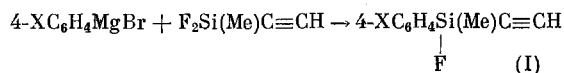


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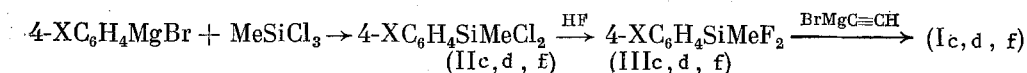
Continuing the investigation of the reactivity of ethynylfluorosilanes [1, 2], we studied the reaction of 4-substituted arylmagnesium bromides with methyl(ethynyl)difluorosilane. The reaction proceeds selectively at the equimolar ratio with the substitution of one F atom, and leads to the 4-substituted aryl(methyl)ethynylfluorosilanes



X = H (a), Me (b), Et (c), EtO (d), F (e).

The compounds (Ic, d), as well as 4-bromophenyl(methyl)-ethynylfluorosilane (If), were obtained by the direct synthesis from the corresponding 4-substituted aryl(methyl)difluorosilanes.

The initial 4-substituted aryl(methyl)difluorosilanes were synthesized by the reaction of the corresponding aryl magnesium bromides with methyltrichlorosilane and the subsequent reaction of the resulting aryl(methyl)dichlorosilanes with 40% HF.



X = Br(f)

TABLE 1. Constants of the Compounds Synthesized

Compound	Yield %	bp, °C (p, mm Hg)	$n_D^{20}$	$d_4^{20}$	Found/Calculated, %				Empirical formula
					C	H	Si	F	
(Ia)	58	69 (12)	1,4871	1,0179	65,31 65,81	5,55 5,52	17,11 17,10	11,55 11,56	C <sub>9</sub> H <sub>9</sub> FSi
(Ib)	55	70 (5)	1,4905	1,0318	67,12 67,37	6,51 6,22	16,08 15,75	10,18 10,66	C <sub>10</sub> H <sub>11</sub> FSi
(Ic)	54	78 (6)	1,4926	1,0500	69,02 68,70	7,11 6,81	14,05 14,61	10,00 9,88	C <sub>11</sub> H <sub>13</sub> FSi
(Id)	57	78 (5)	1,4902	1,0051	63,58 63,42	6,26 6,29	13,97 13,44	9,43 9,12	C <sub>11</sub> H <sub>13</sub> FOSi
(Ie)	56	90 (18)	1,4606	1,0635	58,33 59,31	4,85 4,72	15,59 15,41	20,42 20,85	C <sub>9</sub> H <sub>9</sub> F <sub>2</sub> Si
(If) *	59	91 (3)	1,5216	1,3361	44,11 44,45	3,72 3,31	11,98 11,55	7,43 7,81	C <sub>9</sub> H <sub>9</sub> BrFSi
(IIId)	60	82 (5)	1,5212	1,1710	—	—	—	—	C <sub>9</sub> H <sub>12</sub> Cl <sub>2</sub> OSi
(IIIc)	63	78 (18)	1,4730	1,0967	—	—	—	—	C <sub>9</sub> H <sub>12</sub> F <sub>2</sub> Si
(IIId)	72	68 (15)	1,4558	1,0797	—	—	—	—	C <sub>9</sub> H <sub>12</sub> F <sub>2</sub> OSi
(IIIIf)	72	57 (3)	1,4918	1,4799	—	—	—	—	C <sub>7</sub> H <sub>7</sub> BrF <sub>2</sub> Si

\*Found: Br 33.15%. Calculated: Br 32.87%.

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The constants, analytical data, and yields of the compounds synthesized are presented in Table 1.

#### EXPERIMENTAL

4-Fluorophenyl(methyl)ethynylfluorosilane (Ie). To 10.6 g of  $F_2Si(Me)C\equiv CH$  in 20 ml of abs. ether was added dropwise, with stirring, the Grignard reagent (from 2.43 g of Mg and 17.5 g of 4- $FC_6H_4Br$  in 50 ml of ether). The separated residue was filtered off and washed on the filter with ether; the ether was distilled. A yield of 9.6 g (56%) of (Ie) was obtained by the distillation of the residue in vacuo. The compounds (Ia-d) were obtained analogously (cf. Table 1).

4-Bromophenyl(methyl)ethynylfluorosilane (If). To 11.85 g of 4- $BrC_6H_4SiMeF_2$  in 25 ml of ether was added dropwise, with stirring, monomagnesium bromoacetylene (from 1.21 g of Mg, 5.4 g of EtBr, and  $HC\equiv CH$  in 50 ml of THF). The yield of 7.2 g (59.2%) of (If) was obtained analogously.

4-Ethoxyphenyl(methyl)dichlorosilane (IIId). To 75 g of  $MeSiCl_3$  in 150 ml of ether was added dropwise, with stirring, 4-ethoxyphenylmagnesium bromide (from 12.1 g of Mg and 100 g of 4-bromophenetole in 300 ml of ether). The yield of 70.5 g (60%) of (IIId) was obtained analogously.

The compounds (IIc) [3] and (IIf) [4] were obtained analogously.

4-Ethoxyphenyl(methyl)difluorosilane (IIIId). We added 70 g of 4- $EtOC_6H_4SiMeCl_2$  dropwise to 40 ml of 40% HF in a polyethylene reactor equipped with a reflux condenser and a dropping funnel, stirring the mixture with a magnetic stirrer. The lower layer was separated and distilled in vacuo. The yield of (IIIId) was 43.7 g (71.5%).

The compounds (IIIc, f) were obtained analogously (cf. Table 1).

#### CONCLUSIONS

The reaction of 4-substituted aryl magnesium bromides with methyl(ethyl)difluorosilane, as well as the reaction of ethynyl magnesium bromide with 4-substituted phenyl(methyl)difluorosilanes, led to the synthesis of 4-substituted phenyl(methyl)-ethynylfluorosilanes.

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