$(M - 2CH_3 + H)^+$, 158 (10), 152 (100) $(M - CH_2Cl)^+$, 150 (30), 136 (7), 122 (6), $(M - CH_2Cl - HCl)^+$, 108 $(M - Si(CH_3)_2Cl)^+$, 100 (4), 93 (9) $Si(CH_3)_2Cl^+$, 74 $(M - SiCl(CH_3)CH_2Cl)^+$, 68 (5), 59 (4) $Si(CH_3)_2H^+$. (XII): 167 (25) M^+, 152 (100) $(M - CH_3)^+$, 132 (17) $(M - Cl)^+$, 93 (21) $(CH_3)_2SiCl^+$, 76 (15), 73 (25) $(CH_3)_3Si^+$. (XIII): 191 (18) M^+, 190 (26) $(M - H)^+$, 176 (100) $(M - CH_3)^+$, 160 (6) $(M - 2CH_3 + H)^+$, 130 (32), 117 (37), 102 (18), 100 (14), 86 (7), 73 (12). $(CH_3)_2HSiNHSi(CH_3)_2NHSi(CH_3)_2H$ (XIV): 206 (9) M^+, 191 (100) $(M - CH_3)^+$, 177 (40) $(M - 2CH_3 + H)^+$, 147 (15) $(M - Si(CH_3)_2H)^+$, 132 (11) $(M - NHSi(CH_3)_2H)^+$, 118 (18) $(M - NHSi(CH_3)_2H - CH_3 + H)^+$. $CH_2{=}CH(CH_3)FSiNHSi(CH_3)_2H$ (XVI): 163 (19) M^+, 148 (100) $(M - CH_3)^+$, 133 (24), 119 (62), 115 (3), 105 (7), 103 (6), 99 (10), 77 (10).

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REACTIONS OF ORGANYLTRIFLUORO- AND DIORGANYLDIFLUOROSILANES WITH 1,1,3,3-TETRAMETHYLDISILOXANE

S. V. Basenko, I. A. Gebel', V. Yu. Vitkovskii,
R. G. Mirskov, and M. G. Voronkov

UDC 542.92:543.51:547.1'128'161

1,1,3,3-Tetramethyldisiloxane is decomposed by organyltrifluoro- and diorganyldifluorosilanes already at 20°C in the presence of catalysts with formation of hitherto unknown 1,1-dimethyl-3,3-diorganyl-3-fluoro- and 1,1-dimethyl-3-organyl-3,3-difluorodisiloxanes of general formula $R_{4-n}SiF_{n-1}OSiH(CH_3)_2$ (n = 2-3) in yields of 50-70%. On storing these decomposition products easily disproportionate in various directions, in which their propensity to disproportionation is determined by the nature of the substituents at the silicon atoms and the number of fluorine atoms in the molecule.

In 1957 the catalytic decomposition reaction of the disiloxane moiety Si—O—Si to perorganylsiloxanes by organylchloro- and organylbromosilanes was described [1-5]. The possibility of easy decomposition of that moiety by 1-iodosilatrane was established [6]. Attempts to react tributylfluorosilane in that way was not crowned with success [3]. Nevertheless, it was shown that tetrafluorosilane decomposes hexamethyldisiloxane but under very drastic conditions (3000 atm) [7]. At the same time some organylfluorosilanes decompose hexamethyldisiloxane rather easily [8].

We have found that 1,1-dimethyl-3-organyl-3,3-difluoro- and 1,1-dimethyl-3,3-diorganyl-3-fluorodisiloxanes are formed in yields of 50-90% on reacting organyltrifluoro- and diorganyldifluorosilanes with tetramethyldisiloxane (molar ratio 1:1) at 20°C for 3-4 days according to the scheme

$$RSiF_3 + (CH_3)_2HSiOSiH(CH_3)_2 \rightarrow RSiF_2OSiH(CH_3)_2 + FSiH(CH_3)_2 \quad (1)$$
$$R = ClCH_2,\ C_6H_5.$$

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TABLE 1. Characteristics of Organylfluorodisiloxanes

Compound	Yield, %	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR_D Found/Calculated
$ClCH_2SiF_2OSi(CH_3)_2H$ (I)	64	86–88	1,3710	1,1135	38,83/37,88
$ClCH_2(CH_3)SiFOSi(CH_3)_2H$ (II)	71	128–130	1,3922	1,0311	43,14/43,77
$CH_3CH(CH_3)SiFOSi(CH_3)_2H$ (III)	54	70–72	1,3790	–	– –
$C_6H_5(CH_3)SiFOSi(CH_3)_2H$ (IV)	51	120–122	1,4480	1,0010	57,33/58,75
$C_6H_5SiF_2OSi(CH_3)_2H$ (V)	54	146–148	1,4350	1,0595	53,77/52,86

$$RR'SiF_2 + (CH_3)_2HSiOSiH(CH_3)_2 \rightarrow RR'SiFOSiH(CH_3)_2 + FSiH(CH_3)_2$$

$$R, R' = CH_3,\ ClCH_2,\ CH_2{=}CH,\ C_6H_5. \qquad (2)$$

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

Compounds (I)-(V) (Table 1) that have been synthesized in that way are colorless mobile liquids, readily soluble in organic solvents.

According to data of chromato-mass spectrometry the reaction mixture resulting from reaction of methyl(chloromethyl)difluorosilane with 1,1,3,3-tetramethyldisiloxane also contains a small amount (6%) of 1,1,3-trimethyl-3-chloromethyl-1,3-difluorodisiloxane. Its formation is obviously caused by an exchange reaction according to the scheme

$$\begin{aligned}&CH_3(ClCH_2)SiF[OSiH(CH_3)_2] + CH_3(ClCH_2)SiF_2 \rightarrow\\ &\rightarrow CH_3(ClCH_2)SiHF + CH_3(ClCH_2)SiF[OSiF(CH_3)_2]\end{aligned} \qquad (3)$$

However, we failed to bring about the model reaction of triethylsilane with phenyltrifluorosilane according to scheme 4.

$$(C_2H_5)_3SiH + C_6H_5SiF_3 \dashrightarrow (C_2H_5)_3SiF + C_6H_5SiHF_2 \qquad (4)$$

When reaction (4) is carried out (~20°C, 30 days) up to 10% of benzene is formed.

According to chromato-mass spectral data in reactions (1) and (2) 1,1,3,3,5,5-hexamethyltrisiloxane (yield 3-7%) is also formed. Its formation may be ascribed to disproportionation of 1,1,3,3-tetramethyldisiloxane

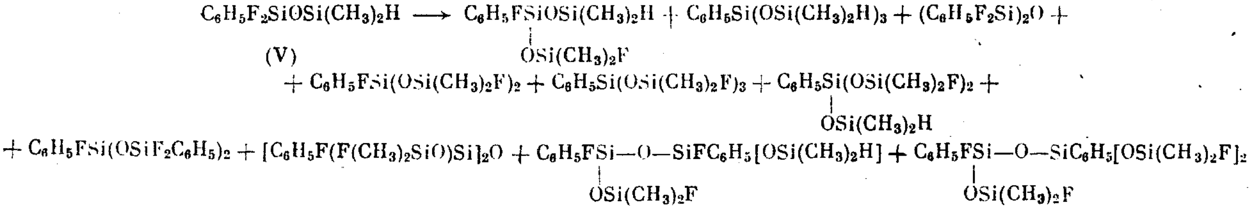
$$2(CH_3)_2HSiOSiH(CH_3)_2 \rightarrow (CH_3)_2HSiOSi(CH_3)_2OSiH(CH_3)_2 + (CH_3)_2SiH_2 \qquad (5)$$

The possibility of an analogous rearrangement of organosilicon compounds R_2SiHX (R = alkyl, X = alkyl, F, Cl) is well known [9-11].

$$2R_2SiHX \rightarrow R_2SiX_2 + R_2SiH_2$$

Substitution of a second and a third fluorine atom in organylfluorosilanes for a dimethylsiloxy group proceeds with great difficulty and in low yields even with two- and threefold excesses of tetramethyldisiloxane. In that case the reaction is complicated by disproportionation processes that are also accelerated by refluxing the reaction mixture.

The prepared 1,1-dimethyl-3,3-diorganyl-3-fluoro- and 1,1-dimethyl-3-organyl-3,3-difluorodisiloxanes (I)-(V) (Table 1) are unstable on storing and, according to chromato-mass spectral data, already disproportionate slowly at 20°C in various directions. Thus, for example, 1,1-dimethyl-3-phenyl-3,3-difluorodisiloxane (V) disproportionates according to the scheme

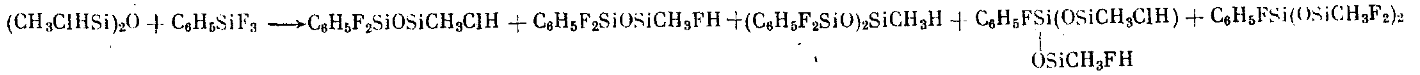


$$\begin{aligned}&\underset{(V)}{C_6H_5F_2SiOSi(CH_3)_2H} \longrightarrow C_6H_5\underset{\overset{|}{OSi(CH_3)_2F}}{FSi}OSi(CH_3)_2H + C_6H_5Si(OSi(CH_3)_2H)_3 + (C_6H_5F_2Si)_2O +\\ &+ C_6H_5FSi(OSi(CH_3)_2F)_2 + C_6H_5Si(OSi(CH_3)_2F)_3 + C_6H_5\underset{\overset{|}{OSi(CH_3)_2H}}{Si}(OSi(CH_3)_2F)_2 +\\ &+ C_6H_5FSi(OSiF_2C_6H_5)_2 + [C_6H_5F(F(CH_3)_2SiO)Si]_2O + C_6H_5F\underset{\overset{|}{OSi(CH_3)_2F}}{Si}{-}O{-}SiFC_6H_5[OSi(CH_3)_2H] + C_6H_5F\underset{\overset{|}{OSi(CH_3)_2F}}{Si}{-}O{-}SiC_6H_5[OSi(CH_3)_2F]_2\end{aligned}$$

The composition of the disproportionation products changes in dependence of the duration of the process. In contrast to disproportionation reactions of 1,1,1-trimethyl-3,3-

diorganyl-3-fluoro- and 1,1,1-trimethyl-3-organyl-3,3-difluorosiloxanes that were studied earlier [12], disproportionation of 1,1-dimethyl-3,3-diorganyl-3-fluoro- and 1,1-dimethyl-3-organyl-3,3-difluorosiloxanes is complicated by the exchange of an Si—H for an Si—F bond, and also by the formation of more branched siloxane structures.

In contrast to tetra- and hexamethyldisiloxane, reaction of phenyltrifluorosilane with 1,3-dimethyl-1,3-dichlorodisiloxane proceeds considerably slower and is accompanied with processes of disproportionation and exchange of Si—H and Si—Cl bonds for an Si—F bond. According to chromato-mass spectral data the reaction proceeds according to the scheme



$$(CH_3ClHSi)_2O + C_6H_5SiF_3 \longrightarrow C_6H_5F_2SiOSiCH_3ClH + C_6H_5F_2SiOSiCH_3FH + (C_6H_5F_2SiO)_2SiCH_3H + \underset{\displaystyle OSiCH_3FH}{C_6H_5FSi}(OSiCH_3ClH) + C_6H_5FSi(OSiCH_3F_2)_2$$

The disproportionation products were identified by chromato-mass spectrometry. In the mass spectra of organylfluorodisiloxanes peaks of ions $(M - CH_3)^+$ are found that have distinct or maximum intensities. Subsequent decomposition of these ions proceeds complexly and in various directions. Thus, in the spectra of the products of the disproportionation reaction of (V) according to the complication of their structures is found a gradual shift of the total fraction of the ion stream to the side of lower masses with concentration of a considerable part of the total stream to fragments that contain one silicon atom. Thereby in the majority of the cases the peak with maximum intensity is the peak of the rearrangement ion with m/z 135, $[C_6H_5Si(CH_3)_2]^+$.

Disproportionation of (IV) yields compounds with more complex structures. Their mass spectra, when at least two C_6H_5 groups are present in the molecule, are characterized by a rearrangement peak with m/z 197, $[(C_6H_5)_2SiCH_3]^+$.

IR spectra of compounds (I)-(IV) contain bands of deformation vibrations at 1260 cm^{-1} that are characteristic of $(CH_3)_2Si$ and CH_3Si groups, bands in the region 1060-1100 cm^{-1} that are characteristic of antisymmetrical valence vibrations of the Si—OSi group, valence vibrations of the Si—H group at 2120-2130 cm^{-1}, bands at 895, 930 cm^{-1} that are characteristic of SiF_2 and SiF fragments, and also bands at 1120, 1430, 1580 cm^{-1} ($Si-C_6H_5$), 1410, 1600 cm^{-1} ($Si-CH=CH_2$), and 610, 750-800 cm^{-1} ($Si-CH_2Cl$). In all the compounds increasing the number of fluorine atoms in the molecule leads to a small enlargement of ν_{as}SiOSi and νSi—H by 10-20 cm^{-1}. A similar effect was found when a phenyl group was substituted for a chloromethyl group.

EXPERIMENTAL

1,1-Dimethyl-3-chloromethyl-3,3-difluorodisiloxane (I). A distillation flask is charged with 13.4 g (0.1 mole) of 1,1,3,3-tetramethyldisiloxane and 13.5 g (0.1 mole) of chloromethyl(trifluoro)silane. The mixture is kept at ~20°C for 3 days after which 7.4 g (95%) of dimethylfluorosilane had distilled into the cooled trap. Distillation of the residue yields 12.2 g (64%) of 1,1-dimethyl-3-chloromethyl-3,3-difluorosiloxane (I).

Compounds (II)-(V) were prepared in much the same way. Physicochemical constants are listed in Table 1.

When the freshly prepared samples were chromatographed organylfluorosiloxane decomposition products were not found, that is, disproportionation on contact with the chromatographic phase does not occur.

Mass Spectra of the Products of the Disproportionation of (I)

(I): 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 the Products of the Disproportionation of (II)

(II): 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). $ClCH_2SiCH_3 \times [OSi(CH_3)_2H]_2$: 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). $ClCH_2(CH_3)FSiOSi[OSi(CH_3)_2H] \times (CH_3)CH_2Cl$: 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 the Products of Disproportionation of (III)

(III): 164 (38) $M^{+\cdot}$, 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 (1) $M^{+\cdot}$, 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) $M^{+\cdot}$, 193 (100) $(M - CH_3)^+$, 133 (14) $(M - OSi(CH_3)_2H)^+$, 199 (5), 73 (86). $[(CH_3)_2HSiO]_2CH_3SiCH{=}CH_2$: 220 (11) $M^{+\cdot}$, 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 the Products of Disproportionation of (IV)

(IV): 214 (40) $M^{+\cdot}$, 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) $M^{+\cdot}$, 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) $M^{+\cdot}$, 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) $M^{+\cdot}$, 353 (20) $(M - CH_3)^+$, 291 (17), 276 (30), 197 (100), 176 (6), 169 (20), 135 (61), 130 (26) $(M - OSi(CH_3)_2F - CH_3)^{++}$, 91 (13), 77 (5), 73 (6). $[C_6H_5(CH_3)FSiO]_2Si(CH_3)C_6H_5$: 430 (8) $M^{+\cdot}$, 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 the Products of Disproportionation of (V)

(V): 218 (100) $M^{+\cdot}$, 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) $M^{+\cdot}$, 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) $M^{+\cdot}$, 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) $M^{+\cdot}$, 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) $M^{+\cdot}$, 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) $M^{+\cdot}$, 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) $M^{+\cdot}$, 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) $M^{+\cdot}$, 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) $M^{+\cdot}$, 399 (4) $(M - CH_3)^+$, 335 (27), 321 (17), 278 (4), 274 (9), 260 (13), 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).

Mass spectra were recorded on a Varian MAT-212 spectrometer at 70 eV, resolution 10^4. Chromatograph Varian-3700, carrier gas helium, phase SE-54. IR spectra were recorded on a Specord 75-IR spectrometer in the region 400-4000 cm^{-1} from thin layers.

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ASYMMETRIC SYNTHESIS OF HETEROORGANIC ANALOGS OF NATURAL COMPOUNDS.

3. GENERAL PREPARATIVE METHOD OF DIASTEREO- AND ENANTIOSELECTIVE SYNTHESIS OF FLUORINE-CONTAINING 2(R),3(S)-β-PHENYLSERINES

V. A. Soloshonok, V. P. Kukhar', S. V. Galushko,
M. T. Kolycheva, A. B. Rozhenko, and Yu. N. Belokon'

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The diastereo- and enantioselective synthesis of the previously unknown 2(R), 3(S)-β-phenylserines containing fluorine atoms, the O—CHF_2—, O—CF_3—, and CF_3 groups in the benzene ring, was carried out by alkylation of a Ni(II) complex of a Schiff base of glycine with (S)-2-N-(N'-benzylprolyl)aminobenzophenone by fluorine-substituted benzaldehydes. The factors influencing the stereochemical result of the reactions studied are not the steric characteristics of the substituents in benzaldehydes, but their electronic nature.

Fluorine-containing β-phenylserines are represented in the literature by racemic o- and p-fluoro derivatives, obtained by condensation of glycine with the corresponding aldehyde in the presence of bases [1-3]. The study of the biological activity of these compounds showed that (D, L)-threo-(p-fluorophenyl)serine inhibits the growth of E. coli [2] and also extends the life span of rats with transplanted Erhlich Ascites [1]. We have previously reported the synthesis of (S)-o-, (S)-m-, (S)-p-fluorophenylalanines and (S)-o-, (S)-m-, (S)-p-fluoro-α-methylphenylalanines by alkylation of glycine and alanine in their Ni(II)-complexes of Schiff bases with chiral regeneratable reagent (S)-2-N-(N'-benzylprolyl)aminobenzophenone [(S)-BBP], by the corresponding fluorine-substituted benzyl chlorides [4]. The aim of the present work was to explore the possibility of using this reagent for diastereo- and enantioselective synthesis of β-phenylserines, containing fluorine atoms, the O—CHF_2—, O—CF_3—, and CF_3 groups in the benzene ring. Moreover, it was also of interest to investigate the influence of the position of these substituents in the benzene ring and their electronic nature on the stereoselectivity of the reaction.

It has been shown earlier [5] that the Ni(II)-complex of the Schiff base of glycine (I) reacts with benzaldehyde in MeOH/THF in the presence of 1.5 N MeONa to give a mixture of (R)-threo- and (S)-threo-β-phenylserines in a ratio of 94:6 (Scheme 1). The corresponding allo-isomers were formed under these conditions in a ~2% yield. It has also been noted in [5] that in view of the reversibility of the reaction of (I) with benzaldehyde, for the complete conversion of (I) a threefold excess of the aldehyde is necessary. Decreasing the excess of the aldehyde used in its condensation with (I) is very important in view of the high cost of the fluorine-substituted benzaldehydes.

Institute of Bioorganic Chemistry and Petrochemistry, Academy of Sciences of the Ukrainian SSR, Kiev. A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1166-1175, May, 1991. Original article submitted April 23, 1990.