

ON THE REACTIONS OF TRIALKYL(ARYL)HYDROSILANES WITH TRIFLUOROACETIC ACID

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Summary

It has been established that the reaction of triethyl-, dimethyl phenyl- and dimethyl benzyl-silanes with trifluoroacetic acid is rather complex and can include not only dehydrocondensation with the formation of acyl oxysilanes, but is also accompanied, to a considerable extent, by thermal transformation of trialkyl(aryl) silyl trifluoroacetates into the corresponding disiloxanes, the splitting of Si—O and Si—C bonds, ionic hydrogenation of the intermediate trifluoroacetic aldehyde, and benzylation of both the initial compounds and the products (in the case of alkyl, benzyl hydrosilanes).

Introduction

Alkyl(aryl) hydrosilanes are known to react with carboxylic acids, forming the corresponding acyl oxysilanes in the presence of such catalysts as Al/I₂ mixture [1], Al halogenides [2], acids and bases [3], colloidal Ni [4–10], metallic Pt, Pd, Rh and other elements of Group VIII, as well as their compounds [2,5,11,12], under the action of irradiation and peroxides [2], of alcohol and alkali [13] and in such electron-donating solvents as pyridine, dimethyl formamide, quinoline, etc. [7,14,15].

At the same time, alkyl(aryl) hydrosilanes are widely used for the purposes of ionic hydrogenation in the medium of trifluoroacetic acid [15–18] (only reviews are cited), the authors, as a rule, being interested only in the final preparative result of hydrogenation. The question of what can happen with various alkyl(aryl) hydrosilanes when they interact directly with trifluoroacetic acid remains, practically, unresolved.

In this communication we present the data obtained by studying the reactions of triethyl-, dimethyl phenyl- and dimethyl benzyl-silanes with trifluoroacetic acid.

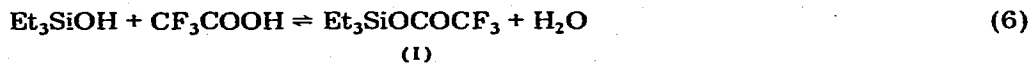
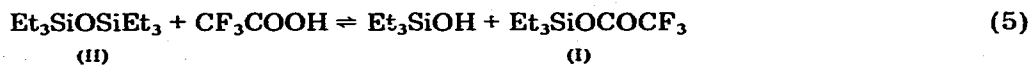
TABLE 1
REACTION OF TRIETHYL SILANE WITH TRIFLUOROACETIC ACID

Initial compounds	Mol. ratio	Reaction temp. (°C)	Reaction time (h)	Ethyl trifluoroacetate (III)	1,1,1-Trifluoroethyl trifluoroacetate (IV)	Trifluoroacetic anhydride (V)	Trifluoroacetic acid	Triethyl silane	Triethyl allyl trifluoroacetate (I)	Hexaethyl disiloxane (II)
Triethyl silane, trifluoroacetic acid	1 : 3	70	10	0.1	5.8	4.1	20.0	6.4	28.0	35.0
Triethyl silane, trifluoroacetic acid, trifluoroacetic anhydride (V)	1 : 3 : 0.5	70	10		20.0		4.8	traces	63.5	21.7
Triethyl allyl trifluoroacetate (I), trifluoroacetic acid	1 : 1	70	10		19.0		2.8		47.0	31.2
Hexaethyl disiloxane (II), trifluoroacetic anhydride (V)	1 : 1	70	10	traces	1.4	0.4			4.1	93.0 ^a
Triethyl silane, trifluoroacetic anhydride (V)	1 : 1	70	3	0.7	4.3	21.0	traces	5.0	45.5	23.5

^a High-boiling products are present (1.1%).

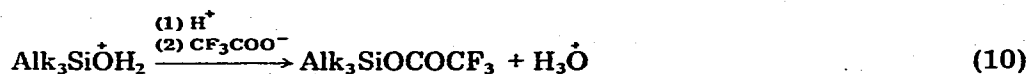
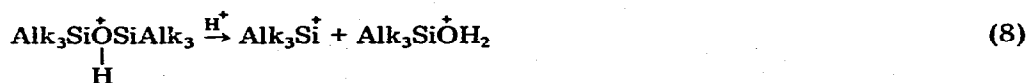
and PMR spectra corresponded to those of the authentic sample, which we synthesized by the reaction of the anhydride (V) with the alcohol (VII).

It has been further established that hexaethyl disiloxane (II) is easily split by trifluoroacetic acid as follows:



We observed the above reactions when studying the interaction of hexamethyl disiloxane with trifluoroacetic acid directly in the PMR tube. With a 1 : 1 mol. ratio of hexamethyl disiloxane to trifluoroacetic acid (reaction without heating) the protons of the methyl groups of trimethyl silyl trifluoroacetate are observed; with a 1 : 3 mol. ratio, the peak, characteristic for the protons of hexamethyl disiloxane, is only slightly present, and the main peak characterizes the protons of trimethyl silyl trifluoroacetate. In addition to this, GLC analysis of the products of the reaction of both hexamethyl- and hexaethyl-disiloxanes with trifluoroacetic acid (mol. ratio 1 : 1) shows the presence of trimethyl silyl trifluoroacetate (up to 43%) and the ester (I) (up to 8%); the reversibility of reactions (5) and (6) is shown by the formation of the corresponding hexaalkyl disiloxanes (seen from the GLC analysis data) during the interaction of trimethyl- and triethyl-silanols with trimethyl- and triethyl-silyl trifluoroacetates; and the reaction of trimethyl- and triethylsilanols with trifluoroacetic acid results in the formation of trialkyl silyl trifluoroacetates and hexaalkyl disiloxanes, trialkyl silanols being absent in the reaction products (according to GLC analysis data).

A possible mechanism of the reaction whereby hexaalkyl disiloxanes are being split by trifluoroacetic acid includes the following [21]:



We are inclined to attribute the fact that the ester (III) is being formed to the possible splitting of the Si—CH₂CH₃ bond by trifluoroacetic acid.

A few remarks on the possible mechanism of reaction (1). We found the decrease in triethyl silane in the reaction with trifluoroacetic acid to depend on the ratio between the reagents (Fig. 1). Thus, with the mol. ratio of silane to the acid equal to 1 : 10 at 50°C, the reaction more or less terminated in 10 min (after 10 min triethyl silane was almost absent in the chromatogram of the reaction products). Analysis of the relationships obtained (Fig. 1) showed it pos-

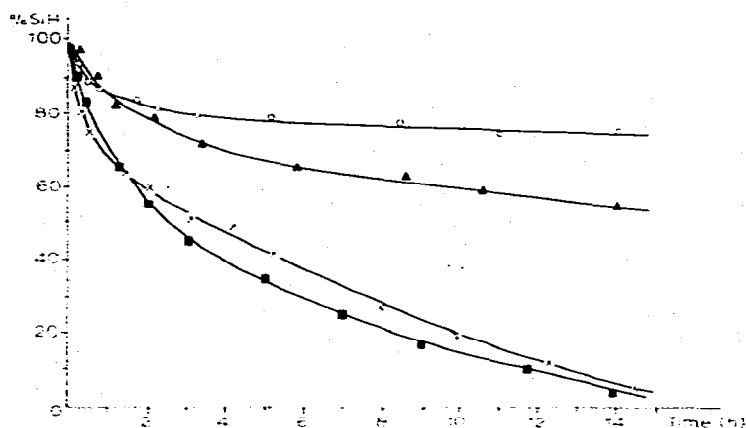
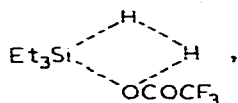


Fig. 1. Decrease in Et_3SiH in reaction with CF_3COOH in the following molecular ratios and temperature $t^\circ\text{C}$: \bullet 1 : 3, 50° ; \times 1 : 3, 50° ; \blacktriangle 1 : 10, 20° ; \blacksquare 1 : 10, 30° .

sible to measure the conversion rate (though rather approximately). With a mol. ratio 1 : 1, the decrease in triethyl silane was found to be a second order process; with the mol. ratio of silane to the acid 1 : 10, the reaction has an apparent second order, which is quite obvious. Taking into account the poor nucleophilic properties of trifluoroacetic acid and its being a strong acid ($H_0 = -3.2$) [22], one would think it unlikely for the rate determining step to be nucleophilic attack by trifluoroacetate anion. In all probability, the reaction proceeds in accordance with the four-centre SNi-Si mechanism [23], as exemplified by the interaction of diorgano-silanes with carboxylic acids in the DMFA medium [24]



the course of the reaction, as it seems, being determined first of all by the stage of the hydride ion detachment from the silicon atom under the action of the proton of the acid, which plays the part of the hydride ion acceptor.

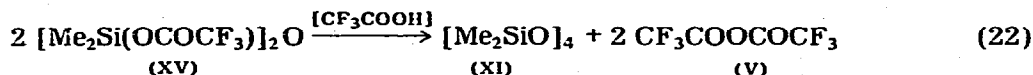
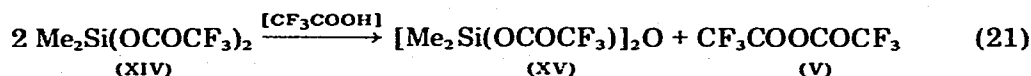
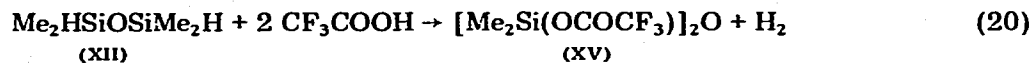
Reaction of dimethyl phenyl silane with trifluoroacetic acid

When the reaction of dimethyl phenyl silane with trifluoroacetic acid is conducted at the mol. ratio of 1 : 3, after heating the mixture at 100°C for 15 h, there are found in the reaction products, along with the unreacted initial compounds, the following: dimethyl phenyl silyl trifluoroacetate (VIII), 25.1%; sym. tetramethyl diphenyl disiloxane (IX), 3.3%; benzene (X), 15.9%; octamethyl cyclotetrasiloxane (XI), 0.8%; sym. tetramethyl disiloxane (XII), 1.9%; and low-boiling substances, 1.9%, constituting, mainly, a mixture of ester (IV) and anhydride (V) (Table 2).

TABLE 2
REACTION OF DIMETHYL PHENYL SILANE WITH TRIFLUOROACETIC ACID

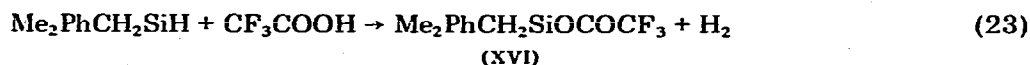
Initial compounds	Mol. ratio	Reac- tion temp. °C	Reac- tion time (h)	Composition of reaction products (wt.%)							
				Low- boiling sub- stances ^a	Sym. tetra- methyl disilo- xane (XII)	Benzeno (X)	Octa- methyl cyclo- tetrasil- oxane (XI)	Trifluoro- acetic acid	Dimethyl phenyl silane	Dimethyl phenyl silyl tri- fluoro- acetate (VIII)	Sym.tetra- methyl di- phenyl siloxane (IX)
Dimethyl phenyl silane, trifluoroacetic acid	1 : 3	100	16	1.0	1.9	16.9	0.8	44.8	6.3	25.1	3.3
Dimethyl phenyl silane, trifluoroacetic acid	3 : 1	100	16	8.6	6.9	16.6		15.2	46.8	5.6	1.4
Dimethyl phenyl silane, trifluoroacetic anhydride (V)	2 : 1	80	3	6.7	11.0	23.4	6.1	3.6	30.4	15.3	3.5
Sym. tetramethyl disiloxane (XII), trifluoroacetic acid	1 : 3	100	4	0.9	12.4			17.5			69.2

^a Mixture of ethyl trifluoroacetate (III), 1,1,1-trifluoroethyl trifluoroacetate (IV) and trifluoroacetic anhydride (V).



Reaction of dimethyl benzyl silane with trifluoroacetic acid

When dimethyl benzyl silane reacts with trifluoroacetic acid at the mol. ratio of 1 : 3, after heating the mixture at 100–120°C for 15 h, there are found in the reaction products, along with the unreacted initial compounds, the following: dimethyl benzyl silyl trifluoroacetate (XVI), 0.6%; sym. tetramethyl dibenzyl disiloxane (XVII), 9.7%; benzyl trifluoroacetate (XVIII), 2.6%; toluene (XIX), 1.8%; sym. tetramethyl disiloxane (XII), 3.4%; octamethyl cyclotetra-siloxane (XI), 4.8%; high-boiling substances: (XX), 0.7% and (XXI), 19.6%; as well as traces of low-boiling substances constituting, mainly, a mixture of the ester (IV) and the anhydride (V) (Table 3). Proceeding from this, one can visualize the following reactions to be taking place:



We could not isolate the ester (XVI) in its pure form even using preparative GLC.

TABLE 3
REACTION OF DIMETHYL BENZYL SILANE WITH TRIFLUOROACETIC ACID

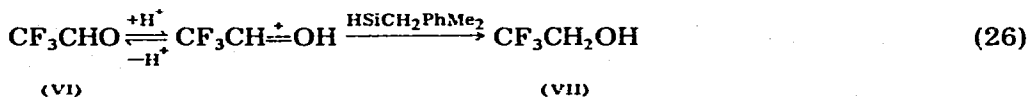
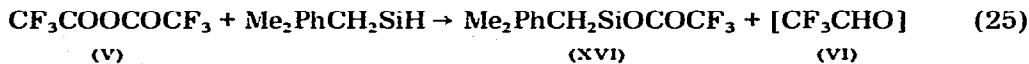
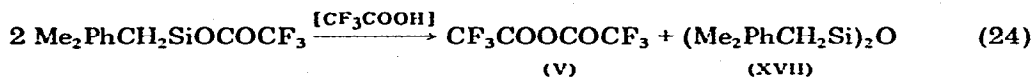
Initial compounds	Mol. ratio	Reaction temp. (°C)	Reaction time (h)	Composition of reaction products, wt. %		
				Low-boiling substances ^a	Sym. tetramethyl disiloxane (XII)	Toluene (XIX)
Dimethyl benzyl silane, trifluoroacetic acid	1 : 3	100–120	15	traces	3.4	1.8
Dimethyl benzyl silane, trifluoroacetic anhydride (V)	2 : 1	80	3	0.9	4.2	3.7
Triethyl silane, trifluoroacetic acid, benzyl trifluoroacetate (XVIII)	1 : 3 : 1	100	10	traces		2.3

^a See footnote to Table 2.

^b Also present: triethyl silane, 1.0%; triethyl silyl trifluoroacetate (I), 27.6%; and hexaethyl disiloxane (II), 6.4%.

But taking the fraction we thought, contained the ester (XVI) and not the initial dimethyl benzyl silane, and processing it with alkali water-methanol solution, we observed the formation of the siloxane (XVII).

Further, similar to what we observed in the reactions of triethyl silane and dimethyl phenyl silane (Table 3).

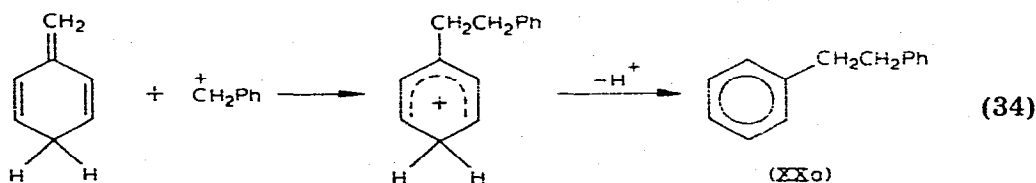
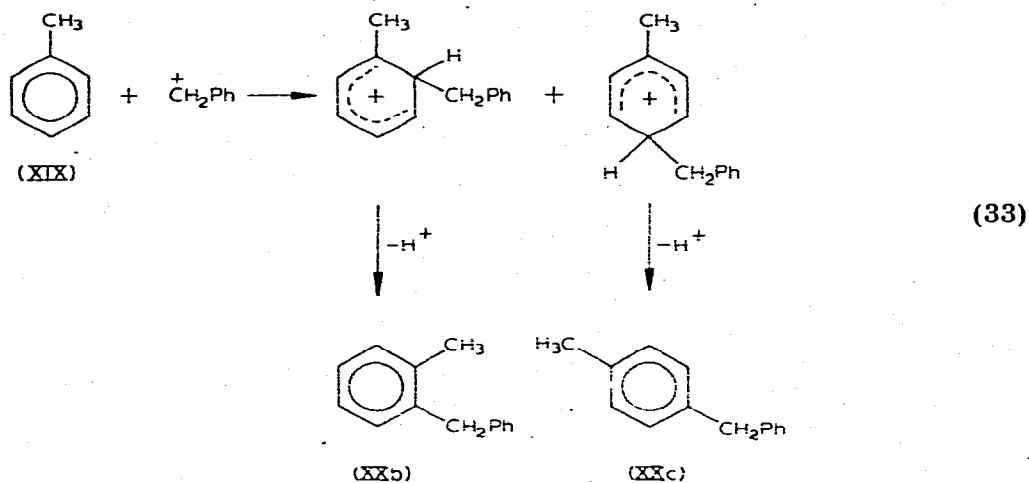


In addition to this, toluene is formed following the reaction * of the Si-benzyl

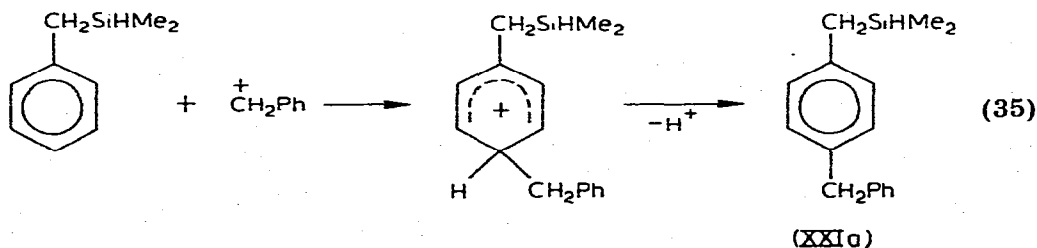


Octa- methyl cyclo- tetrasil- oxane (XI)	Benzyl trifluoro- acetate (XVIII)	Trifluoro- acetic acid	Dimethyl benzyl silane	Dimethyl benzyl silyl trifluoroacetate (XVI)	Sym.tetra- methyl di- benzyl di- siloxane (XVII)	High-boiling compounds	
						(XX)	(XXI)
4.8	2.6	51.0	5.8	0.6	9.7	0.7	19.6
1.4	4.1	1.0	17.6	1.0	54.1	traces	12.0
	traces	43.7					19.0 ^b

* See footnote referring to eqn. 15.

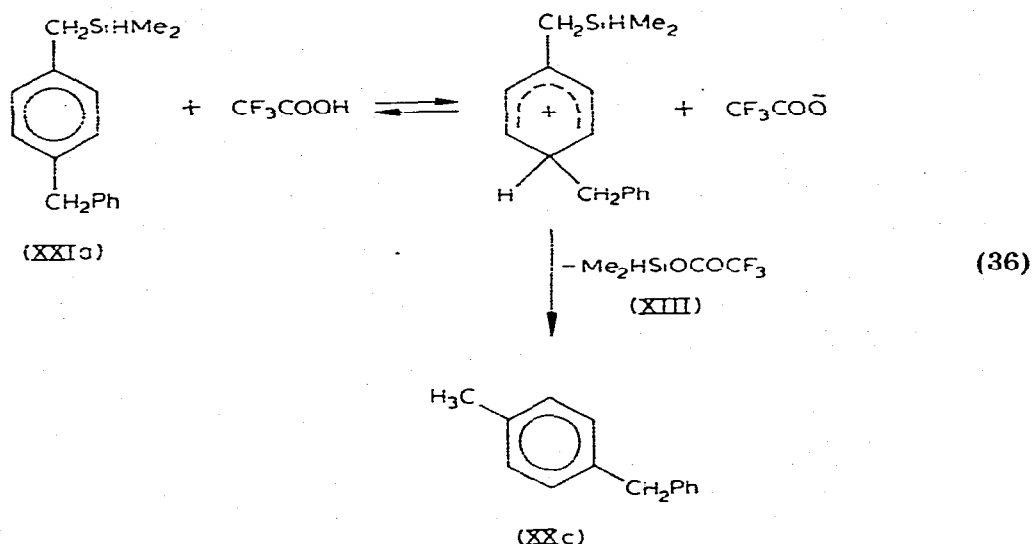


the form of the chromatograms makes the possibility of their preparative separation in our conditions doubtful. Proceeding from the results of studying the reaction of trimethyl benzyl silane with trifluoroacetic acid [27], we assume that, probably, at the interaction of dimethyl benzyl silane, reactions similar to the following can also take place:



The appearance of other compounds is also, obviously, possible. These are, e.g.: *o*-isomers, corresponding siloxanes and silyl trifluoroacetates, formed from the substances of the XXIa type, products of acidic splitting along the Si—benzyl and Si—O—Si bonds, as well as compounds obtained by electrophilic substitution into the aromatic ring with the insertion of two or more benzyl groups, etc.

Along with reaction (33), the formation of substances XXb and XXc is possible as a result of acidic splitting of the Si—benzyl bond in compounds similar to XXIa:



It has, thus, been established that the reaction of triethyl-, dimethyl phenyl- and dimethyl benzyl silanes with trifluoroacetic acid is a rather complex one and can include not only dehydrocondensation with the formation of acyl oxysilanes, but also be accompanied, to a considerable extent, by the splitting of Si—O and Si—C bonds, ionic hydrogenation of the intermediately formed trifluoroacetic aldehyde, benzylation of both the initial compounds and those formed in the reaction (in the case of alkyl benzyl hydrosilanes).

Experimental

Triethyl-, dimethyl phenyl- and dimethyl benzyl silanes, ethyl-, triethyl silyl-, trimethyl silyl-, 1,1,1-trifluoroethyl and benzyl trifluoroacetates, sym. tetramethyl-, sym. tetramethyl diphenyl- and sym. tetramethyl dibenzyl disiloxanes, trimethyl- and triethyl silanols were synthesized following the conventional procedures, the physical constants of these compounds corresponded to those given in the literature. The other compounds, used in the work, were commercially produced in the USSR, 1,1,1-trifluoroethyl alcohol produced by MERK-Schuchardt Co. Trifluoroacetic acid was purified by distillation in a rectifying column, first over silver oxide and then over conc. sulphuric acid. The purity of all the products was checked by GLC. LKhM-8 and LKh-7 analytical chromatographs, PAKh V-5 preparative chromatograph, carrier gas helium, SP-SE-30 (10%) or SKTFT-50 (10%) on Chromosorb-W or Chezasorb AW-HMDS were used. IR spectra were taken on UR-10 and UR-20 spectrophotometers, PMR spectra on Varian T60 and Hitachi-Perkin Elmer R-20 spectrometers.

The results of individual experiments are presented in Tables 1-3. All experiments were conducted in sealed ampules. The overall weight of samples used was 0.3-0.5 g. The content of individual compounds in reaction products is given in wt.% according to GLC data.

Dimethyl phenyl silyl trifluoroacetate (VIII)

The mixture of 4 g (0.027 mol) of dimethyl phenyl silane and 3.4 g (0.029 mol) of trifluoroacetic acid was heated in a refluxer in a N₂ atmosphere for 10 h at 120–130°C. By distillation 2.1 g (28.3%) of the 69–75°C/26 mmHg fraction was isolated; by the last preparative GLC purification (temperature of column 157°C) 1.3 g of VIII, n_D^{20} 1.4471 were obtained. Analysis: Found: C, 48.29; H, 4.55; Si, 10.92. C₁₀H₁₁F₃O₂Si calcd.: C, 48.39; H, 4.42; Si, 11.29%.

1,1,1-Trifluoroethyl trifluoroacetate (IV)

The mixture of 4.2 g (0.029 mol) of dimethyl phenyl silane and 5.8 g (0.028 mol) of trifluoroacetic anhydride (V) was heated in a refluxer in a N₂ atmosphere for 3 h at temperature ≤80°C. By distillation 0.39 g of the 40–51°C fraction was isolated; by the last preparative GLC purification (temperature of column 68°C) 0.21 g of IV were obtained.

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