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Cleavage of siloxanes with organyltrifluoro- and diorganyldifluorosilanes

M.G. Voronkov, S.V. Basenko, I.A. Gebel, V.Yu. Vitkovskii and R.G. Mirskov
Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of Russia, 664033 Irkutsk (Russia)

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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-

Correspondence to: Professor M.G. Voronkov, Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of Russia, 664033 Irkutsk, Russia.

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:

$$RSiF_3 + (CH_3)_3SiOSi(CH_3)_3 \longrightarrow RSiF_2OSi(CH_3)_3 + FSi(CH_3)_3 \quad (1)$$

$R = CH_3, ClCH_2, CH_2{=}CH, CH_2{=}CH{-}CH_2, C_6H_5$

$$RR'SiF_2 + (CH_3)_3SiOSi(CH_3)_3 \longrightarrow RR'SiFOSi(CH_3)_3 + FSi(CH_3)_3 \quad (2)$$

$R,R' = CH_3, ClCH_2, C_6H_5$

Reactions 1 and 2 occur without any catalysts. All attempts to introduce fluorides [$Me_3(PhCH_2)NF$, CsF, AlF_3, 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:

$$ClCH_2SiF_3 > CH_3SiF_3 > CH_3(ClCH_2)SiF_3 > CH_2{=}CHSiF_3 > CH_2{=}CH{-}CH_2SiF_3 > C_6H_5SiF_3 > CH_3(C_6H_5)SiF_2$$

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 $(CH_3)_3SiOSiFRR'$ (**I–VII**, Table 1) are unstable compounds which disproportionate slowly at 20°C (GLC) according to [10]:

$$\underset{\textbf{(I–VII)}}{(CH_3)_3SiOSiFRR'} \longrightarrow \underset{\textbf{(A)}}{(RR'FSi)_2O} + \underset{\textbf{(B)}}{RR'Si[OSi(CH_3)_3]_2} + RR'SiF_2 + RSi[OSi(CH_3)_3]_3 + \underset{\textbf{(C)}}{[(CH_3)_3SiOSiRR']_2O} + \underset{\textbf{(D)}}{[(CH_3)_3Si]_2O} + (CH_3)_3SiF$$

$R,R' = CH_3$, F (**I**); $ClCH_2$, F (**II**); $CH_2{=}CH$, F (**III**); C_6H_5, F (**IV**); CH_3, $ClCH_2$ (**V**); CH_3, C_6H_5 (**VI**); $CH_2{=}CHCH_2$, 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).

$$(CH_3)_3SiOSiCl_2CH_3 \longrightarrow \underset{\textbf{(B)}}{Cl(CH_3)Si[OSi(CH_3)_3]_2} + \underset{\textbf{(D)}}{[(CH_3)_3SiOSiCl(CH_3)]_2O} + (CH_3)_3SiCl \quad (4)$$

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	$CH_2CH(CH_3)SiFOSi(CH_3)_2H$	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. $C_5H_{14}FClOSi_2$ 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 $\rangle SiOSi\langle$ 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.

$$(CH_3)_3SiOSi(CH_3)_2CH_2Cl + ClCH_2SiF_3 + \begin{cases} \longrightarrow (CH_3)_3SiOSi(CH_2Cl)F_2 + FSi(CH_3)_2CH_2Cl \\ \longrightarrow (ClCH_2)F_2SiOSi(CH_3)_2CH_2Cl + (CH_3)_3SiF \end{cases} \quad (5)$$

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).

$$C_6H_5SiF_3 + (CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_3 \longrightarrow C_6H_5SiF_2OSi(CH_3)_2OSi(CH_3)_3 + (CH_3)_3SiF \quad (6)$$

$$C_6H_5SiF_3 + [(CH_3)_3SiO]_4Si \longrightarrow C_6H_5SiF_2OSi[OSi(CH_3)_3]_3 + (CH_3)_3SiF \quad (7)$$

In the reaction of organyltrifluoro- and diorganyldifluorosilanes 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]:

$$RSiF_3 + (CH_3)_2HSiOSiH(CH_3)_2 \longrightarrow RSiF_2OSiH(CH_3)_2 + FSiH(CH_3)_2 \quad (8)$$

$R = ClCH_2, C_6H_5$

$$RR'SiF_2 + (CH_3)_2HSiOSiH(CH_3)_2 \longrightarrow RR'SiFOSiH(CH_3)_2 + FSiH(CH_3)_2 \quad (9)$$

$R,R' = CH_3, ClCH_2, CH_2{=}CH, C_6H_5$

According to GLC, the reactivity of organylfluorosilanes increases in the following order: $ClCH_2SiF_3 > CH_3(ClCH_2)SiF_2 > C_6H_5SiF_3 > CH_3(CH_2{=}CH)SiF_2 > CH_3(C_6H_5)SiF_2$.

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

$$CH_3(ClCH_2)SiF[OSiH(CH_3)_2] + CH_3(ClCH_2)SiF_2 \longrightarrow CH_3(ClCH_2)SiHF + CH_3(ClCH_2)SiF[OSiF(CH_3)_2] \quad (10)$$

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

$$(C_2H_5)_3SiH + C_6H_5SiF_3 \longrightarrow (C_2H_5)_3SiF + C_6H_5SiHF_2 \quad (11)$$

Up to 10% of benzene is formed when reaction 4 ($\sim$ 20°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.

$$2(CH_3)_2HSiOSiH(CH_3)_2 \longrightarrow (CH_3)_2HSiOSi(CH_3)_2OSiH(CH_3)_2 + (CH_3)_2SiH_2 \quad (12)$$

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

$$2R_2SiHX \longrightarrow R_2SiX_2 + R_2SiH_2 \quad (13)$$

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

$$C_6H_5F_2SiOSi(CH_3)_2H \longrightarrow C_6H_5FSi(OSi(CH_3)_2F)OSi(CH_3)_2H + C_6H_5Si[OSi(CH_3)_2H]_3 + (C_6H_5F_2Si)_2O + C_6H_5FSi[OSi(CH_3)_2F]_2 + C_6H_5Si[OSi(CH_3)_2F]_3 + C_6H_5Si(OSi(CH_3)_2H)[OSi(CH_3)_2F]_2 + C_6H_5FSi[OSiF_2C_6H_5]_2 + \{C_6H_5F[F(CH_3)_2SiO]Si\}_2O + C_6H_5FSi(OSi(CH_3)_2F)-O-SiFC_6H_5[OSi(CH_3)_2H] + C_6H_5FSi(OSi(CH_3)_2F)-O-SiC_6H_5[OSi(CH_3)_2F]_2 \quad (14)$$

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

$$(CH_3ClHSi)_2O + C_6H_5SiF_3 \longrightarrow C_6H_5F_2SiOSiCH_3ClH +$$

$$C_6H_5F_2SiOSiCH_3FH + (C_6H_5F_2SiO)_2SiCH_3H + C_6H_5FSi(OSiCH_3ClH) + \begin{matrix} | \\ OSiCH_3FH \end{matrix}$$

$$C_6H_5FSi(OSiCH_3F_2)_2 \qquad (15)$$

GLC–MS analysis of the disproportionation products **A–D** shows that the electron-impact induced decomposition of these compounds proceeds analogously to that of hexaorganylsiloxanes 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 $Si(CH_3)_3^+$ peak is of low intensity or absent. This indicates that the $(M - CH_3)^+$ ion is formed mainly at the expense of the $Si(CH_3)_3$ 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 R = F, Cl, CH_3 and $ClCH_2$).

In the spectra of tri- and tetrasiloxanes (compounds **B**, **C**), the $Si(CH_3)_3^+$ 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 abstaction of $CH_2Si(CH_3)_2O$ and R groups (R = CH_3, CH_2CH).

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), $[(C_6H_5)_2SiCH_3]^+$ 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} (Si–C_6H_5), 1410, 1600 cm (Si–$CH{=}CH_2^1$) and 610, 750–800 cm^{-1} (Si–CH_2Cl). The increase in the number of fluorine atoms in the molecule in all compounds leads to a slight (10–20 cm^{-1}) increase in ν_{as}(SiOSi) and ν(Si–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) $(M - CH_3)^+$, 141 (2) $(M - C_2H_5)^+$, 139(3) $(M - CH_3 - CH_4)^+$, 127(4) $(M - C_3H_7)^+$, 125(4), 81(2) $CH_3SiF_2^+$, 77(3) $(CH_3)_2SiF^+$, 73(9) $(CH_3)_3Si^+$. $(CH_3F_2Si)_2O$ (**IA**): 163(100) $(M - CH_3)^+$, 159(3) $(M - F)^+$, 149(2) $(M - C_2H_5)^+$, 134(2), 129(10), 81(14) $CH_3SiF_2^+$. $CH_3(F)Si[OSi(CH_3)_3]_2$ (**IB**): 225(100) $(M - CH_3)^+$, 209(5) $(M - CH_3 - CH_4)^+$, 195(1), 193(2), 189(1), 151(3) $[M - (CH_3)_3SiO]^+$, 135(2), 133(2), 121(1), 73(64) $(CH_3)_3Si^+$. $CH_3Si[OSi(CH_3)_3]_3$ (**IC**): 295 (42) $(M - CH_3)^+$, 279(4) $(M - CH_3 - CH_4)^+$, 265(1), 263(1), 242(1), 207(100) $[M - (CH_3)_3SiO - CH_2]^+$, 191(4), 73(64) $(CH_3)_3Si^+$.

Mass spectra of products of disproportionation of II. **II**: 189(81) $(M - CH_3)^+$, 175(1), 161(100), 155(2) $(M - ClCH_2)^+$, 147(4), 145(8), 125(19), 81(5) $CH_3SiF_2^+$. $ClCH_2(F)Si[OSi(CH_3)_3]_2$ (**IIC**): 259(100) $(M - CH_3)^+$, 231(44), 225 (12) $(M - ClCH_2)^+$, 216(5), 219(3) $(M - ClCH_2 - CH_2)^+$, 193(7), 87(53) $(CH_3)_2SiOH^+$, 73(100) $(CH_3)_3Si^+$. $[(CH_3)_3SiO(ClCH_2)(F)Si]_2O$ (**IID**): 371(6), $(M - CH_3)^+$, 337(4) $(M - ClCH_2)^+$, 291 (1) $[M - (CH_3)_2SiCl]^+$, 263(4), 271(8), 197(4), 107(7) $(CH_3)_2SiCH_2Cl^+$, 93(10) $(CH_3)_2SiCl^+$, 77(5) $(CH_3)_2SiF^+$, 73(100) $(CH_3)_3Si^+$.

Mass spectra of products of disproportionation of III. **III**: 167(100) $(M - CH_3)^+$, 155(2) $(M - CH_2{=}CH)^+$, 151(2) $(M - C_2H_5)^+$, 141(69) $(M - CH_3 - C_2H_2)^+$, 139(2), 137(3), 127(6), 125(17) $(M - 2CH_3 - CH_2{=}CH)^+$, 113(2), 111(4), 93(2), 86(3), 84(6), 81(4) $CH_3SiF_2^+$, 77(5) $(CH_3)_2SiF^+$, 73(1) $(CH_3)_3Si^+$. $CH_2{=}CH(F)Si[OSi(CH_3)_3]_2$ (**IIIB**): 237(100) $(M - CH_3)^+$, 221(2) $(M - CH_3 - CH_4)^+$, 209(51), 196(18), 195(10), 193(3), 151(3), 137(4), 85(31) $(CH_3)_2SiCH{=}CH_2^+$, 73(29) $(CH_3)_3Si^+$. $CH_2{=}CHSi[OSi(CH_3)_3]_3$ (**IIIC**): 307(28) $(M - CH_3)^+$, 291(1) $(M - CH_3 - CH_4)^+$, 263(1), 219(56) $[M - (CH_3)_2SiO - CH_2]^+$, 207(100) $[M - (CH_3)_3SiO - C_2H_2]^+$, 193(6), 191(4), 133(3), 85(49) $CH_2{=}CHSi(CH_3)_2^+$, 73(80) $Si(CH_3)_3^+$.

Mass-spectrum of IV. **IV**: 232(8) M^+, 217(100) $(M - CH_3)^+$, 201(10) $(M - CH_3$

$-CH_4)^+$, 197(13) $(M-CH_3-HF)^+$, 187(3), 143(3) $[M-(CH_3)_3SiO]^+$, 139(2) $C_6H_5Si(F)CH_3^+$, 124(5) $C_6H_5SiF^+$, 91(6), 77(3) $C_6H_5^+$.

Mass-spectrum of V. V: 185(55) $(M-CH_3)^+$, 157(100), 151(46) $(M-ClCH_2)^+$, 143(3), 141(5), 136(3), 135(4) $(M-ClCH_2-CH_4)^+$, 121(10), 73(4) $(CH_3)_3Si^+$.

Mass spectra of products of disproportionation of VI. **VI**: 228(5) M^+, 213(100) $(M-CH_3)^+$, 197(20) $(M-CH_3-CH_4)^+$, 193(5) $(M-CH_3-HF)^+$, 183(3), 139(4) $[M-(CH_3)_3SiO]^+$, 135(5) $C_6H_5Si(CH_3)_2^+$, 91(5), 77(4) $C_6H_5^+$. $C_6H_5(CH_3)Si[OSi(CH_3)_3]_2$ **(VIB)**: 283(100) $(M-CH_3)^+$, 267(8) $(M-CH_3-CH_4)^+$, 253(2), 251(4), 205(2), 193(4), 135(48) $C_6H_5Si(CH_3)_2^+$, 73(12) $(CH_3)_3Si^+$.

Mass spectra of products of disproportionation of VII. **VII**: 181(10) $(M-CH_3)^+$, 155(53) $(M-CH_2CH{=}CH_2)^+$, 141(63) $(M-CH_2-CH_2CH{=}CH_2)^+$, 127(14), 125(38) $(M-CH_2CH{=}CH_2-2CH_3)^+$, 111(11), 81(14) $CH_3SiF_2^+$, 77(11) $(CH_3)_2SiF^+$, 73(6) $(CH_3)_3Si^+$. $CH_2{=}CHCH_2(F)Si[OSi(CH_3)_3]_2$ **(VIIB)**: 251(100) $(M-CH_3)^+$, 225(41) $(M-CH_2CH{=}CH_2)^+$, 211(16) $(M-CH_2CH{=}CH_2-CH_3)^+$, 209(34), 195(12) $(M-2CH_3-CH_2CH{=}CH_2)^+$, 193(10), 151 (20), 137(16), 135(11), 121(12), 118(14), 105(21), 99(62) $(CH_3)_2SiCH_2CH{=}CH_2^+$, 98(17), 77(19) $(CH_3)_2SiF^+$, 73(91) $(CH_3)_3Si^+$.

Mass spectra of products of disproportionation of VIII. **VIII**: 187(100) $(M-CH_3)^+$, 172(22) $(M-2CH_3)^+$, 171(3) $(M-CH_3-CH_4)^+$, 167(3) $(M-Cl)^+$, 151(5) $(M-CH_3-HCl)^+$, 113(8) $CH_3SiCl_2^+$, 93(25) $(CH_3)_2SiCl^+$, 73(10) $(CH_3)_3Si^+$. $CH_3(Cl)Si[]Si(CH_3)_3]_2$ **(VIIIB)**: 241(96) $(M-CH_3)^+$, 226(12) $(M-2CH_3)^+$, 225(4) $(M-CH_3-CH_4)^+$, 221(4) $(M-Cl)^+$, 189(6), 167(5) $[M-(CH_3)_3SiO]^+$, 133(7), 73(100) $(CH_3)_3Si^+$. $[(CH_3)_3SiO(CH_3)(Cl)Si]_2O$ **(VIID)**: 335(1) $(M-CH_3)^+$, 227(11) $[M-Cl(CH_3)_2SiOCH_2]^+$, 207(2), 192(1), 93(3) $(CH_3)_2SiCl^+$, 73(100) $(CH_3)_3Si^+$.

Mass spectra of products of disproportionation of XI. XI: 189(8) $(M-H)^+$, 175(100) $(M-CH_3)^+$, 161(33) $(M-2CH_3+H)^+$, 146(53), 123(17) $(M-ClCH_2-F+H)^+$, 93(8) $(CH_3)_2FSiO^+$, 81(8), 77(17) $(CH_3)_2SiF$. $ClCH_2SiF[OSi(CH_3)_2H]_2$: 246(1) M^+, 231(7) $(M-CH_3)^+$, 197(2) $(M-ClCH_2)^+$, 133(3) $\{[(CH_3)_2SiH]_2O-H\}^+$, 93(11) $(CH_3)_2FSiO^+$, 73(100) $(CH_3)_3Si^+$.

Mass spectra of products of disproportionation of XII. **XII**: 185(7) $(M-H)^+$, 171(82) $(M-CH_3)^+$, 157(24), 145(13), 143(45), 137(100) $(M-ClCH_2)^+$, 121(8), 107(11) $(M-OSiMeFH)^+$, 93(8) $(M-OSi(CH_3)_2F)^+$, 91(6), 77(13) $(M-OSi(ClCH_2)CH_3H)^+$, 73(8) $(M-OSi(ClCH_2)FH)^+$, 53(7). $ClCH_2SiCH_3[OSi(CH_3)_2H]_2$: 242(1) M^+, 227(3) $(M-CH_3)^+$, 193(14) $(M-ClCH_2)$, 189(33), 161(100), 145(13), 125(23), 81(9), 73(23). $ClCH_2SiCH_3[OSi(CH_3)_2H][OSi(CH_3)_2F]$: 245(4) $(M-CH_3)^+$, 211(4) $(M-ClCH_2)^+$, 195(8), 191(28), 189(72), 163(39), 161(100), 145(13), 125(21), 110(3), 81(8), 77(1), 73(12). $ClCH_2(CH_3)FSiOSi[OSi(CH_3)_2H](CH_3)CH_2Cl$: 293(5) $(M-H)^+$, 255(43) $(M-ClCH_2)^+$, 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) $(M-CH_3)^+$, 137(32) $(M-CH_2{=}CH_2)^+$, 136(20), 123(60), 121(58), 107(20), 91(12), 77(20), 63(20). $[CH_3(CH_2{=}CH)FSi]_2O$: 194(10 M^+, 179(100) $(M-CH_3)^+$, 167(13) $(M-CH{=}CH_2)^+$, 153(23) $(M-CH_3-CH{=}CH_2+H)^+$, 141(44), 125(100), 111(9), 96(14), 81(14). $[(CH_3)_2HSiO]_2Si(CH_3)_2$: 208(15) M^+, 193(100) $(M-CH_3)^+$, 133(14) $(M-OSi(CH_3)_2H)^+$, 199(5), 73(86). $[(CH_3)_2HSiO]_2CH_3Si-$

$CH{=}CH_2$: 220(11) M^+, 205(100) $(M - CH_3)^+$, 193(13) $(M - CH{=}CH_2)^+$, 191(19), 167(53), 145(3) $(M - OSi(CH_3)_2H)^+$, 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) $(M - CH_3)^+$, 197(24), 182(15), 178(5), 137(92) $(M - C_6H_5)^+$, 121(50) $(M - OSi(CH_3)_2F)^+$, 107(6), 99(5), 91(13), 77(16), 73(2). $(C_6H_5(CH_3)FSi)_2O$: 294(5) M^+, 279(34) $(M - CH_3)^+$, 217(7) $(M - C_6H_5)^+$, 201(100), 187(6), 143(9), 140(8), 125(17), 91(33), 81(5), 77(10). $C_6H_5(CH_3)Si[OSi(CH_3)_2F]_2$: 291(67) $(M - CH_3)^+$, 287(10) $(M - F)^+$, 273(53) $(M - CH_3 - F + H)^+$, 210(15), 195(15), 146(2), 143(1), 139(4), 135(100), 129(7), 121(9), 107(3), 91(4), 77(3), 73(13). $C_6H_5(CH_3)FSiOSi[OSi(CH_3)_2H](CH_3)C_6H_5$: 350(13) M^+, 335(77) $(M - CH_3)^+$, 273(73) $(M - C_6H_5)^+$, 258(36), 197(100) $(M - OSi(CH_3)_2H - C_6H_5 + H)^+$, 136(20), 135(77), 121(25), 91(9), 77(5), 73(7). $C_6H_5(CH_3)FSiOSi[OSi(CH_3)_2F](CH_3)C_6H_5$: 368(12) M^+, 353(20) $(M - CH_3)^+$ 291(17), 276(30), 197(100), 176(6), 169(20), 135(61), 130(26) $(M - OSi(CH_3)_2F - CH_3)^{2+}$, 91(13), 77(5), 73(6). $[C_6H_5(CH_3)FSiO]_2Si(CH_3)C_6H_5$: 430(8) M^+, 415(35) $(M - CH_3)^+$, 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) $(M - H)^+$, 203(78) $(M - CH_3)^+$, 197(19) $[(C_6H_5)_2SiCH_3]^+$, 187(42), 183(23), 143(36) $(M - OSi(CH_3)_2H)^+$, 139(91), 125(40), 111(21), 107(16), 101(19), 91(31), 81(21), 78(48), 77(43), 73(13). $C_6H_5F_2SiOSi(CH_3)_2F$: 236(36) M^+, 221(100) $M - CH_3)^+$, 203(45), 183(10), 162(14), 139(55), 91(24), 77(31), 73(40). $C_6H_5FSi[OSi(CH_3)_2H]_2$: 274(10) M^+, 273(18) $(M - H)^+$ 259(48) $(M - CH_3)^+$, 196(53) $(M - C_6H_5)^+$, 181(48) $(M - CH_3 - C_6H_5 + H)^+$, 135(100) $C_6H_5(CH_3)_2Si^+$, 121(50) $[C_6H_5(CH_3)SiH]^+$, 91(13), 77(38), 73(25). $C_6H_5Si[OSi(CH_3)_2H]_3$: 330(5) M^+, 315(4) $(M - CH_3)^+$, 193(40), 161(22), 135(100) $[C_6H_5(CH_3)_2Si]^+$, 121(30) $[C_6H_5(CH_3)SiH]^+$, 77(55), 73(60). $C_6H_5FSi[OSi(CH_3)_2F]_2$: 310(2) M^+, 295(9) $(M - CH_3)^+$, 291(8) $(M - F)^+$, 277(18) $(M - CH_2F)^+$, 214(13) $(M - C_6H_5F)^+$, 199(16), 197(40), 182(27), 135(100), 121(31), 91(6), 77(8), 73(10). $(CH_3)_2FSiOSi(CH_3)_2OSiF_2C_6H_5$: 310(7) M^+, 295(77) $(M - CH_3)^+$, 291(15) $(M - F)^+$, 277(43) $(M - CH_2F)^+$, 214(20) $(M - C_6H_5F)^+$, 199(11), 161(8), 139(20), 135(100), 121(20), 91(8), 77(13), 73(10). $C_6H_5Si[OSi(CH_3)_2F]_3$: 369(23) $(M - CH_3)^+$, 351(8) $(M - CH_3 - F + H)^+$, 273(53) $(M - OSi(CH_3)_2F - F + H)^+$, 211(27) $(M - OSi(CH_3)_2F - SiCH_3F_2 + H)^+$, 139(9) $C_6H_5SiFCH_3^+$, 135(100) $C_6H_5Si(CH_3)_2^+$, 121(17) $C_6H_5SiCH_3H^+$, 91(4) $C_6H_5CH_2^+$, 77(5) C_6H_5, 73(39) $(CH_3)_3Si^+$. $C_6H_5Si[OSi(CH_3)_2F]_2OSi(CH_3)_2H$: 366(1) M^+, 351(1) $(M - CH_3)^+$, 347(3), $(M - F)^+$, 333(3), 273(21), 256(16), 211(10), 197(4), 193(7), 135(100), 121(23), 77(27), 73(32). $C_6H_5Si[OSi(CH_3)_2H]_2OSi(CH_3)_2F$: 348(16) M^+, 333(10) $(M - CH_3)^+$, 329(12) $(M - F)^+$, 286(16), 272(20), 256(18), 254(9), 214(10), 196(9), 135(100), 121(18), 77(6), 73(50). $\{C_6H_5[F(CH_3)_2SiO]FSi\}_2O$: 435(42) $(M - CH_3)^+$, 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). $\{C_6H_5[H(CH_3)_2SiO]FSi\}_2O$: 414(13) M^+, 399(4) $(M - CH_3)^+$, 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). $C_6H_5[F(CH_3)_2SiO]FSi{-}O{-}Si[OSi(CH_3)_2F]_2C_6H_5$: 509(10) $(M - CH_3)^+$, 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). $ClCH_2Si(CH_3)_2F$: 126(5) M^+, 111(6) $(M - CH_3)^+$, 97 $(M - 2CH_3 + H)^+$, 85(29), 81(54), 77(100) Me_2SiF^+. $ClCH_2(CH_3)_2SiOSiF[OSi-$

$(CH_3)_3]CH_2Cl$: 293(19) $(M - CH_3)^+$, 265(12), 251(18), 237(45), 213(6), 191(25), 163(28), 121(14), 107(18) $(CH_3)_2SiCH_2Cl^+$, 93(100) $(CH_3)_2SiCl^+$, 77(83) $(CH_3)_2SiF^+$, 73(67) $(CH_3)_3Si^+$.

References

1 M.G. Voronkov and L.M. Chudesova, Izv. Akad. Nauk SSSR, Otdel Khim., 11 (1957) 1415.
2 M.G. Voronkov, USSR Inventor's Certificate No. 579268, Bull. Izobr., 5 (1958) 36.
3 M.G. Voronkov and L.M. Chudesova, Zh. Obshch. Khim., 28 (1959) 1534.
4 M.G. Voronkov, S.F. Pavlov and E.I. Dubinskaya, Dokl. Akad. Nauk. SSSR, 227 (1976) 362.
5 N.G. Sviridova, G.I. Karpov, Yu.A. Yuzhelevskii, V.P. Mileshkevich and M.G. Voronkov, Zh. Obshch. Khim., 51 (1981) 2149.
6 M.G. Voronkov and S.V. Basenko, Sov. Sci. Rev. B. Chem., 14 (1989) 1.
7 V.A. Pestunovich, L.P. Petukhov, V.I. Rakhlin, B.Z. Shterenberg, R.G. Mirskov and M.G. Voronkov, Dokl. Akad. Nauk. SSSR, 263 (1982) 904.
8 J.J. Mascony and A.G. MacDiarmid, Chem. Commun., (1965) 307.
9 M.G. Voronkov, S.V. Basenko, R.G. Mirskov, M.F. Larin, V.Yu. Vitkovskii, E.I. Brodskaya and D.D. Toryashinova, Zh. Obshch. Khim., 55 (1985) 1206.
10 M.G. Voronkov, S.V. Basenko, V.Yu. Vitkovskii, I.A. Gebel and R.G. Mirskov, Izv. Akad. Nauk SSSR, Ser. Khim., 5 (1987) 1169.
11 J. Goubean and H. Grosse-Ruyken, Z. Anorg. All. Chem., 264 (1951) 230.
12 S.V. Basenko, I.A. Gebel, V.Yu. Vitkovskii, R.G. Mirskov and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., 5 (1991) 1162.
13 B.N. Dolgov, M.G. Voronkov and S.N. Borisov, Zh. Obshch. Khim., 3 (1957) 709.
14 B.N. Dolgov, S.N. Borisov and M.G. Voronkov, Zh. Obshch. Khim., 8 (1957) 2062.
15 M.G. Voronkov, N.A. Keiko and T.A. Kuznetsova, Zh. Obshch. Khim., 8 (1973) 1862.
16 S.N. Borisov and N.G. Sviridova, Plast. Massy, 6 (1965) 24.
17 A.N. Polivanov, A.A. Bernadskii, V.N. Bochkarev, V.I. Zhun and V.D. Sheludyakov, Zh. Obshch. Khim., 3 (1980) 614.
18 A.N. Polivanov, A.A. Bernadskii, N.N. Silkina, B.N. Klimentov and V.N. Bochkarev, Zh. Obshch. Khim., 8 (1980) 1780.