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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/I_2 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.

Reaction of triethyl silane with trifluoroacetic acid

When triethyl silane reacts with trifluoroacetic acid in the mol. ratio 1 : 3, after heating the mixture at 70° C for 10 h, the following reaction products, along with the unreacted initial compounds, are found (wt% determined by GLC analysis): triethyl silyl trifluoroacetate (I), 28%; hexaethyl disiloxane (II), 35%; and low-boiling substances — ethyl trifluoroacetate (III), 0.1%; 1,1,1-trifluoroethyl trifluoroacetate (IV), 5.8% and trifluoroacetic anhydride (V), 4.1% (see Table 1). Hydrogen was also evolved during the reaction, but its quantity was not measured.

What attracts attention is, firstly, that quite a substantial amount of hexaethyl disiloxane (II) is formed, since the reaction was conducted with anhydrous acid and in the conditions excluding moisture penetration, so that the hydrolysis of the ester (I) formed as shown in eqn. 1 is, to a considerable extent, impossible.

$$Et_3SiH + CF_3COOH \rightarrow \underset{(I)}{Et_3SiOCOCF_3} + H_2 \qquad (1)$$

In all probability, the disiloxane (II) is formed as a result of the thermal transformation of the ester (I) [19] as in eqn. (2):

$$\underset{(I)}{2Et_3SiOCOCF_3} \xrightarrow{[CF_3COOH]} \underset{(V)}{CF_3COOCOCF_3} + \underset{(II)}{(Et_3Si)_2O} \qquad (2)$$

Having observed the transformation of the ester (I) into the disiloxane (Table 1), we were convinced that this is actually so.

It should be noted that reaction (2) is, to a certain extent, reversible, as the heating of the disiloxane (II) with the anhydride (V) leads to the formation of the ester (I) in amounts of up to 4% (Table 1).

The decreased yield of the anhydride (V), as compared with that to be expected from equation (2), seems to be caused by the subsequent reactions (see Experimental section);

$$\underset{(V)}{CF_3COOCOCF_3} + Et_3SiH \rightarrow \underset{(I)}{Et_3SiOCOCF_3} + \underset{(VI)}{[CF_3CHO]} \qquad (3)$$

The trifluoroacetic aldehyde formed (VI) participates immediately in ionic hydrogenation [20] as in eqn. (4):

$$\underset{(VI)}{CF_3CHO} \underset{-H^+}{\overset{+H^+}{\rightleftarrows}} CF_3CH{=}^+OH \xrightarrow{HSiEt_3} \underset{(VII)}{CF_3CH_2OH} \qquad (4)$$

The 1,1,1-trifluoroethyl alcohol (VII), formed in the reaction, was isolated as the corresponding ester, $CF_3CH_2OCOCF_3$ (IV). (It is to be noted that, when the ester (IV) was being isolated, the impurity of the alcohol (VII) was present in the chromatograms of the fractions prior to the preparative GLC purification. It is also possible that the $CF_3CH_2OCH_2CF_3$ ester, which we had not detected chromatographically, was also present.)

The appearance of the ester (IV) was rather unexpected, but it was, nevertheless, isolated in its pure form by preparative GLC. Its physical constants, IR

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)	Trifluoacetic acid	Triethyl silane	Triethyl silyl trifluoroacetate (I)	Hexaethyl disiloxane (II)
Triethyl silane, trifluoroacetic acid	1 : 3	70	10	0.1	5.8	4.1	20.6	6.4	28.0	35.0
Triethyl silane, trifluoroacetic acid, trifluoroacetic anhydride (V)	1 : 3 : 0.5	70	10		20.0		4.8	traces	53.5	21.7
Triethyl silyl 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 synthetized by the reaction of the anhydride (V) with the alcohol (VII).

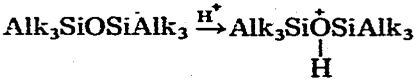
It has been further established that hexaethyl disiloxane (II) is easily split by trifluoroacetic acid as follows:

$$\underset{(II)}{Et_3SiOSiEt_3} + CF_3COOH \rightleftharpoons Et_3SiOH + \underset{(I)}{Et_3SiOCOCF_3} \qquad (5)$$

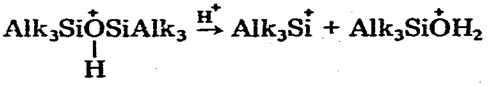
$$Et_3SiOH + CF_3COOH \rightleftharpoons \underset{(I)}{Et_3SiOCOCF_3} + H_2O \qquad (6)$$

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]:


(7)

$$Alk_3SiOSiAlk_3 \xrightarrow{H^+} Alk_3Si\underset{\displaystyle H}{\overset{+}{O}}SiAlk_3 \qquad (7)$$


(8)

$$Alk_3Si\underset{\displaystyle H}{\overset{+}{O}}SiAlk_3 \xrightarrow{H^+} Alk_3\overset{+}{Si} + Alk_3Si\overset{+}{O}H_2 \qquad (8)$$

$$Alk_3\overset{+}{Si} \xrightarrow{CF_3COO^-} Alk_3SiOCOCF_3 \qquad (9)$$

$$Alk_3Si\overset{+}{O}H_2 \xrightarrow{\substack{(1)\ H^+ \\ (2)\ CF_3COO^-}} Alk_3SiOCOCF_3 + H_3\overset{+}{O} \qquad (10)$$

We are inclined to attribute the fact that the ester (III) is being formed to the possible splitting of the $Si{-}CH_2CH_3$ 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-

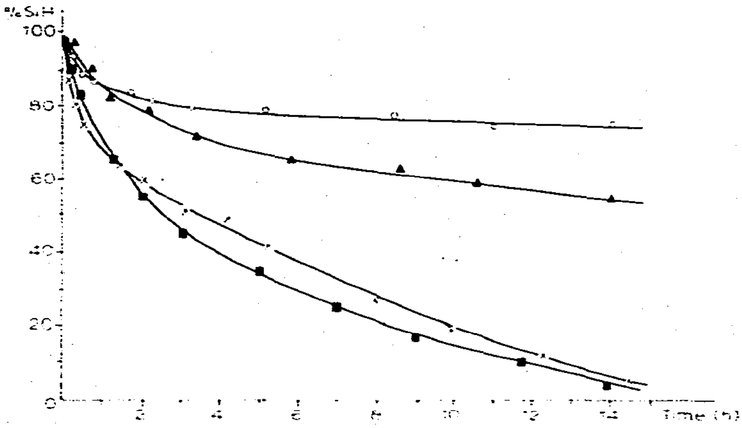
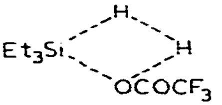


Fig. 1. Decrease in Et_3SiH in reaction with CF_3COOH in the following molecular ratios and temperature t°C: ● 1 : 3, 50°; X 1 : 3, 50°; ▲ 1 : 10, 20°; ■ 1 : 10, 30°.

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]



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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	Reaction temp, °C	Reaction time (h)	Composition of reaction products (wt.%)							
				Low-boiling substances [a]	Sym. tetramethyl disiloxane (XII)	Benzene (X)	Octamethyl cyclotetrasiloxane (XI)	Trifluoroacetic acid	Dimethyl phenyl silane	Dimethyl phenyl silyl trifluoroacetate (VIII)	Sym.tetramethyl diphenyl siloxane (IX)
Dimethyl phenyl silane, trifluoroacetic acid	1 : 3	100	15	1,9	1,9	15,9	0,8	44,8	6,3	25,1	3,3
Dimethyl phenyl silane, trifluoroacetic acid	3 : 1	100	15	8,5	5,9	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			

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

The formation of the above products is possible as a result of the following reactions:

$$Me_2PhSiH + CF_3COOH \rightarrow \underset{(VIII)}{Me_2PhSiOCOCF_3} + H_2 \qquad (11)$$

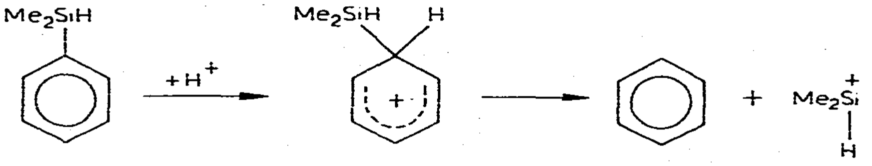
Then, similarly to what we observed in the reactions of triethyl silane (Table 2):

$$2\ \underset{(VIII)}{Me_2PhSiOCOCF_3} \xrightarrow{[CF_3COOH]} \underset{(V)}{CF_3COOCOCF_3} + \underset{(IX)}{(Me_2PhSi)_2O} \qquad (12)$$

$$\underset{(V)}{CF_3COOCOCF_3} + Me_2PhSiH \rightarrow \underset{(VIII)}{Me_2PhSiOCOCF_3} + \underset{(VI)}{[CF_3CHO]} \qquad (13)$$

$$\underset{(VI)}{CF_3CHO} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} CF_3CH\overset{+}{=}OH \xrightarrow{HSiMe_2Ph} \underset{(VII)}{CF_3CH_2OH} \qquad (14)$$

In addition to this, the Si—phenyl bond splitting * reaction is to a large extent taking place [25,26]:



(X)

(15)

The dimethyl silyl trifluoroacetate (XIII) formed * can then participate in the following transformations:

$$2\ \underset{(XIII)}{Me_2HSiOCOCF_3} \xrightarrow{[CF_3COOH]} \underset{(V)}{CF_3COOCOCF_3} + \underset{(XII)}{(Me_2HSi)_2O} \qquad (17)$$

$$\underset{(XIII)}{Me_2HSiOCOCF_3} + CF_3COOH \rightarrow \underset{(XIV)}{Me_2Si(OCOCF_3)_2} + H_2 \qquad (18)$$

Subsequent reactions of compounds XII and XIV can lead to the formation of octamethyl cyclotetrasiloxane:

$$\underset{(XII)}{Me_2HSiOSiMe_2H} + 2\ CF_3COOH \rightleftharpoons 2\ \underset{(XIII)}{Me_2HSiOCOCF_3} + H_2O \qquad (19)$$

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* It is to be noted that the splitting of the Si—phenyl bond does not necessarily have to take place in the initial dimethyl phenyl silane only — other cases are also possible, e.g.:

$$\underset{(IX)}{(Me_2PhSi)_2O} \xrightarrow{2CF_3COOH} \underset{(XV)}{[Me_2Si(OCOCF_3)]_2O} + 2\ \underset{(X)}{PhH} \qquad (16)$$

** We have not isolated the compounds XIII and XIV, but a fraction containing disoloxane (XII) and an impurity of an unknown substance has been isolated. The IR spectrum of this fraction contains the absorption band characteristic of valence vibrations of the C=O groups in esters. At the same time, absorption in the 3300—3600 cm^{-1} region is absent.

$$\underset{\text{(XII)}}{Me_2HSiOSiMe_2H} + 2\,CF_3COOH \rightarrow \underset{\text{(XV)}}{[Me_2Si(OCOCF_3)]_2O} + H_2 \qquad (20)$$

$$2\,\underset{\text{(XIV)}}{Me_2Si(OCOCF_3)_2} \xrightarrow{[CF_3COOH]} \underset{\text{(XV)}}{[Me_2Si(OCOCF_3)]_2O} + \underset{\text{(V)}}{CF_3COOCOCF_3} \qquad (21)$$

$$2\,\underset{\text{(XV)}}{[Me_2Si(OCOCF_3)]_2O} \xrightarrow{[CF_3COOH]} \underset{\text{(XI)}}{[Me_2SiO]_4} + 2\,\underset{\text{(V)}}{CF_3COOCOCF_3} \qquad (22)$$

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 cyclotetrasiloxane (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:

$$Me_2PhCH_2SiH + CF_3COOH \rightarrow \underset{\text{(XVI)}}{Me_2PhCH_2SiOCOCF_3} + H_2 \qquad (23)$$

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).

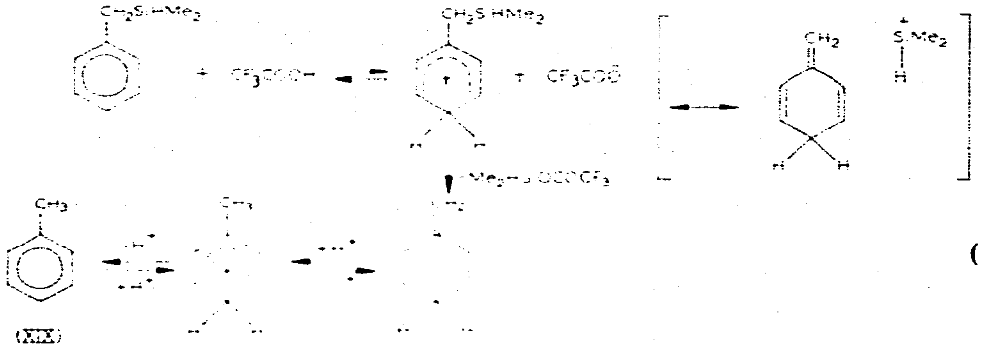
Further, similar to what we observed in the reactions of triethyl silane and dimethyl phenyl silane (Table 3).

$$2\ Me_2PhCH_2SiOCOCF_3 \xrightarrow{[CF_3COOH]} \underset{(V)}{CF_3COOCOCF_3} + \underset{(XVII)}{(Me_2PhCH_2Si)_2O} \qquad (24)$$

$$\underset{(V)}{CF_3COOCOCF_3} + Me_2PhCH_2SiH \rightarrow \underset{(XVI)}{Me_2PhCH_2SiOCOCF_3} + \underset{(VI)}{[CF_3CHO]} \qquad (25)$$

$$\underset{(VI)}{CF_3CHO} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} CF_3CH\overset{+}{=}OH \xrightarrow{HSiCH_2PhMe_2} \underset{(VII)}{CF_3CH_2OH} \qquad (26)$$

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


(XIX)

(27)

Octa-methyl cyclo tetrasil-oxane (XI)	Benzyl trifluoro-acetate (XVIII)	Trifluoro-acetic acid	Dimethyl benzyl silane	Dimethyl benzyl silyl triflu-oroacetate (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}	

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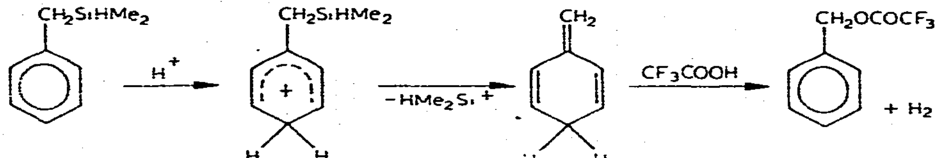
* See footnote referring to eqn. 15.

bond splitting [27] (for conciseness, here and further, *o*-substitution is not considered).

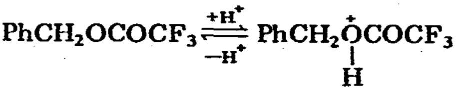
We are inclined to explain the formation of benzyl trifluoroacetate (XVIII) in a way similar to what has been previously substantiated [27], taking into account the results of other studies [28,29]:



(XVIII)

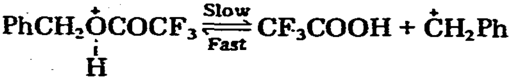
(28)

It is necessary to note that the amount of toluene, obtained at the splitting of the Si—benzyl bond under the action of trifluoroacetic acid upon trimethyl benzyl silane [27,30], is smaller than in the given case (with dimethyl benzyl silane). Therefore, a possibility is not excluded of toluene being additionally formed in accordance with the reaction of ionic hydrogenation of the ester (XVIII):



$$PhCH_2OCOCF_3 \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} PhCH_2\underset{\displaystyle H}{\overset{+}{O}}COCF_3 \qquad (29)$$

The oxonium cation formed can then be subjected to monomolecular heterolysis in a way, similar to what was observed in the case of benzyl acetate and concentrated sulphuric acid [31]:



$$PhCH_2\underset{\displaystyle H}{\overset{+}{O}}COCF_3 \underset{Fast}{\overset{Slow}{\rightleftharpoons}} CF_3COOH + \overset{+}{C}H_2Ph \qquad (30)$$

$$\overset{+}{C}H_2Ph \xrightarrow{HSiMe_2CH_2Ph} \underset{(XIX)}{CH_3Ph} + \overset{+}{Si}Me_2CH_2Ph \qquad (31)$$

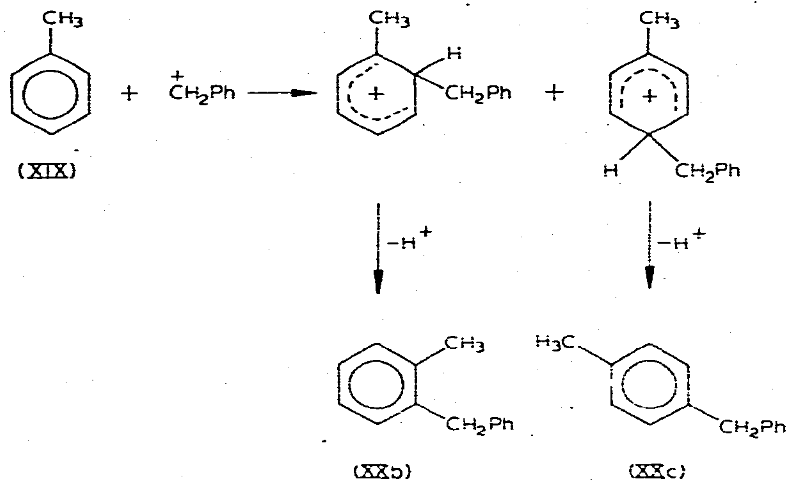
We see indications that reactions (29—31) are taking place: firstly, in that the formation of toluene and the same high-boiling products is also observed at the interaction of triethyl silane, benzyl trifluoroacetate (XVIII) and trifluoroacetic acid:

$$Et_3SiH + \underset{(XVIII)}{CF_3COOCH_2Ph} \xrightarrow{CF_3COOH} \underset{(XIX)}{CH_3Ph} + (XX) \qquad (32)$$

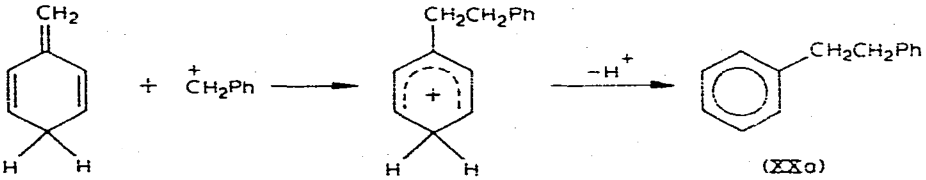
Secondly, the high-boiling products of the reactions (XX) consist of dibenzyl (XXa), *o*- and *p*-methyl diphenyl methanes (XXb) and (XXc), which indicates that the reaction of the benzylation of toluene and intermediate methylene cyclohexadiene is taking place [27].

The formation of sym. tetramethyl disiloxane (XII) and octamethyl cyclotetrasiloxane (XI) is possible as a result of reactions similar to (16—22).

A few remarks about the high-boiling substances (XXI). First of all, GLC analysis shows not less than eight substances to be present in fraction XXI. But

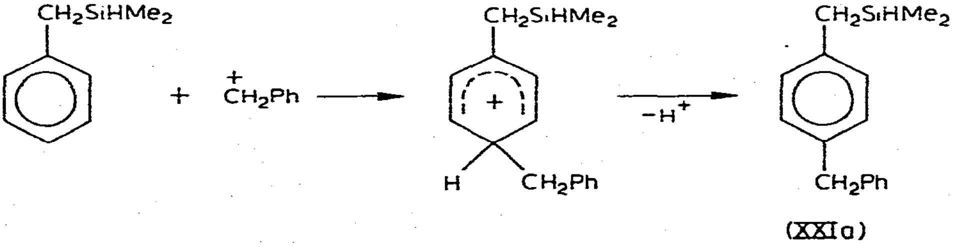


(33)



(34)

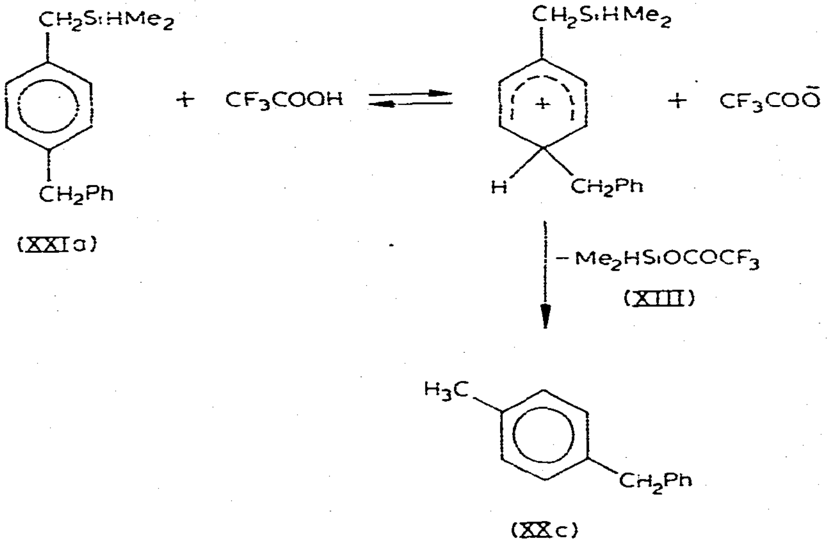
the form of the chromatograms makes the possibility of their preparative separation in our conditions doubtful. Proceeding from the results of studying the reaction of trimethyl benzyl silane with trifluoroacetic acid [27], we assume that, probably, at the interaction of dimethyl benzyl silane, reactions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



(35)

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:



(36)

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 synthetized 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 N_2 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. $C_{10}H_{11}F_3O_2Si$ 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 N_2 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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