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Selective Reduction of Halopolyfluorocarbons by Organosilicon Hydrides

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It is demonstrated that silicon hydrides can be used for reduction of polyfluorinated halocarbons. For example, the reaction between CF_3CCl_2F and excess triethylsilane, catalyzed by benzoyl peroxide, leads to the formation of a mixture containing CF_3CHClF (major), CF_3CH_2F, and $ClSi(C_2H_5)_3$. On the other hand, the reaction of chlorofluoroalkanes, containing an internal $-CCl_2-$ group readily proceeds with reduction of both chlorines, leading to compounds such as $(CF_3)_2CH_2$ and $CF_3CH_2C_2F_5$. In contrast to chlorofluoroalkanes, bromofluoroalkanes are much more reactive and reaction with hydrosilane rapidly proceeds without the catalyst at elevated temperature.

Introduction

Conversion of chloro- and bromopolyfluorocarbons into the corresponding hydropolyfluorocarbons can be carried out by several methods. Reduction by tributyltin hydride[1−3] and catalytic[4] or high temperature[5] hydrodehalogenation by hydrogen are probably the most widely employed methods. A common disadvantage of thermal reduction is low selectivity, and the method based on tin hydrides, although rather powerful, involves the use and handling of toxic organotin compounds.

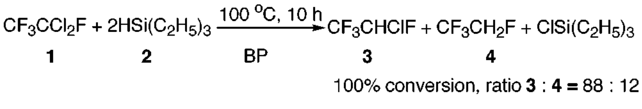
Silicon hydrides are a relatively cheap class of compounds of low toxicity, and the reduction of alkyl halides by silicon hydrides in the presence of radical initiators has been known for a long time.[6] In contrast to the use of organotin hydrides, reductions with these reagents do not find wide application in organic synthesis, due to a significantly lower activity of silicon hydrides compared to tin hydrides. On the other hand, silicon hydrides can be used successfully for the selective reduction of polychloroalkanes.[7,8] For example, reduction of CF_2Cl_2 by silicon hydrides under radical conditions (copyrolysis or mercury photosensitization of the Si−H bond)[9] and selective reduction of $ClCF_2CFCl_2$[8] by $C_6H_5SiH(CH_3)_2$ in the presence of benzoyl peroxide afford monohydroproducts in high yield. This seems to be the only reported example of such reductions of fluorinated substrates.

The reaction of halofluoroalkanes with hydrosilanes in the presence of radical initiators has been investigated as a general method for the preparation of hydrofluoroalkanes.

Results

Chloropolyfluorocarbons were found to be much more active in this reaction than alkyl chlorides. In general, the reaction of chlorofluorocarbons with silanes proceeds rapidly at elevated temperature in the presence of peroxide initiators.

For instance, CF_3CCl_2F (**1**) reacts with an excess of triethylsilane (**2**) in the presence of 5 mol % of benzoyl peroxide (BP) to give a mixture of CF_3CHFCl (**3**), CF_3CH_2F (**4**), and $ClSi(C_2H_5)_3$ (Table 1, entry 1).



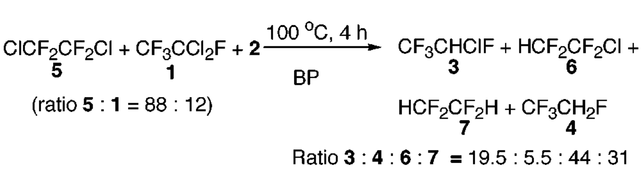
$$\underset{\mathbf{1}}{CF_3CCl_2F} + \underset{\mathbf{2}}{2HSi(C_2H_5)_3} \xrightarrow[\text{BP}]{100\ ^oC,\ 10\ h} \underset{\mathbf{3}}{CF_3CHClF} + \underset{\mathbf{4}}{CF_3CH_2F} + ClSi(C_2H_5)_3$$

100% conversion, ratio **3** : **4** = 88 : 12

BP - $[C_6H_5C(O)O-]_2$

(1)

The isomeric 1,2-dichlorotetrafluoroethane (**5**) is less active in this process, as the reaction between a mixture of **1** and **5** and excess reducing agent leads to a mixture of products **3**, **4**, **6**, and **7**, with a higher conversion of the *gem*-dichloride **1** (96% vs 71%; Table 1, entries 1 and 2).



$$\underset{\mathbf{5}}{ClCF_2CF_2Cl} + \underset{\mathbf{1}}{CF_3CCl_2F} + \mathbf{2} \xrightarrow[\text{BP}]{100\ ^oC,\ 4\ h} \underset{\mathbf{3}}{CF_3CHClF} + \underset{\mathbf{6}}{HCF_2CF_2Cl} + \underset{\mathbf{7}}{HCF_2CF_2H} + \underset{\mathbf{4}}{CF_3CH_2F}$$

(ratio **5** : **1** = 88 : 12)

Ratio **3** : **4** : **6** : **7** = 19.5 : 5.5 : 44 : 31

(2)

Reduction of 1,1,2-trichlorotrifluoroethane (**8**) by **2** (ratio 1:1), although not highly selective, produces monohydrogenated ethane **9** as a major product, along with small amounts of dihydrocompounds **11** and **12**.

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(1) Krespan, C. G. In *Chemistry of Organic Fluorine Compounds II*; Hudlicky, M., Pavlath, A. E., Eds.; ACS Monograph 187; American Chemical Society: Washington, DC, 1995; p. 297.

(2) Dolbier, W. R. *Chem. Rev.* **1996**, *96*, 1557.

(3) Van Der Puy, M.; Belter, R. K.; Borowski, R. J.; Ellis, L. A. S.; Pershichini, P. J., III; Poss, A. J.; Rygas T. P.; Tung, H. S. *J. Fluorine Chem.* **1995**, *71*, 59.

(4) Lunin, V. V.; Lokteva, E. S. *Izv. Akad. Nauk, Ser. Khim.* **1996**, 1609.

(5) Rao, V. N. M. In *Organofluorine Chemistry. Principles and Commercial Applications*; Banks, R. E., Smart, B. E., Tatlow, J. C., Eds.; Plenum Press: New York, 1994; p 159.

(6) Weber, W. P. *Silicon Reagents for Organic Chemistry*; Springer-Verlag: New York, 1983; pp 323−324.

(7) Nagai, Y.; Yamazaki, K.; Shiojima, I.; Kobori, N.; Nagashi, M. *J. Organomet. Chem.* **1967**, *9*, P21.

(8) Nagai, Y.; Yamazaki, K.; Shiojima, I. *J. Organomet. Chem.* **1967**, *9*, P25.

(9) Clark, M. P.; Conqueror, M.; Morgan, G. H.; Davidson, I. M. T. *J. Organomet. Chem.* **1996**, *521*, 395.

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Table 1. Reduction of Halopolyfluoroalkanes by Organosilanes

entry no.	compd	silane	molar ratio	initiator (mol %)	temp (°C) (time, h)	conver (%)	products (wt % in mixture)
1	**1**	**2**	1:2	BP[a] (5)	80 (10)	100	**3** (88), **4** (12)
2	**5** + **1**[b]	**2**	1:2	BP (8.6)	100 (4)	**5** (96), **1** (71)	**3** (19.5), **4** (5.5), **6** (44), **7** (31)
3	**8**	**2**	1:2	BP (4)	80 (10)	82	**9** (90), **10** (2), **11** (1.2), **12** (6.8)
4	**8**	PS[c]	1:2	BP (4)	80 (10)	67	**9** (97), **10** (2), **12** (1)
5	**8**	$C_6H_5Si(CH_3)_2H$	1:2	BP (5)	80 (10)	85	**9** (97), **10** (3)
6	**13**	**2**	1:2	BP	100 (12)	96	**14** (64), **15** (26.5), **16** (9.5)
7	**17**	**2**	1:2	BP (8)	100 (12)	100	**18** (28), **18a** (5), **19** (49), **19a** (5), **20** (10.5), unknown (2.5)
8	**21**	**2**	1:2	BP (4)	100 (12)	100	**22** (94), **23** (6)
9	**24**	**2**	1:2	BP (3)	120 (13)	100	**25** (75), **25a** (3), **26** (21), **26a** (1)
10	**21**	$(CH_3)_2SiH_2$	1:1	TBP[d] (4)	120 (12)	93	**22** (7.5), **23** (92.5)
11	**21**	Cl_3SiH	1:2	TBP (6)	120 (12)	6	**23**
12	**21**	**2**	1:2	$H_2PtCl_6{\cdot}6H_2O$ (1)	120 (12)	99.5	**22** (32.5), **23** (67.5)
13	**13**	**2**	1:2	Pd/C[e]	120 (12)	83	**14** (62), **15** (19), **16** (11), $CFH{=}CFCF_3$ (8)
14	**5** + **27**[f]	**2**	1:2.5	BP (4)	100 (12)	**27** (100), **5** (83)	**28** (40), **6** (48), **7** (12)
15	**29**	**2**	1:2	BP (5)	120 (13)	100	**26** (95), **27** (5)
16	**29**	PS[c]	1:2	BP (4)	120 (13)	75	**30** (70), **31** (30)
17	**29**	TMS[g]	1:1	BP (4)	120 (12)	90	**30** (85), **31** (15)
18	**32**	**2**	1:2		100 (12)	50	**33**
19	**34**	**2**	1:2		80 (5)	100	**35** (95)[i]

[a] Benzoyl peroxide. [b] Ratio 88:12. [c] Poly(methylsiloxane), $[-(H)Si(CH_3)O-]_n$, trimethylsilyl-terminated, equivalent weight 70. [d] *tert*-Butyl peroxide. [e] 0.5 wt % of Pd on carbon, 0.5 g. [f] Ratio 65:35. [g] Tetramethylsiloxane. [i] **35** was isolated in 86% yield.

$$\underset{\mathbf{8}}{ClCF_2CCl_2F} + \mathbf{2} \xrightarrow[BP]{80\,^{\circ}C,\ 10\,h} \underset{\mathbf{9}}{ClCF_2CHClF} + \underset{\mathbf{10}}{HCF_2CCl_2F} + \underset{\mathbf{11}}{ClCF_2CH_2F} + \underset{\mathbf{12}}{HCF_2CHFCl} \quad (3)$$

Ratio **9** : **10** : **11** : **12** = 90 : 2 : 1.2 : 6.8

Poly(methylhydrosiloxane), $[-(H)Si(CH_3)O-]_n$, was also shown to be an efficient reducing agent. The reaction of this material with **8** was slower (67% conversion) but slightly more selective for **9** (97% vs 90%) compare to reaction of **8** and **2**, (Table 1, entries 3 and 4).

$$\underset{\mathbf{8}}{ClCF_2CCl_2F} + [-(H)Si(CH_3)O-]_n \xrightarrow[BP]{80\,^{\circ}C,\ 10\,h} \mathbf{9} + \mathbf{10} + \mathbf{11} \quad (4)$$

Ratio **9** : **10** : **11** = 97 : 1.9 : 1.1

The reaction of **8** with dimethylphenylsilane was reported to proceed with exclusive reduction of one chlorine in the $-CCl_2F$ group.[8] The present work confirms that the interaction of **8** with dimethylphenylsilane under conditions similar to those used in ref 8 is indeed highly selective and leads to monohydrogenated products in high yield. However, this process is not entirely regiospecific and results in the formation of a small amount of **10** along with compound **9**.

$$\mathbf{8} + C_6H_5Si(CH_3)_2H \xrightarrow[BP]{80\,^{\circ}C,\ 10\,h} \mathbf{9} + \mathbf{10} \quad (5)$$

Conversion 85%, ratio **9** : **10** = 97 : 3

Reaction of 1,2-dichlorohexafluoropropane (**13**) with a 2-fold excess of silane **2** leads to a mixture of two isomeric monohydropropanes **14** and **15** as major products, along with small amount of dihydropropane **16**.

$$\underset{\mathbf{13}}{CF_3CFClCF_2Cl} + \mathbf{2} \xrightarrow[BP]{100\,^{\circ}C,\ 12\,h} \underset{\mathbf{14}}{CF_3CFHCF_2Cl} + \underset{\mathbf{15}}{CF_3CFClCF_2H} + \underset{\mathbf{16}}{CF_3CFHCF_2H} \quad (6)$$

Conversion 96%, ratio **14** : **15** : **16** = 64 : 26.5 : 9.5

1,2,3-Trichloropentafluoropropane (**17**) with excess of silane **2** (ratio 1:2) behaves similarly, producing a mixture of alkanes **18**−**20** along with small amounts (2.5%) of unidentified product (Table 1, entry 7).

$$\underset{\mathbf{17}}{ClCF_2CFClCF_2Cl} + \mathbf{2} \xrightarrow[BP]{100\,^{\circ}C,\ 12\,h} \underset{\mathbf{18}}{ClCF_2CFHCF_2Cl} + \underset{\mathbf{18a}}{ClCF_2CFClCF_2H} + \underset{\mathbf{19}}{ClCF_2CFHCF_2H} + \underset{\mathbf{19a}}{HCF_2CFClCF_2H} + \underset{\mathbf{20}}{HCF_2CFHCF_2H}$$

Conversion 100%, ratio **18** : **18a** : **19** : **19a** : **20** = 28 : 5 : 49 : 5 :10.5 (7)

The ratios of alkanes **14**/**15** (eq 6), **18**/**18a**, and **19**/**19a** in the crude reaction mixtures are indicative of a higher rate of reduction of internal −CFCl− groups than of terminal $-CF_2Cl$ group in this process, as befits a free radical process.

An internal dichloromethylene group $-CCl_2-$ of polychlorofluorocarbons was found to be even more active in the reduction, which is also in accord with a free radical mechanism for this process. Compound **21**, for example, was reduced to $(CF_3)_2CH_2$ by reaction with 2 mol of **2**. Only a small amount of monohydropropane **23** was found in this reaction mixture.

$$\underset{\mathbf{21}}{(CF_3)_2CCl_2} + \mathbf{2} \xrightarrow[BP]{100\,^{\circ}C,\ 12\,h} \underset{\mathbf{22}}{(CF_3)_2CH_2} + \underset{\mathbf{23}}{(CF_3)_2CHCl} + ClSi(C_2H_5)_3$$

Conversion 100%, ratio **22** : **23** = 94 : 6 (8)

The reduction of compound **24** by a 2-fold excess of **2** results in the formation of a mixture of compounds **25** and **26** as major products, along with small amounts of **25a** and **26a**.

The preferential formation of compounds **25** and **26** may be interpreted as evidence for the higher reactivity of the −CHCl− group compared to the $-CF_2Cl$ group.

Reduction of a mixture of **5** and butane **27** with an excess of **2** is another example. Under conditions similar

$$\underset{\mathbf{24}}{\mathrm{ClCF_2CCl_2CF_2CF_3}} + 2 \xrightarrow[\text{BP}]{120\ ^\circ\text{C, 13 h}} \underset{\mathbf{25}}{\mathrm{ClCF_2CH_2CF_2CF_3}} + \underset{\mathbf{25a}}{\mathrm{HCF_2CH_2CF_2CF_3}} + \underset{\mathbf{26}}{\mathrm{ClCF_2CHClCF_2CF_3}} + \underset{\mathbf{26a}}{\mathrm{HCF_2CHClCF_2CF_3}} \tag{9}$$

Conversion 100%, ratio **25** : **25a** : **26** : **26a** = 75 : 3 : 21 :1

to reduction of **21** a complete conversion of **27** into dihydrobutane **28** was observed in contrast to 83% conversion of **5** (Table 1, entry 14).

$$\mathbf{5} + \underset{\mathbf{27}}{\mathrm{CF_3CCl_2CF_2CF_3}} + \mathbf{2} \xrightarrow[\text{BP}]{120\ ^\circ\text{C, 12 h}} \underset{\mathbf{28}}{\mathrm{CF_3CH_2CF_2CF_3}} + \mathbf{6} + \mathbf{7} \tag{10}$$

Ratio **28** : **6** : **7** = 40 : 48 :12

Conversion : **27** -100%; **5** - 83%

The reactivity of the silane has a significant effect on the reduction process. For example, in the reaction of **21** catalyzed by *tert*-butyl peroxide (TBP), the replacement of **2** by diethylsilane (ratio 1:1) changes the selectivity of the reaction, and the monohydropropane **23** becomes the major product.

$$\mathbf{21} + \mathrm{H_2Si(C_2H_5)_2} \xrightarrow[\text{TBP}]{120\ ^\circ\text{C, 12 h}} \mathbf{22} + \mathbf{23} \tag{11}$$

Conversion - 93%, ratio **22** : **23** = 7.5: 92.5

TBP - $[(\mathrm{CH_3})_3\mathrm{CO}\text{-}]_2$

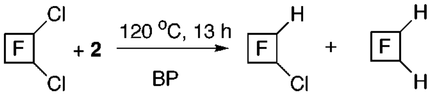
Trichlorosilane has the lowest activity among silanes used in this study. The reaction of $HSiCl_3$ and **21** is slow and leads to the formation of **23** in low yield (Table 1, entry 11).

$$\mathbf{21} + \mathrm{HSiCl_3} \xrightarrow[\text{TBP}]{120\ ^\circ\text{C, 12 h}} \mathbf{23} \tag{12}$$

Conversion - 6%

The reaction of chloropolyfluoroalkanes with silanes requires a radical initiator. No interaction between **21** and **2** was observed without peroxide initiator even at elevated temperature (100 °C, 12 h). However, the reduction also proceeds rapidly in the presence of "classical" hydrogenation catalysts such as hexachloroplatinic acid or Pd/C. Reaction of **21** and **2** catalyzed by hexachloroplatinic acid produced a mixture of **22** and **23**, while reaction of **13** and **2** catalyzed by Pd/C formed a substantial amount of $CFH{=}CFCF_3$ along with a mixture of compounds **14**−**16** (Table 1, entries 12 and 13).

1,2-Dichlorohexafluorocyclobutane (**29**) was also reacted with an excess of triethylsilane, producing 1,2-dihydrohexafluorocyclobutane (**30**) along with a small amount of monohydrocyclobutane **31**.



29 **31** **30** (13)

Conversion 100%, ratio **30** : **31** = 95 :5

Reactions of **29** with poly(methylsiloxane) and tetramethylsiloxane proceed similarly, but they are less selective (see Table 1, entries 16 and 17). Bromopolyfluorocarbons are more active than chloropolyfluoroalkanes, and reaction with **2** usually proceeds without catalyst. Dibromodifluoromethane (**32**) was converted into hydrobromodifluoromethane (**33**) simply by heating a mixture of reagents.

$$\underset{\mathbf{32}}{\mathrm{CF_2Br_2}} + 2\ \mathrm{HSi(C_2H_5)_3} \xrightarrow{100\ ^\circ\text{C, 12 h}} \underset{\mathbf{33}}{\mathrm{CF_2HBr}} \tag{14}$$

100% selectivity, 50% conversion

The corresponding dihydropentane **35** was isolated in high yield from a noncatalyzed reaction of 2,2-dibromooctafluoropentane (**34**) with a 2-fold excess of $HSi(C_2H_5)_3$ (Table 1, entry 19).

Discussion

Reduction of halopolyfluoroalkanes by hydrosilanes such as triethylsilane probably occurs by a radical chain mechanism. A radical derived from the decomposition of the initiator starts the radical chain by abstraction of a hydrogen atom from the silane, leading to the formation of a silyl radical **36** (Scheme 1).

Scheme 1

Initiation:

a) $\mathrm{RO^{\cdot}} + \mathrm{HSi(C_2H_5)_3} \longrightarrow \mathrm{ROH} + \underset{\mathbf{36}}{{}^{\cdot}\mathrm{Si(C_2H_5)_3}}$

Propagation:

b) $\mathbf{36} + \mathrm{R_f(R_f')CCl_2} \longrightarrow \mathrm{(C_2H_5)_3SiCl} + \underset{\mathbf{37}}{\mathrm{R_f(R_f')CCl^{\cdot}}}$

c) $\mathbf{37} + \mathrm{HSi(C_2H_5)_3} \longrightarrow \underset{\mathbf{38}}{\mathrm{R_f(R_f')CClH}} + \mathbf{36}$

The propagation steps involve abstraction of a chlorine atom from chloropolyfluoroalkane by radical **36** to form triethylchlorosilane and fluoroalkyl radical **37**. Abstraction of $H^{\bullet}$ from silane by **37** leads to the formation of hydrochloropolyfluoroalkane **38** and regeneration of the silyl radical **36**. Alkane **38** can be either an intermediate or final product of the reaction. The order of decreasing activity of different groups in the reduction ($-CCl_2- > -CClF- \geq -CClH- > -CF_2Cl$) can be correlated to the stability of corresponding radical intermediates and is in good agreement with a radical mechanism for the process. The fact that reduction of chloropolyfluoroalkanes is catalyzed by peroxides is, of course, also indicative of a radical chain mechanism, which is very efficient, based on the amount of peroxide (5−6 mol %) necessary to complete the reduction.

Primary alkyl radicals are known to be much less reactive in hydrogen abstraction than polyfluorinated radicals,[2,4] and this is why the reduction of alkyl halides usually requires much more powerful reagents than silane **2**, examples being tributyltin hydride,[13] tris(trimethylsilyl)silane,[14] and pentamethyldisilane.[15]

The relative reactivity of silanes in reduction of chloropolyfluoroalkanes is also an important factor; the significant difference in activity between Cl_3SiH and **2**

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(10) Paleta, O.; Dadak, V.; Dedek, V. *J. Fluorine Chem.* **1988**, *39*, 397.

(11) Dedek, V.; Chvatal, Z. *J. Fluorine Chem.* **1986**, *31*, 363.

(12) Ramig, K.; Quiroz, F.; Vernice, G. G.; Rozov, L. A. *J. Fluorine Chem.* **1980**, *80*, 101.

(13) Kuivila, H. G. *Synthesis* **1970**, 499.

(14) Ballestri, M.; Chatgilialogu, C.; Clark, K. B.; Griller, D.; Giese, B.; Kopping, B. *J. Org. Chem.* **1991**, *56*, 678.

(15) Lusztyk, J.; Maillard, B.; Ingold, K. U. *J. Org. Chem.* **1986**, *51*, 2457.

is probably the result of a much slower hydrogen transfer from trichlorosilane to the polyfluoroalkyl radical.

In reductions of chloropolyfluoroalkanes, triethylsilane is less reactive than tributyltin hydride since the latter effectively replaces several chlorine atoms in chloropolyfluorocarbons under mild conditions.[3] This difference in hydrodechlorination reactivity is not surprising, since the latter was shown to be more than 200 times more active as a hydrogen transfer agent in reactions involving polyfluorinated radicals.[2] An advantage of the less reactive silanes lies in the greater selectivities available with them in the reduction of chloropolyfluoroalkanes.

The radical chain mechanism proposed for the reduction of halopolyfluoroalkanes by organosilanes is similar to that offered for the reduction of polychloroalkanes by silanes[7,8] and for polychloro- and chloropolyfluoroalkanes or polyfluorinated ethers by 2-propanol[10−12] under UV-irradiation. All of these processes were shown to have a radical chain mechanism involving the formation of electrophilic polyhalogenated radicals[6,7,12] as intermediates.

On the other hand, the mechanism for the reduction of chloropolyfluoroalkanes catalyzed by H_2PtCl_6 and Pd/C may be much more complex. There are several possibilities including formation of active metal clusters as a result of reduction by H_2PtCl_6, followed by oxidative addition of the C−Cl bond of chloropolyfluoroalkane to an electron-rich metal center and further formation of a polyfluoroalkyl σ-complex of Pt (or Pd). A polyfluoroalkyl derivative of the metal may be converted to final product either through the sequence of formation of metal hydride complex and reductive elimination of polyfluoroalkane or as a result of the homolysis of a carbon−metal bond with generation of fluoroalkyl radical. Unfortunately, experimental data are not sufficient to choose between these mechanisms.

The experimental results obtained in this work are in excellent agreement with a recently published opinion based on an analysis of the reactivity of polyfluorinated radicals that triethylsilane may be “a very useful agent for relatively slow chain processes involving fluorinated radicals”.[2] Much lower reactivity of silicon hydrides vs tin hydrides in radical reductions can be compensated for by much higher reactivity of polyfluorinated radicals vs the corresponding hydrocarbon radicals, since the reactivities of fluorinated radicals approach that of the highly electronegative *tert*-butoxy radical.[2]

Experimental Section

^{19}F and ^{1}H NMR spectra were recorded using $CFCl_3$ as internal standard and either chloroform-*d* or acetone-*d* as a lock solvent. Silanes, poly(methylhydrosiloxane) (Gelest), peroxides, and compounds **1**, **5**, **13**, **29**, and **32** were commercial and used without further purification. Compounds **21**, **27**, **34**,[16] and **24**[17] were prepared using known procedures. Products **3**, **4**, **6**, **7**, **9**−**12**, **19a**,[18] **20**,[3] and **28**[19] were identified by comparison of ^{1}H and ^{19}F data with reported values. Materials **15**, **16**, **22**, **23**, **30**, and **33** were identified by comparison with authentic samples.

Caution! We did not experience any problems in this work; however, use a peroxide initiator and general consideration of radical chain mechanism of reduction polyfluoroalkanes by silanes suggest that the reaction under certain conditions can be hard to control. *Reductions should be carried behind a shield or in a barricade.*

Reduction of Polyhalofluoroalkanes by Oranosilanes Hydrides. (General Procedure). A mixture of polyhalofluoroalkane (0.05−0.2 mol) and silane (0.05−0.4 mol) was placed in Hastelloy reactor, and initiator/catalyst was added. The reactor was closed, purged with N_2, and kept 1 h at 25 °C and 6−13 h at 80−120 °C. The reactor was cooled to −78 °C and unloaded. The crude reaction mixture was analyzed by GC and ^{1}H and ^{19}F NMR spectroscopy. Reaction conditions, ratio of reagents, and products are given in Table 1.

Since compounds **18**, **19**, and **19a** were previously reported in patent literature only, they were characterized by ^{19}F NMR.

18: −63.91 (2F, dm, 176 Hz), −64.82 (2F, dm, 176 Hz), −193.66 (1F, dm, 56 Hz).

19: −61.94 (1F, dm, 187 Hz), −65.38 (1F, dm, 187 Hz), −129.10 (1F, dm, 326 Hz), −130.75 (1F, dm, 326 Hz), −206.71 (1F, dm, 57 Hz).

19a: −132.55 (4F, dm, 54 Hz), −147.13 (1F, m).

Compounds **25** and **26** were not isolated but were characterized in mixture by ^{19}F NMR spectroscopy.

25: −49.77 (2F, m; 11 Hz), −86.82 (3F, s), −118.15 (2F, m).

26: −54.18 (1F, dm; 168 Hz), −57.00 (1F, dm; 168 Hz), −78.68 (3F, m), −116.08 (1F, dm; 272 Hz), −121.50 (1F, dm; 272 Hz).

Reduction of 34 by Triethylsilane. 10 mL of $HSi(C_2H_5)_3$ was added dropwise to 10 g of **34** with stirring at 80 °C over 10 min. The reaction mixture was kept at this temperature for 5 h, collecting the crude product which passed a short reflux water condenser in a cold trap (−78 °C). Collected product (based on GC and NMR data **35** was 95% purity) was redistilled to give 4.8 g (86%) of **35**.

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(16) Petrov, V. A.; Krespan, C. G.; Smart, B. E. *J. Fluorine Chem.* **1998**, *89*, 125.

(17) Sievert, A. C.; Nappa, M. J. PCT WO 95/16656, 1995 (to Dupont); *Chem. Abstr.* **1995**, *123*, 339128.

(18) Weigert F. J. *J. Fluorine Chem.* **1990**, *46*, 375.

(19) Burdon, J.; Ezmirly, S. T.; Huckerby, T. N. *J. Fluorine Chem.* **1988**, *40*, 283.