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The electron-withdrawing effect of the trifluorosilyl group in phenyltrifluorosilane is a consequence of the strong polarization of the Si-C bond and the ready cleavage of this bond by electrophilic reagents [1].

In the present work, we synthesized (aroxymethyl)trifluorosilanes and methyl(aroxymethyl)fluorosilanes with the general formula  $XC_6H_4OCH_2SiMe_nF_{3-n}$  (n = 0, 1) and studied their reactions with electrophilic reagents. These compounds were synthesized by the action of fluorinating agents such as 40% HF,  $Et_2O \cdot BF_3$ , and  $SbF_3$  on the corresponding (aroxymethyl)trimethoxysilanes and methyl(aroxymethyl)methoxysilanes. The best yields (85%) were obtained using  $Et_2O \cdot BF_3$ 

 $\begin{array}{rl} {\rm XC}_{6}{\rm H}_{4}{\rm OCH}_{2}{\rm SiMe}_{n}({\rm OMe})_{3-n}\,+\,n/3{\rm Et}_{2}{\rm O}\cdot{\rm BF}_{3}\rightarrow\\ &\rightarrow {\rm XC}_{6}{\rm H}_{4}{\rm OCH}_{2}{\rm SiMe}_{n}{\rm F}_{3-n}\,+\,n/3{\rm B}({\rm OMe})_{3}\\ &({\rm I}),\ ({\rm II})\\ ({\rm I}):\,n\,=\,0,\,\,{\rm X}\,=\,{\rm H}\ ({\rm a}),\,\,{\rm H}^{*}\ ({\rm b}),\,\,4\text{-Me}\ ({\rm c}),\,\,2\text{-OAc}\ ({\rm d}),\\ 4\text{-NO}_{2}\ ({\rm e}),\,\,4\text{-Br}\ ({\rm f}\ );\ ({\rm II}):\,\,n\,=\,1,\,\,\,{\rm X}\,=\,{\rm H}\ ({\rm a}),\,\,4\text{-F}\ ({\rm b}),\,\,4\text{-Cl}\ ({\rm c}),\\ &4\text{-Br}\ ({\rm d}),\,\,4\text{-Me}\ ({\rm e}),\,\,2\text{-OAc}\ ({\rm f}).\\ \end{array}$ 

Silanes (Ia-f) are stable, colorless, high-boiling liquids, (IIa) and (IIb) are liquids, while (IIc-f) are colorless crystalline compounds which fume in the air but are rather stable upon storage in a sealed ampul. The yields, physicochemical properties, and elemental analysis data of the compounds synthesized are given in Table 1.

The replacement of the methoxy groups in (aroxymethyl)trimethoxysilanes and methyl(aroxymethyl)methoxysilanes by fluorine atoms does not cause a significant change in the polarization of the Si-C bond and does not facilitate the splitting of this bond by electrophilic reagents. Mercuration of the aromatic ring occurs upon the reaction of Hg(OAc)<sub>2</sub> with (aroxymethyl)trifluorosilanes and methyl(aroxymethyl)fluorosilanes

$$(AcO)_{2}Hg + XC_{6}H_{4}OCH_{2}SiMe_{n}F_{3-n} \rightarrow AcOHg(X)C_{6}H_{3}OCH_{2}SiMe_{n}F_{3-n}$$

The benzene ring is brominated upon the reaction of these compounds with N-bromosuccinimide

$$CH_{2}CO$$

$$NBr + XC_{6}H_{4}OCH_{2}SiMe_{n}F_{3-n} \rightarrow Br(X)C_{6}H_{3}OCH_{2}SiMe_{n}F_{3-n}$$

$$CH_{2}CO$$

(Aroxymethyl)trifluorosilanes react with alkali metal fluorides and ammonium fluoride to give the corresponding aroxymethylpentafluorosilicates containing a hexacoordinated silicon atom

 $2MF + XC_6H_4OCH_2SiF_3 \rightarrow M_2[XC_6H_4OCH_2SiF_5]$  $M = NH_4, KF, Na.$ 

Aroxymethylpentafluorosilicates are colorless crystalline compounds which are readily soluble in water but have low solubility in organic solvents.

The results of an IR spectral, mass spectral, and x-ray diffraction structural study of the compounds synthesized will be published separately.

\*In XC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiF<sub>3</sub>.

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TABLE	l. Silan	es XC <sub>6</sub> F	l40CH2SiF3	(Ia-f) an	nd XC <sub>6</sub> H <sub>4</sub> O	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	SiF3.				
Com- pound	X	Yield, 🖗	bp. °C /n mm He)	$n_D^{20}$	$a_k^{20}$		Four	nd <b>/Calcula</b> te	d, ∳₀		Chemical
-			(Brt mm •d)	1		σ	H	Si	Ε4	Cl (Br)	
(Ia)	Ħ	82	60(20)	1,3998	1,171	$\frac{43,09}{43,74}$	4,47	14,49 14,61	$\frac{29,13}{29,63}$	1	$C_7H_7OSiF_3$
(q1)	* H	62	106(20)	I	1	49,38 49,08	5,23 5,03	12,43	25,89 25,88	I	C <sub>9</sub> H <sub>11</sub> OSIF <sub>3</sub>
(Ic)	4-Me	71,3	91 (30)	I	ł	46,79 46,59	4,49	<u>11,87</u> <u>13,61</u>	$\frac{27,31}{27,64}$	1	C <sub>8</sub> H <sub>9</sub> OSIF <sub>3</sub>
(Id)	2-0Ac	73,6	140(20)	I	l	$\frac{43,11}{43,19}$	3,88 3,63	$\frac{10,93}{11,22}$	$\frac{21,81}{22,77}$	ł	C <sub>9</sub> H <sub>9</sub> O <sub>3</sub> SiF <sub>3</sub>
(I.e)	4-NO2	81,4	mp. 52		1	$\frac{36,12}{35,44}$	$\frac{2,81}{2,55}$	$\frac{11,64}{11,84}$	$\frac{23,98}{24,03}$	5,87(N) 5,90(N)	$C_7H_6O_3SiF_3N$
(If)	4-Br	69	тр. 67	1	l	$\frac{31,02}{30,99}$	3,01 2,81	9,98 10,36	$\frac{20,78}{21,03}$	29,78 29,51	C <sub>7</sub> H <sub>6</sub> OSiF <sub>3</sub> Br
(IIa)	H	83	88 (20)	1,4601	1,151	$\frac{51,14}{51,04}$	5,53 5,35	$\frac{14,29}{14,92}$	20,20 20,18	l	C <sub>8</sub> H <sub>10</sub> OSiF <sub>2</sub>
(qII)	4-F	79,2	92 (24)	1,4458	1,229	46,65 46,59	4,33	$\frac{13,47}{13,62}$	27,64 27,64	í	C <sub>8</sub> H <sub>9</sub> OSiF <sub>3</sub>
(IIc)	4-CI	74	126 (26)	1,4794	1,265	43,29	4,02	12,31 12,61	<u>17,22</u> 17,06	$\frac{15,76}{15,92}$	C <sub>8</sub> H <sub>9</sub> OSiF <sub>2</sub> Cl
(IId)	4-Br	75,4	124(15)	1,4996	1,511	$\frac{36,23}{35,97}$	$\frac{3,43}{3,39}$	10,15 10,51	$\frac{14,42}{14,21}$	29,67 29,91	C <sub>8</sub> H <sub>9</sub> OSiF <sub>2</sub> Br
(IIe)	4-Me	74,6	105 (20)	1,4636	1,121	54,07 53,44	6,13 5,98	13,90 13,88	<u>18,67</u> 18,79	l	C <sub>9</sub> H <sub>12</sub> OSiF <sub>2</sub>
(III)	2-0Ac	81,7	133(6)	1,4816	1,273	48,87 48,77	4,98	$\frac{11,17}{11,40}$	$\frac{15,47}{15,12}$	1	$ C_{10}H_{12}O_{3}SiF_{2} $
*In XC	6H40CH2S:		нз <b>.</b>								

Silanes XC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>SiF<sub>3</sub> (Ia-f) and XC<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>CH<sub>2</sub>SiF<sub>3</sub>.

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## EXPERIMENTAL

Samples of (aroxymethyl)trimethoxysilanes and methyl(aroxymethyl)methoxysilanes were obtained according to our previous procedure [2].

<u>Methyl(phenoxymethyl)difluorosilane (IIa)</u>. a) A sample of 5.31 g (0.025 mole) methyl-(phenoxymethyl)dimethoxysilane was added dropwise with stirring to 7.09 g (0.05 mole)  $Et_20$ • BF<sub>3</sub> and the mixture was heated for 3 h. Vacuum distillation gave 3.93 g (81.3%) (IIa).

b) A sample of 5.31 g (0.025 mole) methyl(phenoxymethyl)dimethoxysilane was added dropwise with stirring to 2.0 g (0.05 mole) 40% HF cooled to 0°C. Vacuum distillation gave 2.49 g (53%) (IIa).

c) A sample of 5.31 g (0.025 mole) methyl(phenoxymethyl)dimethoxysilane was added to 4.47 g (0.025 mole) SbF<sub>3</sub> and the mixture was heated for 2 h. Vacuum distillation gave 3.1 g (65.8%) (IIa).

Analogous procedures gave (Ia-f) and (IIb-f).

<u>Mercuration of Methyl(phenoxymethyl)difluorosilane.</u> A mixture of 3.57 g (0.01 mole)  $(AcO)_2Hg$  and 2.58 g (0.01 mole) (IIa) in 30 ml abs. benzene was stirred for 5 h at about 20°C. Evaporation in vacuum gave 2.86 g (67%) [(acetoxymercuri)phenoxymethyl]difluorosilane, which is an oily liquid. Found: C 26.01; H 2.31; Si 5.93; F 8.30; Hg 44.11%.  $C_{10}H_{12}O_3SiF_2Hg$ . Calculated: C 26.88; H 2.71; Si, 6.28; F 8.5; Hg 44.89%.

Bromination of Methyl(phenoxymethyl)difluorosilane. A sample of 5.27 g (0.028 mole) (IIa) was added to 5.34 g (0.03 mole) N-bromosuccinimide in 50 ml abs.  $CHCl_3$  and the mixture was stirred for 0.5 at 20°C. Vacuum distillation gave 6.2 g (83%) methyl(bromophenoxymethyl)-difluorosilane, bp 248°C,  $n_D^{2°}$  1.4996,  $d_4^{2°}$  1.511. Found: C 35.87; H 3.44; Si 10.27; F 14.19; Br 30.56%.  $C_8H_9OSiF_2Br$ . Calculated: C 35.97; H 3.39; Si 10.51; F 14.22; Br 29.91%.

<u>Ammonium(phenoxymethyl)pentafluorosilicate.</u> A mixture of 3.7 g (0.1 mole) NH<sub>4</sub>F and 9.61 g (0.05 mole) (Ia) in 30 ml CHCl<sub>3</sub> was stirred for 7 h at 20°C. Vacuum distillation gave 9.19 g (69%) product, mp 260°C. Found: C 32.09; H 6.11; Si 11.03; F 36.02; N 11.01%.  $C_7H_{15}OSiF_5N_2$ . Calculated: C 31.67; H 5.68; Si 10.75; F 35.78; N 10.91%.

## CONCLUSIONS

(Aroxymethyl)trifluorosilanes and methyl(aroxymethyl)fluorosilanes with the general formula  $XC_6H_4OCH_2SiM_nF_3-n$  (n = 0, 1) were synthesized and their reactivity with electrophilic reagents was studied.

## LITERATURE CITED

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