

## THE REACTIVITY OF FLUORINE IN ( $\omega$ -FLUOROALKYL)-SUBSTITUTED SILANES\*

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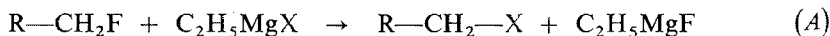
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Yields of the exchange  $R-CH_2F + C_2H_5MgX = R-CH_2X + C_2H_5MgF$  ( $R = (CH_3)_3Si-$ ,  $(CH_3)_3Si(CH_2)_2-$ ,  $(CH_3)_3Si(CH_2)_4-$ ,  $n-C_6H_{13}-$ ,  $(CH_3)_3C-$ ;  $X = Cl, Br, I$ ) and initial relative rate constants of this reaction for  $X = Br$  were determined. The facility of the reaction decreases in the order  $I > Br > Cl$  for all the compounds, neopentyl fluoride being unreactive. The reactivity of ( $\omega$ -fluoroalkyl)silanes decreases with increasing distance between the silicon and fluorine. Results are interpreted in agreement with physico-chemical properties of above compounds.

Properties of ( $\omega$ -fluoroalkyl)silanes  $R_3Si(CH_2)_nF$  are of interest especially in view of anomalous behaviour of compounds which contain fluorine in the  $\alpha$  position to silicon (the  $\alpha$ -effect). Physico-chemical properties of these compounds were already studied by us by NMR spectroscopy ( $^{19}F$ -NMR, ref.<sup>1,2</sup>,  $^1H$ -,  $^{13}C$ -, and  $^{29}Si$ -NMR, ref.<sup>2</sup>) and by measurements of proton-accepting ability of fluorine atom by IR spectroscopy<sup>3</sup>. Interpretation of observed properties was based on quantum chemical calculations of electron systems of these compounds by Del Re (ref.<sup>2</sup>) and CNDO/2 (ref.<sup>4</sup>) methods.

The aim of this work was to verify interpretation of physico-chemical properties of ( $\omega$ -fluoroalkyl)-substituted silanes and complement these data concerning chemical manifestation of their electronic structure. An analogy to the chemical reactivity of the C—Cl bond in the compounds  $R_3Si(CH_2)_nCl$  cannot be always utilized, since studies using various reaction systems for substitution reaction of C—Cl bond are controversial<sup>5,6</sup>. In the present work we chose an exchange reaction of fluorine atom for a halogen of the Grignard reagent which we studied earlier<sup>7</sup> (Eq. (A)). We have measured the equilibrium



\* Part CXLII in the series Organosilicon Compounds; Part CXLI: This Journal 41, 2701 (1976).

yields and relative rate constants of this exchange reaction for the model series  $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{F}$  ( $n = 1, 3, 5$ ) and for neopentyl fluoride and *n*-heptyl fluoride as organic standards.

## EXPERIMENTAL

Synthesis of some model organosilicon compounds and carbon analogues was described earlier: ( $\gamma$ -fluoropropyl)trimethylsilane<sup>8</sup>, ( $\epsilon$ -fluoropentyl)trimethylsilane<sup>1</sup>, *n*-heptyl fluoride<sup>7</sup>, and neopentyl fluoride<sup>1</sup>. (Fluoromethyl)trimethylsilane was prepared from trimethylsilylmethanol by the action of freshly prepared Yarovenko reagent<sup>9</sup> ( $\text{ClFHCCF}_2\text{N}(\text{C}_2\text{H}_5)_2$ ). Trimethylsilylmethanol (30 g, 0.29 mol) and 50 ml of ether were placed into a flask to which a solution of 61 g (0.32 mol) of the Yarovenko reagent in 50 ml of ether was added dropwise. After an exothermic reaction had subsided, the reaction mixture was kept under reflux for 2 h and then a portion boiling to 130°C was distilled off. This portion was fractionated with the use of an adiabatic column filled with silver spirals to give 16 g (0.15 mol, 52%) of (fluoromethyl)trimethylsilane (b.p. 60°C, ref.<sup>10</sup> 64°C) and 3.8 g of the rearranged product, ethyldimethylfluorosilane (0.035 mol, 12%).

Preparation of Grignard reagents along with the method for determining equilibrium yields of fluorine-halogen exchange were similar to those reported earlier<sup>7</sup>. Ethylmagnesium bromide was used to determine relative rate constants of fluorine exchange since its action does not lead to side reactions. To the known amount of an organosilicon compound and *n*-heptyl fluoride taken in an appropriate ratio (a total of about 3 mmol), 40 ml of 0.3M ether solution of ethylmagnesium bromide were added and the mixture stirred under reflux for 20–45 min, depending upon reactivity of a given compound. The mixture was then hydrolysed with 50 ml of water acidified by addition of 2 ml of sulphuric acid. After washing and drying, the most of the ether was distilled off and the sample was analysed by gas chromatography using 15% Sil E-302 on Celite as a stationary phase. The relative rate constant  $k_{rel}$  was calculated from the elution peak areas according to the relation (1) where  $a$  and  $y$  are the initial and final

$$k_{rel} = k_1/k_0 = \log(a/a_0)/\log(y/y_0) \quad (1)$$

concentrations of the organosilicon compound and standard, respectively. The yields and relative rate constants listed in Tables I and II are given with 7% relative error.

## RESULTS AND DISCUSSION

Concerning equilibrium yields presented in Table I it should be added that during the exchange with ethylmagnesium iodide both ( $\omega$ -fluoroalkyl)silane and *n*-heptyl fluoride react completely but products of this exchange undergo partial decomposition under reaction conditions and during work-up of the sample. As to neopentyl fluoride, neopentyl bromide did not form in more than 0.5% yield. The rearranged product, tert-amyl bromide has not been found in the reaction mixture and the products of consecutive dehydrohalogenation cannot be detected in the ether solution.

The reactivity of halogens of Grignard reagents increases in the order  $\text{Cl} < \text{Br} < \text{I}$  for all the organosilicon models, irrespective of the distance between the silicon and fluorine. This order corresponds to the energy gains of the exchange, as reported

earlier<sup>7</sup>. First two organosilicon models give higher exchange yields than does carbon standard, n-heptyl fluoride. Differences in the yields for the  $\alpha$ - and  $\gamma$ -derivatives are smaller than differences in the initial relative rate constants for the exchange reaction with ethylmagnesium bromide (Table II). The yield of the  $\varepsilon$ -derivative (Table I) is even somewhat lower than that of n-heptyl fluoride. The initial relative rate constants show, however, that both compounds are similarly reactive. These results are analogous to the observation by Copper<sup>5</sup> that (chloromethyl)trimethylsilane is in  $S_N2$  reaction with KI in acetone 20 to 30 times more reactive than n-butyl chloride. Mironov<sup>11</sup> has reported for the same reaction that (chloromethyl)trimethylsilane gives

TABLE I

Yields of Products of Exchange Reaction

$RF + C_2H_5MgX \rightarrow R-X + C_2H_5MgF$  and Energy Gains for the Exchange (Ether solution, reflux, 25–30 fold excess of  $C_2H_5MgX$ ).

Starting compound	Yield, %		
	Cl <sup>a</sup>	Br <sup>b</sup>	I
$(CH_3)_3SiCH_2F$	55.8 (0)	94.1	100
$(CH_3)_3Si(CH_2)_3F$	42.1 (22.8)	97.7	100
$(CH_3)_3Si(CH_2)_5F$	7.0 (0)	36.8	100
n-C <sub>7</sub> H <sub>15</sub> F	16.0 (20.1)	44.6	100
Energy gain <sup>c</sup> (kcal/mol)	14	14	18

<sup>a</sup> Yields of alkylation products ( $R-C_2H_5$ ) are given in parentheses. <sup>b</sup> Neopentyl fluoride affords less than 0.5% of neopentyl bromide. <sup>c</sup> Energy gains for the exchange are calculated from the bond energies recorded in ref.<sup>7</sup>.

TABLE II

Relative Rate Constants of the Exchange with Ethylmagnesium Bromide

Compound	$k_{rel}$	<sup>19</sup> F, p.p.m. <sup>a</sup>
$(CH_3)_3SiCH_2F$	33.8	–270.37
$(CH_3)_3Si(CH_2)_3F$	5.56	–215.09
$(CH_3)_3Si(CH_2)_5F$	0.992	–218.06
n-C <sub>7</sub> H <sub>15</sub> F	1.000	–218.19
neo-C <sub>5</sub> H <sub>11</sub> F	—	–222.29

<sup>a</sup> Ref.<sup>1</sup>, relative to  $CFCl_3$ , positive value denotes a paramagnetic shift.

under conditions of competition experiments 7 times higher exchange yield than ( $\gamma$ -chloropropyl)trimethylsilane. The trimethylsilyl group is particularly strongly activating when attached to the  $\alpha$  position and acts thus by its positive inductive effect. In agreement with this,  $^{19}\text{F}$ -NMR spectra show that fluorine atom in the  $\alpha$  position to silicon is substantially more shielded compared to the  $\gamma$  position<sup>1</sup> (Table II). However, neopentyl fluoride is essentially inactive, although according to its  $^{19}\text{F}$ -chemical shift the reactivity of this compound ought to lie between the  $\alpha$ - and  $\gamma$ -derivative. The low reactivity of neopentyl halogenides in  $\text{S}_{\text{N}}2$  reactions can obviously be attributed to steric reasons. The steric demands of (fluoromethyl)trimethylsilane are smaller due to the longer Si—C bond, similarly as it was already observed by Sommer<sup>6</sup> for  $\text{S}_{\text{N}}2$  reactions of the chloro analogue. The unreactivity of neopentyl fluoride thus confirms earlier considerations<sup>7,12</sup> about a concerted four-center transition state of this exchange reaction.

As follows from Table I, in the case of ethylmagnesiumchloride we have observed a side reaction, ethylation of the fluoro compound to give  $\text{R}-\text{C}_2\text{H}_5$  compounds. The alkylation as a consecutive reaction of the type  $\text{R}-\text{Cl} + \text{C}_2\text{H}_5\text{MgCl} \rightarrow \text{R}-\text{C}_2\text{H}_5 + \text{MgCl}_2$  was excluded by the experiment with the starting substrate, *n*-heptyl chloride.

In the Experimental we report on the synthesis of (fluoromethyl)trimethylsilane by means of the Yarovenko reagent. This complements data about preparation of analogous compounds, neopentyl fluoride and (fluoromethyl)trimethylsilane by the two methods: decomposition of the tosylate with potassium fluoride and by displacement of the hydroxy group by the Yarovenko reagent (Table III). Both methods

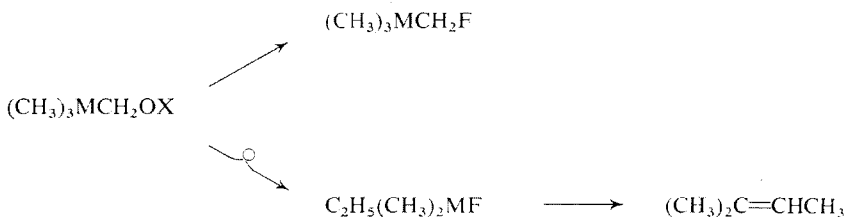
TABLE III  
Comparison of Syntheses of  $(\text{CH}_3)_3\text{SiCH}_2\text{F}$  and  $(\text{CH}_3)_3\text{CCH}_2\text{F}$

Starting compound	Reagent	Solvent <sup>a</sup>	Temperature	Yield, %	Product, rel. %	
					normal	rearranged
$(\text{CH}_3)_3\text{CCH}_2\text{OR}^b$	KF	DEG	100	39	54	46
$(\text{CH}_3)_3\text{SiCH}_2\text{OR}^b$	KF	DEG	100	49	77	23
$(\text{CH}_3)_3\text{CCH}_2\text{OH}$	Yarovenko reag.	DEGE	100	50	12	88
$(\text{CH}_3)_3\text{SiCH}_2\text{OH}$	Yarovenko reag.	DEE	35	64	81	19

<sup>a</sup> DEG = diethylene glycol, DEGE = diethylene glycol diethyl ether, DEE = diethyl ether.

<sup>b</sup> R = *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$ -.

lead during preparation to formation of rearranged products which in the case of the carbon compound is accompanied by consecutive dehydrohalogenation (Scheme 1). Comparison of the effect of the Yarovenko reagent on the extent of the rearrangement is affected by different reaction temperature and solvents which were used in preparations.



M = C, Si; X = H, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>-

SCHEME 1

Migration ability of the methyl group of the silicon compound is lower than that of the carbon compound, although (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>OX reacts easier and formation of the rearranged product is energetically more favourable, since it leads to formation of the stronger Si—F bond compared to the C—F one. Spatial release caused by migration of the methyl group from the tertiary to primary carbon in the neopentyl group is, however, more advantageous. This type of rearrangement that was kinetically studied with (chloromethyl)trimethylsilane by Bott<sup>13</sup> and Hairstone<sup>14</sup> requires transient formation of a charged particle able to rearrange, followed by nucleophilic attack at silicon. During exchange reaction with Grignard reagents we have not observed formation of rearranged products from (fluoromethyl)trimethylsilane, *i.e.* ethyldimethylhalogenosilanes (dimethyldiethylsilane after ethylation, Table I). This shows that the exchange of halogens for fluorine is a concerted process taking place without participation of a carbonium ion.

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