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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 disproportionate 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:



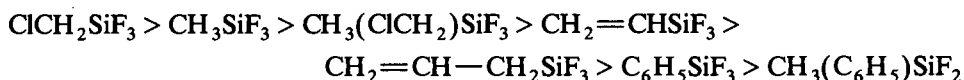
R = CH₃, ClCH₂, CH₂=CH, CH₂=CH—CH₂, C₆H₅



R, R' = CH₃, ClCH₂, C₆H₅

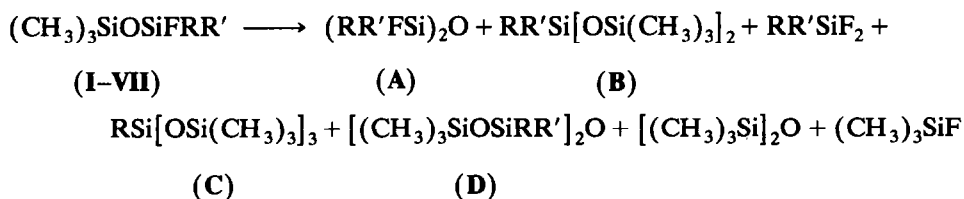
Reactions 1 and 2 occur without any catalysts. All attempts to introduce fluorides [Me₃(PhCH₂)NF, CsF, AlF₃, SbF₃] or to carry out the reaction in a solvent of different dielectric constant were not a success.

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 (CH₃)₃SiOSiFRR' (I–VII, Table 1) are unstable compounds which disproportionate slowly at 20°C (GLC) according to [10]:



R, R' = CH₃, F (I); ClCH₂, F (II); CH₂=CH, F (III); C₆H₅, F (IV);

CH₃, ClCH₂ (V); CH₃, C₆H₅ (VI); CH₂=CHCH₂, F (VII) (3)

In this connection it should be borne in mind that, at room temperature, hexafluorodisiloxane disproportionates very readily to SiF₄ and SiO₂ [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).

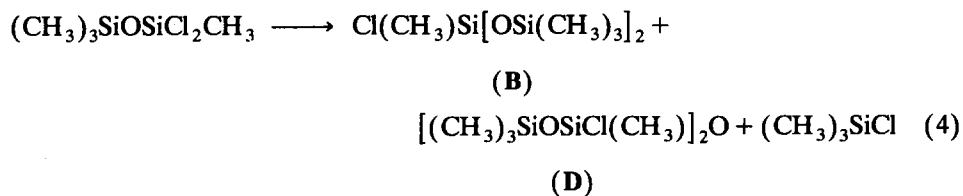


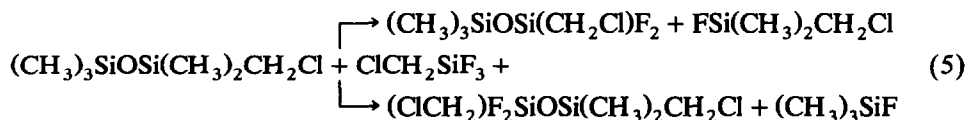
Table 1

Physico-chemical constants of the organylfluorodisiloxanes

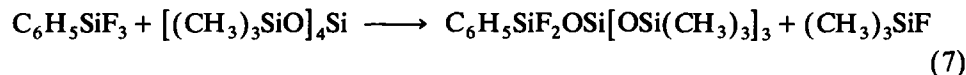
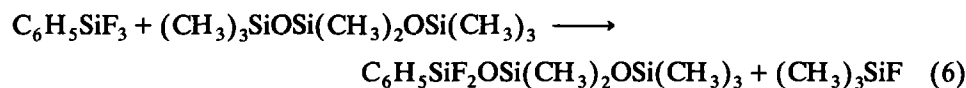
N	Organylfluorodisiloxanes	Yield (%)	m.p. (°C)	n_D^{20}	d_4^{20}	MR_D	
						Found	Calc.
I	$CH_3SiF_2OSi(CH_3)_3$	57	60–62	1.3750	0.9930	39.26	37.44
II	$ClCH_2SiF_2OSi(CH_3)_3$	64	124–127	1.3670	1.0891	42.21	42.28
III	$CH_2CHSiF_2OSi(CH_3)_3$	97	85–88	1.3600	0.9650	41.70	41.60
IV	$C_6H_5SiF_2OSi(CH_3)_3$	92	186–190	1.4258	1.0449	56.96	57.26
V	$ClCH_2(CH_3)SiFOSi(CH_3)_3^a$	85	135–138	1.3910	0.9481	50.39	51.40
VI	$C_6H_5(CH_3)SiFOSi(CH_3)_3^b$	86	196–200	1.4562	1.0319	60.19	63.15
VII	$CH_2CHCH_2SiF_2OSi(CH_3)_3$	70	99–100	1.3630	0.9680	45.09	46.41
VIII	$CH_3SiCl_2OSi(CH_3)_3^c$	62	127–128	1.4000	1.0080	–	–
IX	$C_6H_5SiF_2OSi(CH_3)_2OSi(CH_3)_3^d$	55	70–72/3	1.4180	1.0432	74.05	76.06
X	$C_6H_5SiF_2OSi[OSi(CH_3)_3]_3^e$	68	95–97/3	1.4138	–	–	–
XI	$ClCH_2SiF_2OSi(CH_3)_2H$	64	86–88	1.3710	1.1135	38.83	37.88
XII	$ClCH_2(CH_3)SiFOSi(CH_3)_2H$	71	128–130	1.3922	1.0311	43.14	43.77
XIII	$CH_3CH(CH_3)SiFOSi(CH_3)_2H$	54	70–72	1.3790	–	–	–
XIV	$C_6H_5(CH_3)SiFOSi(CH_3)_2H$.51	120–122	1.4480	1.0010	57.33	58.75
XV	$C_6H_5SiF_2OSi(CH_3)_2H$	54	146–148	1.4350	1.0595	53.77	52.86

^a Anal. Found: C, 30.02; H, 7.10; Cl, 17.68; F, 9.64; Si, 27.69. $C_5H_{14}ClFOSi_2$ calc.: C, 29.90; H, 7.04; Cl, 17.65; F, 9.46; Si, 27.97%. ^b Anal. Found: Si, 24.83. $C_{16}H_{17}FOSi_2$ calc.: Si, 24.59%. ^c Ref. [16]: m.p. 128–129°C; n_D^{20} 1.4009; d_4^{20} 1.0046. ^d Anal. Found: C, 43.10; H, 6.54; F, 12.25; Si, 27.54. $C_{11}H_{20}F_2O_2Si_3$ calc.: C, 43.09; H, 6.59; F, 12.39; Si, 27.49%. ^e Anal. Found: C, 39.58; H, 7.00; F, 8.74; Si, 30.28. $C_{15}H_{32}F_2O_4Si_5$ calc.: C, 39.60; H, 7.10; F, 8.35; Si, 30.87%.

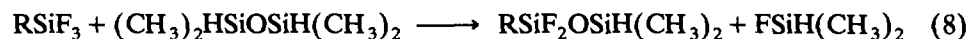
Chloromethyltrifluorosilane fails to break the >SiOSi< group in 1,1,1-trimethyl-, 3-vinyl-, 3,3-difluoro- and 1,1,3,3-tetramethyl-, 1,3-dichloromethylsiloxane at 20°C whilst in 1,1,1,3,3-pentamethyl-, 3-chloromethylsiloxane cleavage follows mainly direction F.



The reaction of phenyltrifluorosilane with 1,1,1,3,3,5,5-octamethyltrisiloxane leads to 1,1,1,3,3-pentamethyl-5,5-difluoro-, 5-phenyltrisiloxane (53% yield) whereas with tetrakis(trimethylsiloxy)silane, it gives tris(trimethylsiloxy)difluoro (phenyl) silane (68% yield).



In the reaction of organyltrifluoro- and diorganyl difluorosilanes with tetramethyldisiloxane (1:1 molar ratio, 20°C, 3–4 days), 1,1-dimethyl-, 3-organyl-, 3,3-difluoro- and 1,1-dimethyl-, 3,3-diorganyl-, 3-fluorodisiloxanes, respectively, are formed in 50–90% yield according to the following scheme [cf. 12]:



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 (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) $\text{CH}_3\text{SiF}_2^+$. $\text{CH}_3(\text{F})\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$ (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) $(\text{CH}_3)_3\text{Si}^+$. $\text{CH}_3\text{Si}[\text{OSi}(\text{CH}_3)_3]_3$ (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) $\text{CH}_3\text{SiF}_2^+$. $\text{ClCH}_2(\text{F})\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$ (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) $(\text{CH}_3)_3\text{Si}^+$. $\text{CH}_2=\text{CH}(\text{F})\text{Si}[\text{OSi}(\text{CH}_3)_3]_2$ (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) $(\text{CH}_3)_3\text{Si}^+$. $\text{CH}_2=\text{CHSi}[\text{OSi}(\text{CH}_3)_3]_3$ (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) $(\text{CH}_3)_3\text{Si}^+$. $\text{CH}_3(\text{Cl})\text{Si}[\text{Si}(\text{CH}_3)_3]_2$ (VIIIb): 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) $(\text{CH}_3)_3\text{Si}^+$. $[(\text{CH}_3)_3\text{SiO}(\text{CH}_3\text{XCl})\text{Si}]_2\text{O}$ (VIIIc): 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). $[(\text{CH}_3)_2\text{HSiO}]_2\text{CH}_3\text{Si}$

CH=CH₂: 220(11) M⁺, 205(100) (M - CH₃)⁺, 193(13) (M - CH=CH₂)⁺, 191(19), 167(53), 145(3) (M - OSi(CH₃)₂H)⁺, 133(15), 119(9), 73(67), 59(27).

Mass spectra of products of disproportionation of XIV. XIV: 214(40) M⁺, 213(32) (M - H)⁺, 199(100) (M - CH₃)⁺, 197(24), 182(15), 178(5), 137(92) (M - C₆H₅)⁺, 121(50) (M - OSi(CH₃)₂F)⁺, 107(6), 99(5), 91(13), 77(16), 73(2). (C₆H₅(CH₃)FSi)₂O: 294(5) M⁺, 279(34) (M - CH₃)⁺, 217(7) (M - C₆H₅)⁺, 201(100), 187(6), 143(9), 140(8), 125(17), 91(33), 81(5), 77(10). C₆H₅(CH₃)Si[OSi(CH₃)₂F]₂: 291(67) (M - CH₃)⁺, 287(10) (M - F)⁺, 273(53) (M - CH₃ - F + 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). C₆H₅(CH₃)FSiOSi[OSi(CH₃)₂H](CH₃)C₆H₅: 350(13) M⁺, 335(77) (M - CH₃)⁺, 273(73) (M - C₆H₅)⁺, 258(36), 197(100) (M - OSi(CH₃)₂H - C₆H₅ + H)⁺, 136(20), 135(77), 121(25), 91(9), 77(5), 73(7). C₆H₅(CH₃)FSiOSi[OSi(CH₃)₂F](CH₃)C₆H₅: 368(12) M⁺, 353(20) (M - CH₃)⁺, 291(17), 276(30), 197(100), 176(6), 169(20), 135(61), 130(26) (M - OSi(CH₃)₂F - CH₃)²⁺, 91(13), 77(5), 73(6). [C₆H₅(CH₃)FSiO]₂Si(CH₃)C₆H₅: 430(8) M⁺, 415(35) (M - CH₃)⁺, 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 - H)⁺, 203(78) (M - CH₃)⁺, 197(19) [(C₆H₅)₂SiCH₃]⁺, 187(42), 183(23), 143(36) (M - OSi(CH₃)₂H)⁺, 139(91), 125(40), 111(21), 107(16), 101(19), 91(31), 81(21), 78(48), 77(43), 73(13). C₆H₅F₂SiOSi(CH₃)₂F: 236(36) M⁺, 221(100) (M - CH₃)⁺, 203(45), 183(10), 162(14), 139(55), 91(24), 77(31), 73(40). C₆H₅FSi[OSi(CH₃)₂H]₂: 274(10) M⁺, 273(18) (M - H)⁺, 259(48) (M - CH₃)⁺, 196(53) (M - C₆H₅)⁺, 181(48) (M - CH₃ - C₆H₅ + H)⁺, 135(100) C₆H₅(CH₃)₂Si⁺, 121(50) [C₆H₅(CH₃)SiH]⁺, 91(13), 77(38), 73(25). C₆H₅Si[OSi(CH₃)₂H]₃: 330(5) M⁺, 315(4) (M - CH₃)⁺, 193(40), 161(22), 135(100) [C₆H₅(CH₃)₂Si]⁺, 121(30) [C₆H₅(CH₃)SiH]⁺, 77(55), 73(60). C₆H₅FSi[OSi(CH₃)₂F]₂: 310(2) M⁺, 295(9) (M - CH₃)⁺, 291(8) (M - F)⁺, 277(18) (M - CH₂F)⁺, 214(13) (M - C₆H₅F)⁺, 199(16), 197(40), 182(27), 135(100), 121(31), 91(6), 77(8), 73(10). (CH₃)₂FSiOSi(CH₃)₂OSiF₂C₆H₅: 310(7) M⁺, 295(77) (M - CH₃)⁺, 291(15) (M - F)⁺, 277(43) (M - CH₂F)⁺, 214(20) (M - C₆H₅F)⁺, 199(11), 161(8), 139(20), 135(100), 121(20), 91(8), 77(13), 73(10). C₆H₅Si[OSi(CH₃)₂F]₃: 369(23) (M - CH₃)⁺, 351(8) (M - CH₃ - F + H)⁺, 273(53) (M - OSi(CH₃)₂F - F + H)⁺, 211(27) (M - OSi(CH₃)₂F - SiCH₃F₂ + H)⁺, 139(9) C₆H₅SiFCH₃⁺, 135(100) C₆H₅Si(CH₃)₂⁺, 121(17) C₆H₅SiCH₃H⁺, 91(4) C₆H₅CH₂⁺, 77(5) C₆H₅, 73(39) (CH₃)₃Si⁺. C₆H₅Si[OSi(CH₃)₂F]₂OSi(CH₃)₂H: 366(1) M⁺, 351(1) (M - CH₃)⁺, 347(3), (M - F)⁺, 333(3), 273(21), 256(16), 211(10), 197(4), 193(7), 135(100), 121(23), 77(27), 73(32). C₆H₅Si[OSi(CH₃)₂H]₂OSi(CH₃)₂F: 348(16) M⁺, 333(10) (M - CH₃)⁺, 329(12) (M - F)⁺, 286(16), 272(20), 256(18), 254(9), 214(10), 196(9), 135(100), 121(18), 77(6), 73(50). {C₆H₅[F(CH₃)₂SiO]FSi}₂O: 435(42) (M - CH₃)⁺, 431(27) (M - 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). {C₆H₅[H(CH₃)₂SiO]FSi}₂O: 414(13) M⁺, 399(4) (M - CH₃)⁺, 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). C₆H₅[F(CH₃)₂SiO]FSi-O-Si[OSi(CH₃)₂F]₂C₆H₅: 509(10) (M - CH₃)⁺, 505 (M - F)⁺, 487(3) (M - 2F + 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). ClCH₂Si(CH₃)₂F: 126(5) M⁺, 111(6) (M - CH₃)⁺, 97 (M - 2CH₃ + H)⁺, 85(29), 81(54), 77(100) Me₂SiF⁺. ClCH₂(CH₃)₂SiOSiF[OSi-

$(\text{CH}_3)_3\text{CCH}_2\text{Cl}$: 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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