH}_3)_2\text{F}$: 236(36) M^+ , 221(100) $(M - \text{CH}_3)^+$, 203(45), 183(10), 162(14), 139(55), 91(24), 77(31), 73(40). $\text{C}_6\text{H}_5\text{FSi}[\text{OSi}(\text{CH}_3)_2\text{H}]_2$: 274(10) M^+ , 273(18) $(M - \text{H})^+$, 259(48) $(M - \text{CH}_3)^+$, 196(53) $(M - \text{C}_6\text{H}_5)^+$, 181(48) $(M - \text{CH}_3 - \text{C}_6\text{H}_5 + \text{H})^+$, 135(100) $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}^+$, 121(50) $[\text{C}_6\text{H}_5(\text{CH}_3)\text{SiH}]^+$, 91(13), 77(38), 73(25). $\text{C}_6\text{H}_5\text{Si}[\text{OSi}(\text{CH}_3)_2\text{H}]_3$: 330(5) M^+ , 315(4) $(M - \text{CH}_3)^+$, 193(40), 161(22), 135(100) $[\text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}]^+$, 121(30) $[\text{C}_6\text{H}_5(\text{CH}_3)\text{SiH}]^+$, 77(55), 73(60). $\text{C}_6\text{H}_5\text{FSi}[\text{OSi}(\text{CH}_3)_2\text{F}]_2$: 310(2) M^+ , 295(9) $(M - \text{CH}_3)^+$, 291(8) $(M - \text{F})^+$, 277(18) $(M - \text{CH}_2\text{F})^+$, 214(13) $(M - \text{C}_6\text{H}_5\text{F})^+$, 199(16), 197(40), 182(27), 135(100), 121(31), 91(6), 77(8), 73(10). $(\text{CH}_3)_2\text{FSiOSi}(\text{CH}_3)_2\text{OSiF}_2\text{C}_6\text{H}_5$: 310(7) M^+ , 295(77) $(M - \text{CH}_3)^+$, 291(15) $(M - \text{F})^+$, 277(43) $(M - \text{CH}_2\text{F})^+$, 214(20) $(M - \text{C}_6\text{H}_5\text{F})^+$, 199(11), 161(8), 139(20), 135(100), 121(20), 91(8), 77(13), 73(10). $\text{C}_6\text{H}_5\text{Si}[\text{OSi}(\text{CH}_3)_2\text{F}]_3$: 369(23) $(M - \text{CH}_3)^+$, 351(8) $(M - \text{CH}_3 - \text{F} + \text{H})^+$, 273(53) $(M - \text{OSi}(\text{CH}_3)_2\text{F} - \text{F} + \text{H})^+$, 211(27) $(M - \text{OSi}(\text{CH}_3)_2\text{F} - \text{SiCH}_3\text{F}_2 + \text{H})^+$, 139(9) $\text{C}_6\text{H}_5\text{SiFCH}_3^+$, 135(100) $\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2^+$, 121(17) $\text{C}_6\text{H}_5\text{SiCH}_3\text{H}^+$, 91(4) $\text{C}_6\text{H}_5\text{CH}_2^+$, 77(5) C_6H_5 , 73(39) $(\text{CH}_3)_3\text{Si}^+$. $\text{C}_6\text{H}_5\text{Si}[\text{OSi}(\text{CH}_3)_2\text{F}]_2\text{OSi}(\text{CH}_3)_2\text{H}$: 366(1) M^+ , 351(1) $(M - \text{CH}_3)^+$, 347(3), $(M - \text{F})^+$, 333(3), 273(21), 256(16), 211(10), 197(4), 193(7), 135(100), 121(23), 77(27), 73(32). $\text{C}_6\text{H}_5\text{Si}[\text{OSi}(\text{CH}_3)_2\text{H}]_2\text{OSi}(\text{CH}_3)_2\text{F}$: 348(16) M^+ , 333(10) $(M - \text{CH}_3)^+$, 329(12) $(M - \text{F})^+$, 286(16), 272(20), 256(18), 254(9), 214(10), 196(9), 135(100), 121(18), 77(6), 73(50). $\{\text{C}_6\text{H}_5[\text{F}(\text{CH}_3)_2\text{SiO}]\text{FSi}\}_2\text{O}$: 435(42) $(M - \text{CH}_3)^+$, 431(27) $(M - \text{F})^+$, 416(8), 353(29), 339(100), 278(63), 274(31), 260(31), 209(64), 197(21), 139(58), 135(83), 121(42), 91(17), 77(17), 73(17). $\{\text{C}_6\text{H}_5[\text{H}(\text{CH}_3)_2\text{SiO}]\text{FSi}\}_2\text{O}$: 414(13) M^+ , 399(4) $(M - \text{CH}_3)^+$, 335(27), 321(17), 278(4), 274(9), 260(14), 244(6), 240(4), 197(15), 183(28), 135(100), 121(44), 91(5), 77(4), 73(12). $\text{C}_6\text{H}_5[\text{F}(\text{CH}_3)_2\text{SiO}]\text{FSi-O-Si}[\text{OSi}(\text{CH}_3)_2\text{F}]_2\text{C}_6\text{H}_5$: 509(10) $(M - \text{CH}_3)^+$, 505 $(M - \text{F})^+$, 487(3) $(M - 2\text{F} + \text{H})^+$, 427(3), 426(3), 412(16), 395(6), 351(16), 335(14), 317(6), 276(8), 274(10), 218(5), 214(11), 197(16), 183(7), 150(8), 135(100), 121(12), 91(5), 77(5), 73(19). $\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{F}$: 126(5) M^+ , 111(6) $(M - \text{CH}_3)^+$, 97 $(M - 2\text{CH}_3 + \text{H})^+$, 85(29), 81(54), 77(100) Me_2SiF^+ . $\text{ClCH}_2(\text{CH}_3)_2\text{SiOSiF}[\text{OSi}(\text{CH}_3)_2\text{F}]_2\text{C}_6\text{H}_5$: 509(10) $(M - \text{CH}_3)^+$, 505 $(M - \text{F})^+$, 487(3) $(M - 2\text{F} + \text{H})^+$, 427(3), 426(3), 412(16), 395(6), 351(16), 335(14), 317(6), 276(8), 274(10), 218(5), 214(11), 197(16), 183(7), 150(8), 135(100), 121(12), 91(5), 77(5), 73(19).

$(\text{CH}_3)_3\text{CH}_2\text{Cl}$: 293(19) ($M - \text{CH}_3$)⁺, 265(12), 251(18), 237(45), 213(6), 191(25), 163(28), 121(14), 107(18) $(\text{CH}_3)_2\text{SiCH}_2\text{Cl}^+$, 93(100) $(\text{CH}_3)_2\text{SiCl}^+$, 77(83) $(\text{CH}_3)_2\text{SiF}^+$, 73(67) $(\text{CH}_3)_3\text{Si}^+$.

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