THE EXCHANGE OF FLUORINE IN (γ-FLUOROPROPYL)TRIALKYLSILANES AND n-HEPTYL FLUORIDE FOR HALOGENS OF GRIGNARD REAGENTS

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The title substances were used as model compounds for determination of relative yields of the exchange of terminal fluorine atom for halogens of the Grignard reagents C_2H_5MgX (X = Cl, Br, I). The ease of the exchange increases in the order Cl < Br < I; n-heptyl fluoride < (γ-fluoropropyl)triethylsilane. With C_2H_5MgI, this exchange is quantitative. The mechanism of the exchange reaction is proposed and the importance of this reaction in preparation of the Grignard reagents from alkyl fluorides is discussed.

When preparing substituted (ω-fluoroalkyl) silanes *via* alkylation of (ω-fluoroalkyl)-halogenosilanes with Grignard reagents, we obtained unexpectedly low yields of (ω-fluoroalkyl)alkylsilanes and observed that the alkylation products contain chlorine or bromine in the alkyl chain in place of fluorine, depending on the Grignard reagent used. As (ω-fluoroalkyl)silanes of the above types have not yet been synthesized, with the exception of (fluoromethyl)trimethylsilane[1] and (fluoromethyl)triethylsilane[2], the exchange of fluorine in (ω-fluoroalkyl)silanes, which makes the preparative utilization of (ω-fluoroalkyl)halogenosilanes in the organosilicon chemistry difficult, has not been observed.

A similar problem of the loss of fluorine from alkyl chain was encountered by Hoffmann[3] in the year 1949 in his attempts to prepare Grignard reagents from α-halogeno-ω-fluoroalkanes (halogen was chlorine, bromine or iodine). The author found that the hydrolysate of the Grignard reagent prepared in the usual way from 1-bromo-5-fluoropentane (the assumed ω-fluoropentyl-magnesium bromide) contains 60% of the initial fluorine in the form of fluoride ion. In order to explain this loss of fluorine from the alkyl chain, he reacted 1-bromo-5-fluoropentane with an equimolar amount of phenylmagnesium bromide and found that the hydrolysate contained all the fluorine from 1-bromo-5-fluoropentane transformed to fluoride ion, while only 60% of the bromine of phenylmagnesium bromide was converted to bromide ion. Hoffmann assumed that the initial step in the preparation of ω-fluoropentylmagnesium bromide is a transient formation of ω-fluoroalkylmagnesium bromide which exchanges bromine for the fluorine of the un-

reacted 1-bromo-5-fluoropentane or for that of the ω-fluoropentylmagnesium bromide. The fluorine exchange by added Grignard reagent, phenylmagnesium bromide, was described in the following way:

$$F(CH_2)_5Br + C_6H_5MgBr \rightarrow Br(CH_2)_5Br + C_6H_5MgF \rightarrow Br(CH_2)_5C_6H_5 +$$
$$+ MgBrF$$
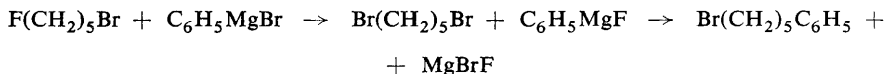
The problem was not studied further by the author and the mechanism proposed by him has not been convincingly proved because of lack of relevant experimental data.

Recently, French authors[4,5] have reported on the exchange of fluorine in benzyl fluoride and allyl fluoride effected by anhydrous magnesium salts MgX_2 in ether and tetrahydrofuran which produced $C_6H_5CH_2X$ and $CH_2=CHCH_2X$ (X = Br, Cl), respectively. The reaction of R'MgBr with $C_6H_5CH_2F$ and $CH_2=CHCH_2F$ yielded predominantly alkylation products.

If a similar exchange of fluorine for halogens *via* the action of MgX_2 or R'MgX (X = Cl, Br, I) is proved to take place also with alkyl fluorides not having an electron-rich system of unsaturated bonds (which stabilizes electron density changes during the halogen exchange reaction) in the α-position to the fluorine-substituted carbon then also some earlier studies on preparation of the Grignard reagents RMgF would be more comprehensible.

Pattison[6−8] studied the synthesis of Grignard reagents from α-halogeno-ω-fluoroalkanes $(F(CH_2)_nMgX)$ and reported on the effect of the carbon chain length and halogens upon the reaction yields. The reaction of the Grignard reagent prepared from α-halogeno-ω-fluoroalkanes with carbon dioxide gave in addition to ω-fluoro-substituted acids also the acids substituted with other halogens. This was explained by competitive formation of the Grignard reagent both from the C—F and C—Hal bonds and these reactions were considered to be the first example of formation of the Grignard reagents from organic fluorides. This explanation has been — obviously rightly — critisized[9].

The Grignard reagents from unsubstituted alkyl fluorides (R—F) have been prepared only recently. The methods employed were the so-called conjugate preparation (mostly with C_2H_5Br) or initiation by I_2 and $BrCH_2CH_2Br$ (ref.[10,11]), good results being obtained after several day reaction. Yields of the Grignard reagents were affected strongly by the solvent. The conjugate method with C_2H_5Br was used with success to prepare Grignard reagents from polyfluoroaromatic compounds[12−14], although in some cases the ethylation[15] was predominant reaction.

On the basis of our experience with the synthesis of ω-fluoroalkylsilanes and of the above studies, in the present work we attempted to explain mechanism of the loss of fluorine from the molecule of organic fluoride, using two model compounds, (γ-fluoropropyl)triethylsilane and n-heptyl fluoride.

$$F(CH_2)_3Si(C_2H_5)_3 + C_2H_5MgX \rightarrow X(CH_2)_3Si(C_2H_5)_3 + C_2H_5MgF$$
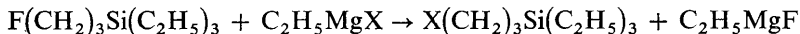
Specific effect of the silicon atom of the former model compound bears upon the possibility of its γ-elimination to cyclopropane[16]:

$$X(CH_2)_3SiR_3 \rightarrow (CH_2)_3 + X\text{-}SiR_3 .$$
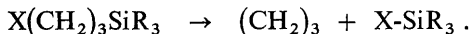
EXPERIMENTAL

Model Compounds

(γ-Fluoropropyl)triethylsilane. (γ-Chloropropyl)triethylsilane[17] was prepared by treating (γ-chloropropyl)trichlorosilane[16] (34 g, 0·16 mol) with excess ethylmagnesium bromide (0·8 mol) in a sealed apparatus from which all the gases evolved during the ethylation and the hydrolysis of the reaction mixture with 5% hydrochloric acid were introduced into absorption vessel containing cooled carbon tetrachloride which would dissolve the product of an eventual γ-elimination, cyclopropane. It was found by NMR analysis that the above elimination did not take place; also tetraethylsilane was not present among reaction products. After usual work-up of the ether layer a rectification afforded 21 g (0·109 mol, 68%) of (γ-chloropropyl)triethylsilane, b.p. 119 to 120°C/26 Torr (ref.[17] b.p. 87·5—88·5°C/8 Torr, n_D^{20} 1·4542 (ref.[17] n_D^{20} 1·4565). The product (19·5 g, 0·10 mol) was reacted with 15 g (0·25 mol) of potassium fluoride in 50 ml of ethylene glycol in the apparatus described above. The γ-elimination did not take place at 180°C while stirring the mixture for 3 h. The distillate formed two layers, the lower one being ethylene glycol. Rectification of the upper layer on a column filled with ceramic rings gave 5·3 g (0·03 mol), 30%) of (γ-fluoropropyl)triethylsilane, b.p. 124—126°C/82 Torr (ref.[16] records 47°C/7 Torr) and n_D^{20} 1·4288 (ref.[16] records 1·4305). For $Si_1C_9H_{21}F$ (176·4) calculated: 61·29% C, 12·00% H, 15·93% Si; found: 60·90% C, 11·75% H, 15·09% Si. Its structure was confirmed by ^1H-NMR spectra. The reaction products were contaminated by a small amount of the starting (γ-chloropropyl)triethylsilane.

γ-Fluoropropyl)triethylsilane was also prepared such that 25 g (0·13 mol) of (γ-fluoropropyl)-trichlorosilane (obtained by addition of trichlorosilane to allyl fluoride[16]) were slowly added to a solution of ethylmagnesium bromide (0·65 mol) in ether placed in the above apparatus. The reaction mixture was hydrolysed with aqueous ammonium chloride solution, the ether layer was worked-up in the usual way and rectified on a column filled with ceramic rings. NMR analysis of the tetrachloromethane solution showed that cyclopropane was not formed during the ethylation. The solution saturated with gases during the hydrolysis with ammonium chloride contained small amounts of cyclopropane, indicating limited elimination reaction. By rectification and gas chromatographic analysis of the reaction mixture it was found that the mixture contains (γ-fluoropropyl)triethylsilane (3 g, 0·017 mol, 13%), (γ-chloropropyl)triethylsilane (1·25 g, 0·006 mol, 5%), (γ-bromopropyl)triethylsilane (7·45 g, 0·031 mol, 24%), and tetraethylsilane (0·03 mol, 23%). The analysis of the fraction containing (γ-bromopropyl)triethylsilane and boiling at 146°C : : 54 Torr gave for $Si_1C_9H_{21}Br$ (237·3): calculated: 45·56% C, 8·92% H, 33·68% Br; found: 45·71% C, 8·92% H, 30·19% Br; n_D^{20} 1·4673 (recorded[18] b.p. 96°C/2 Torr).

(γ-Fluoropropyl)trimethylsilane. Similarly as in the previous case, 11·4 g (0·058 mol) of (γ-fluoropropyl)trichlorosilane were methylated with 0·3 mol of methylmagnesium chloride. During the methylation and hydrolysis with saturated aqueous ammonium chloride solution the mixture was cooled to 0 to +5°C. A distillation yielded 1·6 g (0·012 mol, 21%) of (γ-fluoropropyl)tri-methylsilane, b.p. 50—53°C/12 Torr, n_D^{20} 1·4070 (ref.[16] b.p. 107—109°C, n_D^{20} 1·3936). The structure of this product was confirmed by NMR spectroscopy. For $Si_1C_6H_{15}F$ (134·3) calculated: 53·67% C, 11·26% H, 20·92% Si, 14·15% F; found: 53·66% C, 11·26% H, 20·92% Si, 14·16% F. The second fraction (5 g, 0·033 mol, 57%), b.p. 76—78°C/12 Torr, n_D^{20} 1·4298, d_D^{20} 0·8789 was assigned the structure of (γ-chloropropyl)trimethylsilane based on its physical constants and NMR spectrum (ref.[19] gives b.p. 150·5°C/744 Torr, n_D^{20} 1·4319, d_D^{20} 0·8789).

n-*Heptyl fluoride* was prepared from 25 g (0·22 mol) of n-heptanol to which a solution of 46 g (0·24 mol) of the Yarovenko reagent[20] in 100 ml of diethyl ether were dropwise added. The mixture was refluxed for 2 h and then the products and the ether were distilled off. The ether solu-

tion was rectified on a column equipped with silver spirals to give 13 g (50%) of n-heptyl fluoride, b.p. 120°C, n_D^{20} 1·3852 (ref.[21] records b.p. 119°C/755 Torr, $n_D^{21·5}$ 1·3855).

Grignard reagents. Ethylmagnesium chloride, bromide, and iodide solutions in diethyl ether were prepared in the usual way in 1·1 mol/l concentration from appropriate alkyl halogenides and magnesium. Anhydrous magnesium bromide partially soluble in the ether was obtained by the Grignard reaction from 1,2-dibromoethane and magnesium. Triethylchlorosilane[22] and triethyliodosilane[23] (prepared from triethylsilane and n-heptyl iodide[24]) were used as chromatographic standards.

Halogen Exchange Reactions

(γ-Fluoropropyl)triethylsilane or n-heptyl fluoride (0·2—0·4 g; 1·1—3·4 mmol) was added to 50 ml of 1·1M ether solution of ethylmagnesium halogenide (55 mmol). The mixture was refluxed and stirred for 6 h, allowed to stand overnight and hydrolysed with 60 ml of 5% hydrochloric acid. The ether layer was washed five times with water, dried over anhydrous magnesium sulphate and the ether removed by distillation through a short column. The residual mixture was analysed on a chromatograph equipped with density balances using the column filled with 7·5% dinonyl phthalate + 7·5% Benton B-34 on Cellite 545. Percentual composition of the final mixture was determined from the areas of chromatographic peaks. Each experiment was at least once repeated. The fluoride ion concentration in the hydrolysate corresponded roughly to the loss of the fluorine from the organic layer.

The following data were obtained by the product balance of the starting and final mixture on the basis of the composition of the mixture after the exchange reaction: *a*) the amount of the original substrate which exchanged its fluorine in the alkyl chain for halogen of the Grignard
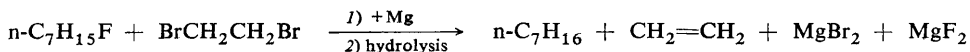
TABLE I

Fluorine Exchange in (γ-Fluoropropyl)triethylsilane and n-Heptyl Fluoride Effected by Ethylmagnesium Halogenides (Composition of the Final Reaction Mixture)

Compound	X = Cl (%)	X = Br (%)	X = I (%)
(γ-Fluoropropyl)triethylsilane			
$F(CH_2)_3Si(C_2H_5)_3$	42·2	4·0	0
$X(CH_2)_3Si(C_2H_5)_3$	31·3	84·6	—[a]
$(C_2H_5)_4Si$	10·2	11·4	12·8
$CH_3(CH_2)_4Si(C_2H_5)_3$	16·3	0	0
n-Heptyl fluoride[b]			
$n\text{-}C_7H_{15}F$	63·9	55·4	0
$n\text{-}C_7H_{15}X$	16·0	44·6	—[a]
$n\text{-}C_9H_{20}$	20·1	0	0

[a] Iodo-substituted products underwent decomposition; [b] the final mixture contained 3% (max.) of n-heptane.

reagent. This amount was calculated per 1 mol of the starting compound and expressed in per cent, *b*) the amount of the starting silane which decomposed by γ-elimination to triethylfluoro-silane and cyclopropane (the final mixture after ethylsilicon contains tetraethylsilane), calculated again per 1 mol of the starting silane and expressed in per cent.

Preparation of the Grignard Reagent from n-Heptyl Fluoride

$$\text{n-C}_7\text{H}_{15}\text{F} + \text{BrCH}_2\text{CH}_2\text{Br} \xrightarrow[\text{2) hydrolysis}]{\text{1) + Mg}} \text{n-C}_7\text{H}_{16} + \text{CH}_2{=}\text{CH}_2 + \text{MgBr}_2 + \text{MgF}_2$$

In a series of experiments, n-heptyl fluoride and $\text{BrCH}_2\text{CH}_2\text{Br}$ taken in varying molar ratio were reacted with 200% molar excess of Mg turnings (calculated with respect to the sum of the fluoride and the dibromo compound). A solution of $\text{BrCH}_2\text{CH}_2\text{Br}$ in 25 ml of diethyl ether was dropwise added during 2 h to a mixture consisting of magnesium turnings, 25 ml of the ether, the total amount of n-heptyl fluoride, and the gas chromatographic internal standard, n-nonane. The mixture was stirred and refluxed both during the addition and for another 4 h. Then it was allowed to stand overnight. After hydrolysis with 60 ml of water, washing and drying, the ether was partially removed by distillation through a short column, while the temperature of the water bath did not raise above 50°C. The sample of the mixture was analysed on a gas chromatograph and the amount of n-heptane formed by decomposition of n-heptylmagnesium fluoride was determined with the aid of the internal standard.

RESULTS AND DISCUSSION

Exchange Reactions

As follows from Table I, the exchange of fluorine in $\text{F(CH}_2)_3\text{Si(C}_2\text{M}_5)_3$ is taking place during the reaction with $\text{C}_2\text{H}_5\text{MgX}$ even when X is chlorine. If X = I, the starting $\text{F(CH}_2)_3\text{Si(C}_2\text{H}_5)_3$ loses its fluorine quantitatively; $\text{I(CH}_2)_3\text{Si(C}_2\text{M}_5)_3$ undergoes, however, decomposition to $(\text{C}_2\text{M}_5)_3\text{SiI}$ during work-up of the sample. With all the halogens, this cleavage during the reaction with $\text{C}_2\text{H}_5\text{MgX}$ proceeds to a similar extent, as shown by comparable amounts of tetraethylsilane found in the final mixtures. This is in harmony with the results obtained in the preparation of $\text{F(CH}_2)_3\text{Si(C}_2\text{H}_5)_3$ and $\text{F(CH}_2)_3\text{Si(CH}_3)_3$ by alkylation with ethylmagnesium bromide and methylmagnesium chloride. In the first case, in which also (γ-chloropropyl)triethylsilane was found among reaction products, the chlorine atoms attached originally to the silicon take part in the exchange.

n-Heptyl fluoride exchanges its fluorine for halogen of Grignard reagents approximately twice less compared to the organosilicon derivative. Trends in relative amounts of individual halogens are, however, similar in both cases. Ethylmagnesium iodide replaces fluorine again quantitatively. The n-heptyl iodide formed decomposes during the reaction and the work-up of the sample to give n-heptane. This was confirmed also by treating the sample of n-heptyl iodide in the same way as in the case of the exchange reaction of n-heptyl fluoride. Nearly identical yields of n-heptyl bro-

mide as with ethylmagnesium bromide were obtained by the exchange with equimolar amount of $MgBr_2$ (ether solution, 39.2% n-heptyl bromide). French authors[4] have reported, however, that benzyl fluoride exchanges fluorine for bromine with methyl-magnesium bromide substantially less (65%) than with $MgBr_2$ (95%) and that the Grignard reagent acts as an alkylating agent (25% ethylbenzene). In our case we have observed alkylation only during the exchange reaction with ethylmagnesium chloride (the products were also n-nonane and n-pentyltriethylsilane). Due to the Schlenk equilibrium in a solution of Grignard reagents[25] $2\ R'MgX \rightleftarrows R'_2Mg + MgX_2$, it is difficult to decide whether the exchange by $R'MgX$ is caused solely by MgX_2 or whether also $R'MgX$ participates in this reaction.

The results for the reactions (Table I)

$$RCH_2F + R'MgX \rightarrow RCH_2X + R'MgF$$
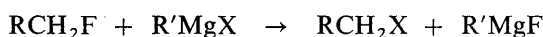
are comprehensible if they are compared with the energy gains calculated as the difference between the energies of the bonds formed and cleaved (Table II). In the exchange of the fluorine attached to the carbon atom for chlorine by a given reaction, the energy gain is 14 kcal/mol (difference in solvation energies of fluoro- and chloro--substituted compounds have not been considered), for the fluorine-bromine exchange it is 14 kcal/mol, and for the fluorine-iodine exchange this gain is 18 kcal/mol. We have also examined the exchange reaction between (γ-chloropropyl)triethylsilane and ethylmagnesium bromide or ethylmagnesium iodide. With ethylmagnesium bro-

TABLE II

Bond Energies (kcal/mol)

| Bond	Energy[26]		Bond	Energy[a]
C—F	107		Mg—F	141
C—Cl	81		Mg—Cl	101
C—Br	68		Mg—Br	88
C—I	57		Mg—I	73

[a] Energies of Mg—Hal bonds were calculated from the heats of combustion of magnesium halogenides according to the relation

$$\Delta H_{comb.} = [\sum(n_i\varepsilon_i)_{starting\ compd.} + \sum s_i(\Delta H_{evap.})_i] - \sum(m_i\varepsilon_i)_{products},$$

where $\Delta H_{comb.}$ is the heat of combustion of the gaseous compound, $n_i m_i$ is the number of bonds with energies ε_i in the starting and final compounds, s_i is the number of the elements which should be evaporated and whose heat of evaporation is $\Delta H_{evap.}$ (ref.[27]). The heats of combustion and evaporation were taken from ref.[28]. The energies for the cleavage of halogen molecules were taken from ref.[27].

mide, the exchange reaction product, (γ-bromopropyl)triethylsilane, was not formed, while with ethylmagnesium iodide the respective exchange took place only to a small extent. The calculated energy gains (Table II) agree with this finding, since for the exchange $RCH_2Cl + R'MgBr \rightarrow RCH_2Br + R'MgCl$ there is no gain, and for the exchange $RCH_2Cl + R'MgI \rightarrow RCH_2I + R'MgCl$ it has a value of 4 kcal/mol.

The agreement between the ease of the exchange reactions and their energy gains indicates that the reaction may proceed *via* a four-centre intermediate *A*, as it has been recently proposed for the exchange of fluorine in benzyl fluoride for bromine[5].
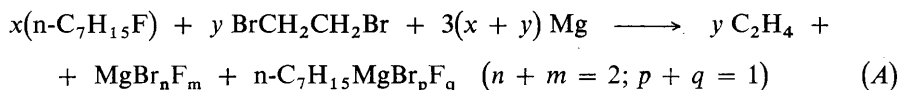
$$R\text{—}CH_2\cdots X$$
$$F\cdots\cdots Mg\text{—}R'$$
$$O(C_2H_5)_2$$
$$A$$
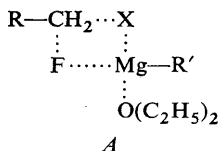
From comparison of the yields of the fluorine exchange for (γ-fluoropropyl)triethylsilane and n-heptyl fluoride it follows that the rate-determining step of the exchange is affected by electron density on the terminal fluorine (in the fluoroalkylsilane this density is higher owing to the $+I$ effect of the triethylsilyl group) and thus by the ability of fluorine to coordinate to magnesium atom instead of solvent molecule.

Preparation of the Grignard Reagent from n-*Heptyl Fluoride*

The knowledge of the course of the displacement of fluorine from an alkyl chain of an organic molecule by halogen of Grignard reagents renders it possible to discuss in somewhat different way the role of the catalysts or the function of the auxiliary Grignard reagent in conjugate preparation of Grignard reagents from alkyl fluorides. The action of catalytic amounts of I_2, $BrCH_2CH_2Br$, C_2H_5Br and other salts[11,12] in formation of the Grignard reagent from alkyl fluoride has not yet been explained in detail. The influence of the auxiliary reagent in the conjugate synthesis has frequently been ascribed to an increased solubility of the sparsely soluble and not easily obtainable Grignard reagent[9] and to a continuous restoration of magnesium surface by reaction with the auxiliary halogenide[9,13]. The catalyst or the auxiliary halogenide reacts with the magnesium to form MgX_2 or $R'MgX$; as proved above, this can exchange fluorine from the alkyl fluoride for X and the R-X formed is active in formation of RMgX which can further exchange its halogen with R-F.

To support this assumption, we have studied reactions of n-heptyl fluoride with excess magnesium in the presence of $BrCH_2CH_2Br$ (equation (*A*)). In this case the yield of

$$x(\text{n-}C_7H_{15}F) + y\,BrCH_2CH_2Br + 3(x+y)\,Mg \longrightarrow y\,C_2H_4 +$$
$$+\ MgBr_nF_m + \text{n-}C_7H_{15}MgBr_pF_q \quad (n+m=2;\ p+q=1) \quad (A)$$

the Grignard reagent was determined chromatographically as the yield of the n-heptane obtained by hydrolysis of the reaction mixture (diethyl ether, 6 h, reflux). The composition of the final mixture after hydrolysis depends on the x/y ratio in the following way (the values are an average of $3-5$ measurements):

x/y	1/2	1/1	1/0.75	2/1	4/1
% n-heptane	72	18	14	9	7

From these results it is evident that n-heptyl fluoride does react with magnesium, in the case of excess $BrCH_2CH_2Br$ even relatively well. The yields of n-heptane fall down markedly with decreasing amount of the auxiliary halogenide. This is in harmony with the study by Ashby[11]. The author observed that in the reaction of hexyl fluoride with magnesium (the auxiliary halogenide was ethyl bromide) in tetrahydrofuran (1·5 days) the yields decrease from 91% (113 mol.% C_2H_5Br) to 0% (2·2% C_2H_5Br). If catalytic amounts of the auxiliary halogenide are used, high yields are obtained only after prolonged reaction time (sometimes tens of days). From comparison of the rates of fluorine-bromine and fluorine-iodine exchange reactions for $R'MgX$ the observation by Ashby[10,11] that iodine is the most active catalyst for formation of RMgF can also be explained. The exchange reaction can also account for the results obtained by Pattison[6-8] in the study of synthesis of Grignard reagents from α-halogeno-ω-fluoroalkanes, in which case halogen of the same molecule acts as the auxiliary halogenide in conjugate preparation of Grignard reagents.

As to preparative purposes in the chemistry of ω-fluoroalkyl-substituted silanes, from the present study it follows that it is advantageous to use such a sequence of individual reaction steps which avoids interaction of fluoroalkyl-substituted derivatives with Grignard reagents. If ω-fluoroalkyl-substituted silanes should be alkylated, the reagents prepared from alkyl chlorides are superior to those obtained from alkyl bromides or alkyl iodides.

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