Trimethyl(pentafluorophenyl)silane
$C_6F_5Si(CH_3)_3$

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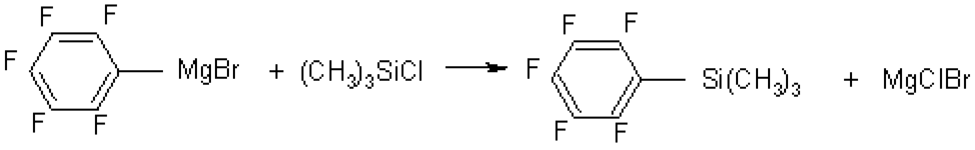
Trimethyl(pentafluorophenyl)silane (here and after referred to as silane) is a colorless liquid with a boiling point of 60 ^{o}14 mm Hg (1), 170 ^{o}Ñ (2), 64,5^{o}Ñ/14 mm Hg, 172-173 ^{o}C (3), 170 ^{o}C/ 693 mm Hg (4) and specific mass n^{25}_{d} of 1,4317 g/cm^{3} (4).

Silane is used as a reagent for introduction of a pentafluorophenyl group and as a reagent for protection of functional groups, the NH group for example (5), under conditions of nucleophilic catalysis.

Some data of its production are in papers including encompassing information (6-9)

1. Methods of silane production

1. Through a Grignard reagent, pentafluorophenyl magnesium bromide (10), when to its ether solution at vigorous stirring and a temperature of -10 - - 20^{o}C trimethylsilane is added dropwise. The target product was produced in 42% yield (1). According to other data (2), the silane yield produced by this method was 33% in terms of pentafluorophenyl bromide, the initial product for producing pentafluorophenyl magnesium. Studying the influence of the reaction conditions, the authors of (3) concluded that using the Grignard reagent freshly made provided a high yield of silane:up to 78%. Using the Grignard reagent after 16.5 hours after its preparation resulted in a decrease of the silane yield down to 46.5%.



2. By the reaction of pentafluorophenyltribromosilane with the alkyl Grignard reagent

$$C_6F_5SiBr_3 + 3CH_3MgJ \rightarrow C_6F_5Si(CH_3)_3 + 3MgBrJ \quad (11)$$

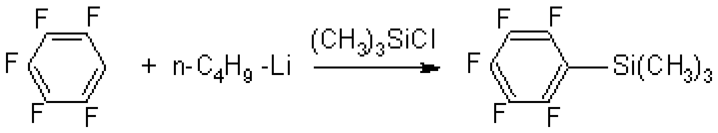
To produce initial pentafluorophenyltribromosilane from pentafluorophenyl bromide and silicone at a temperature of 600-650^{o}C, it was proposed to use a mixture of silicon and copper powders, which content in the pressed and caked mixture was 5-40%.

3.By the interaction of hexafluorobenzene with trimethylsilane under UV irradiation, which source was a Hanovia 500 W mercury lamp (2). The yield of silane was 53% as the initial hexafluorobenzene. The interaction of hexafluorobenzene with bis(trimethylsilyl) mercury under UV induction (an Hanovia UVS 500 W was the source of UV irradiation) in a 3-4-fold excess of hexafluorobenzene provided the yield of silane up to 91% (12). The reaction of hexafluorobenzene with trimethylsilane hydride under UV radiation resulted in 53% silane yield (13).

$$C_6F_6 + (CH_3)_3SiH \xrightarrow{UV} C_6F_6\text{-}Si\text{-}(CH_3)_3$$

4.By the reaction of bis(trimethylsilyl) mercury with pentafluoro bromide in the dark for 7 days at 20^{o}C. The yield of silane is 67% (14).

5. By the interaction of pentafluorobenzene with n-butyllithium followed by the addition of chlorotrimethylsilane into the reaction mixture. The yield was 66% (4).



6. By interaction of pentafluorophenyl bromide, chlorotrimethylsilane and trsi(diethylamino)phosphine (15,16). Paper (17) reported about possibility of such a reaction and described producing trifluoromethyltrimethyl silane. This reaction was studied in detail by Siberian Branch of the academy of Science of the USSR (16,18,19). During producing silane by treatment of a mixture of $Br(J)C_6F_5$ è $Cl(Br, J)Si(CH_3)$ with the equimolar quantity of tris(diethylamino)phosphine in a solvent at room temperature there were determined the reaction conditions and found that the yield of silane is influenced by the solvent nature in which the reaction was carried out. The yield of silane in pentane, hexane and dichloromethane after purification reached 63-68% whereas that in benzene and acetonitrile was up to 30%. Also it was found that chloropentafluorobenzene under the same conditions did not enter the reaction. The authors believed this reaction convenient to get polyfluorophenyl-containing silanes, germanes and stannanes though the use of tris(diethylamino)phosphine, a compound of high cancinogenity (20).

2. Silane reactions with various compounds.

2.1. Interaction of silane with carbonyl compounds.

Silane reacts with benzaldehyde in the absence of catalyst at 165-170^{o}C for 4 days to form sylil ether: phenyl(pentafluorophenyl)-trimethylsiloxy methane ($C_6F_5(C_6H_5)CHO\sim SiMe_3$) in 62% yield (21).

In the presence of catalysts this reaction proceeds under mild conditions (18-20^{o}C) for less than 4 days according to S_F I (N) (22) type. Researchers of the Siberian branch of the

Academy of Science of the USSR studied the reactions of silane with carbonyl compounds in the presence of a cyanide-anion which source was a complex of KCN*18 crown-6ethers (5, 23-33, 34). The authors studied the influence of the carbonyl group and solvent (reaction medium), space and electron factors and a number of other parameters, studied the mechanism of the reactions with an aryl anion participation.

In dependence on the ability of the carbonyl compounds to enolization, there are formed either trimethylsilyl ethers of enols and pentafluorobenzene or silane adducts to the carbonyl group. The reaction medium is of great importance. Thus, silane with enolazable ketones (acetophenone, cyclohexanone, tretbutylmethylketone and diisopropylketone) in diethyl ether forms appropriate trimethylsilylenol ethers and polymeric products, polytetrafluorophenylene, in tetrahydrofurane (THF) (24,25,33)

The yield and content of the products depends on the stereochemical ratio of the initial reagents (26,28,31,33).

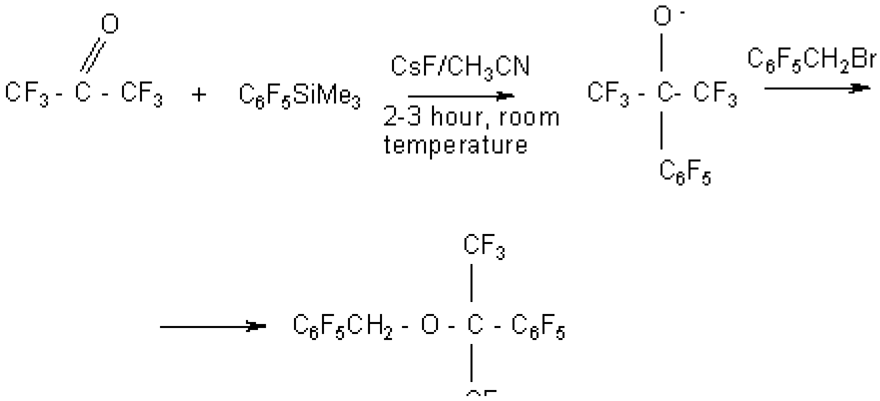
The interaction of silane with carbonyl compounds under initiation with KCN*18-crown-6

N	Initial carbonyl compound	Products produced	Yield, medium	References
1	2	3	4	5
1	Diacetoamide(equimolar quantity)	N[1(trimethylsiloxy)ethylidene]acetamide	Diethyl ether	26,27,28
2	N-trimethylsilylsuccinamide	2,5 bis(trimethylsiloxy)-N-trimethylsilylpyrrole		28
3	mathylmesitylketone	1,1-mesityltrimethylsiloxyethene	THF	29
4	3-pyridine aldehyde	Mixture of *pyridil*(pentafluorophenyl)trimethylsiloxy methane and è 1,2-bis(trimethylsiloxy)-1,2-bis (3-pyridil)ethene	Diethyl ether 45% 16%	29
5	Trifluoro-substituted acetophenone	1-phenyl-1-pentafluorophenyl-1-trimethylsiloxy- 2,2,2-trifluoroethane	Acetonitrile 85%	30,33
6	Acetophenone	1-phenyl-1-trimethylsiloxyethene	Diethyl ether 81,2 % 68,1 %	23 24
7	p-aminoacetophenone in the ratio of 1:1 to silane	4-N-trimethylsilyl aminoacetophenone	MeCN 69,8 %	33

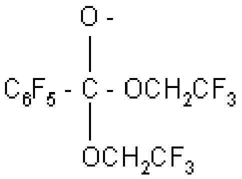
	the ratio of 1:2 to silane	trimethylsiloxyethene	85 %	
9	4 -nitroacetophenone	1-(4-nitrophenyl)-1-trimethylsiloxyethane	MeCN 82-84 %	33
10	2,3,4,5,6-pentafluoroacetophenone	1-pentafluorophenyl-1-trimethylsiloxyethene	Diethyl ether 66 %	33
11	2,4,6-trimethyl-α,α,α-trifluoroacetophenone	Tetrafluoropolyphenylene	THF 98 %	33
12	2,2-dimethylbutanone	3,3-dimethyl-2-trimethylsiloxybutene	Diethyl ether 88,6 %	23,24
13	Cyclohexanone	1-trimethylsiloxy-cyclohexene-1	Diethyl ether 36,5 %	23,24
14	Benzaldehyde	Phenyl(trimethyl-siloxy)pentafluorophenylmethane	Diethyl ether 56,5 %	23
15	1-hexine-3-one	3-trimethylsiloxy-3-hexene-1-ine	Diethyl ether	24
16	2-methylpropanal	1-pentafluorophenyl-1-trimethylsiloxy-2-methylpropane	37,3 %	24

The reaction of silane with carbonyl compounds is also catalyzed with fluoride ions, which sources are KF, CsF, RbF.

The synthesis of polyfluoroaromatic ethers is made through an intermediate polyfluoroalkooxide, a product of interaction of a perfluorocarbonyl compound with silane, which reacts in situ with pentafluorobenzyl bromide in 40% yield..

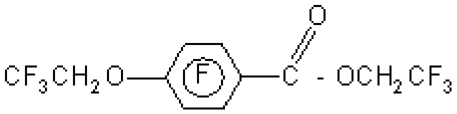


At the same time in the reaction of bis(trifluoroethyl) carbonate with silane in the presence of CsF there is formed the intermediate compound



$$C_6F_5-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle OCH_2CF_3}{|}}{C}}-OCH_2CF_3$$

which generates CF3CH2O^{-}anion. The latter substitute the fluorine atom in the pentafluorophenyl group in *para* position. In this case there is no interaction with pentafluorobenzyl bromide and diether is formed in 27% yield (35).



Paper (36) describes the addition of pentafluorophenyl group to benzaldehyde in the presence of TASF catalyst (tris(diethylamino)sulfonium difluorotrimethylsilane ($(R_2N)_3S^+Me_3SiF_2$-) in a THF medium. In the author's opinion, the yield of phenyltrimethylsiloxy pentafluorophenylmethane with the use of this catalyst is higher (87%) than that with use of different catalysts.

2.2. Interaction of silane with a number of other non-carbonyl electrophilic compounds.

The interaction of compounds containing S,O and the active S-Cl(F) bond with silane was carried out in the presence of KF and TBAF(n-tetrabutylamino fluoride) catalysts. The following pentafluorophenylsulfoxides and pentafluorophenylsulfones were produced in a 75-95% yield:

- Pentafluorophenylsulfinyl fluorides from $SOCl_2$ and SOF_2
- Pentafluorosulfinyl fluorides from SO_2Cl_2 and SOF_2
- Trifluoromethyl(pentafluorophenyl)sulfoxides and trifluoromethyl (pentafluorophenyl) sulfones from $CF_3S(O)F$ and CF_3SO_2Cl respectively (37).

γ - SO_3 freshly made also readily reacts with silane to form $C_6F_5SO_2OSi(CH_3)_3$ in 69% yield (38).

CsF was found an effective catalyst in the reactions with electrophilic compounds (39):

Initial product	Compound obtained	Yield, %
I_2	Iodopentafluorobenzene	59
Br_2	Bromopentafluorobenzene	93
D_2O	Deuteropentafluorobenzene	38
CH_3I	Pentafluorotoluene	59
$C_6F_5CF_3$	perfluoro-4-methyldiphenyl	50
$C_6F_5HgOCOCF_3$	Perfluorodiphenyl mercury	62

IF_5	Pentafluorophenyliodide tetrafluoride (40)

$$IF_5 + C_6F_4\text{-}Si\text{-}(CH_3)_3 \longrightarrow C_6F_5\text{-}I\text{-}F_4$$

Reactions of silane with HF, $AlCl_3$, $AlBr_3$, $HCl\text{-}AlCl_3$, $Br_2\text{-}AlBr_3$ in a medium of halohydrocarbons have been studied (41).

2.3. Interaction of silane with electrofilic compounds containing multiple bonds.

Silane reacts with polyfluoroalkenes in acetonitrile in the presence of CsF with substitution of the vinyl atoms of fluorine with the pentafluorophenyl group. The interaction of silane with perfluoro-4-methyl-2-pentene results in formation of perfluoro-4-methyl-2-phenyl-2-pentene in equal amount together with perfluoro-1,1,3-trimethylindane (42).

Fluorine-containing ethylene compounds in the presence of CsF react with silane with substitution of the fluorine atom at the 1 position with pentafluorophenyl group. As a result of the reaction, 7,8-dichloroperfluoro-1-octene converts into cis,trans-7,8-dichloroperfluoro-1-phenyl-1-octene in 84% yield. The side chain of perfluoroallylbenzene is arylated to form cis and trans perfluoro-1,3-diphenylpropene in 39% yield. In perfluoroisobutene the both vinyl atoms of fluorine are subsequently substituted to form perfluoroisobutenylbenzene, perfluorodiphenylisobutene and perfluoro-4-isobutenyl-diphenyl, a product of fluorine substitution in the pentafluorophenyl ring of perfluoroisobutenylbenzene:

CF2=C(CF3)2 + C6F5Si(CH3)3 → C6F5-CF=C(CF3)2 (33 %) +

+ (C6F5)2C=C(CF3)2 (7 %) + 4- C6F5C6F4 CF=C (CF3)2 (10 %)

Internal perfluoroalkenes react with silane under more hard conditions: at 55-60^{o}C. So, perfluoro-2-methyl-2-pentene is arylated into 2-methyl-3-phenyl-2-pentene in 63% yield (43). Studying the reactions of silane with internal perfluoroalkenes, the authors of (44) have found that azoalkenes, perfluoro-3-azapentene-2 and perfluoro-azanonene-4 in the presence of CsF at 20^{o}C are converted into appropriate perfluorophenylazaalkenes in 63% and 56% yield respectively.

Azenes in a medium of acetonitrile in the presence of CsF at 25^{o}C form pentafluorophenyl substituted azenes under the influence of silane.

Initial azene	Product produced	Yield, %
$CF_3(C_2F_5)NN=C(Cl)CF_3$	$CF_3(C_2F_5)NN=C(CF_3)\text{-}C_6F_5$	65
$(CF_3)_2NN=C(Cl)C_2F_5$	$(CF_3)_2NN=C(CF_3)C_6F_5$	68
$SF5N=C(Cl)C_2F_5$	$SF5N=C(C_2F_5)C_6F_5$	55

Sulfimides react with silane readily as well.

$$CF_3N=SF_2 \xrightarrow[\substack{CH_3CN\\ 250^{o}C}]{CsF} CF_3N=S(C_6F_5)_2 \quad (45)$$

2.4. Interaction of silane with nucleophilic compounds.

In the study of the reactions of silane with N^-,O^-,S^-,Si^- and C^- nucleophiles on examples of sodilum ethylate, sodium propanethiolate, piperidine, piperidyllithium, butyllithium, lithiumalumohydride and triphenylsilyllithium (Ph_3SiLi) the authors have concluded that the nature of a nucleophile is the determining factor in the course of these reactions. Thus, O^- and S^- nucleophiles attack the Si atom whereas Si^- and C^-nucleophiles, lithium alumohydride and piperidyllithium attack C-4 atom of the pentafluorophenyl group and piperidine affects both centers (46,47).

Similar results in the reactions of n-butyllithium (48) and triphenylsilyllithium (49) were obtained earlier: butyllithium in hexane reacted with silane to give 1-(trimethylsilyl)n-butyltetrafluorobenzene in 54% and triphenylsilyllithium in THF gave 1-(trimethylsilyl)-4-(triphenylsilyl)-tetrafluorobenzene in 42.5% yield.

2.5. Interaction of silane with xenone difluoride

A reaction of silane with XeF_2 in acetonitrile in the presence of fluoride ions (CsF, KF, RbF) results in evolution of xenone, trimethylfluorosilane and formation of pentafluorobenzene (58%) and decafluorodiphenyl (11%) (50,51). Silane does not react with XeF_2 in fluorotrichloromethane, sulfuryl fluoride even in the presence of CsF.

The reactivity of xenone difluoride increases sharply in methylene chloride in the presence of boron trifluoride due to polarization of the Xe-F bond and already at room temperature silane is converted into 1-trimethylsilylheptafluoro-1,4-cyclohexadiene in 74% yield (52).

2.6. Other silane reactions.

The reaction of phenylacetylene with silane in the presence of a cyanide-ion is described in paper (25):

$$PhC\equiv CH + C_6F_5Si(CH_3)_3 \longrightarrow PhC\equiv CSi(CH_3)_3$$

Silane reacts with potassium hexafluorobromate according to the following equation:

$$KBrF_6 + C_6F_5Si(CH_3)_3 \longrightarrow KBrF_4 + C_6F_6 + (CH_3)_3SiF \quad (54)$$

Silane was used for the production of anionic complexes of tetrakis(pentafluorophenyl)indium $[In(C_6F_5)_4]^-$by interaction of $In(C_6F_5)_3$ * D, where D= MeCN, ET_2O, with silane in the presence of CsF in acetonitrile (55,56).

$$In(C_6F_5)_3{}^* MeCN + C_6F_5Si(CH_3)_3 \xrightarrow{CsF,\ CH_3CN} [In(C_6F_5)_4]-$$

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