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THE SYNTHESIS OF 3,3-DIFLUOROALLYL DERIVATIVES OF SILICON BY AN ORGANOPHOSPHORUS ROUTE *

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Summary

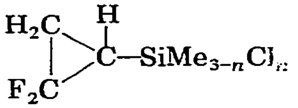
3,3-Difluoroallyl derivatives of silicon have been prepared by the reaction of difluorochloromethane with ylides of type $Ph_3P{=}CHCH_2SiR_3$ (SiR_3 = $SiMe_3$, $SiMe_2H$, $SiMe_2OSiMe_3$, $SiMe(OSiMe_3)_2$). Also prepared by this procedure was $Me_3SiCH_2C(CH_3){=}CF_2$, but $Me_3SiCH_2C(C_6H_5){=}CF_2$ could not be prepared in this way, probably because the ylide, $Ph_3P{=}C(C_6H_5)CH_2SiMe_3$, was not sufficiently basic to deprotonate HCF_2Cl. The thermal stability of $Me_3SiCH_2CH{=}CF_2$ was assessed and a few of its reactions examined: addition of CCl_2 and CBr_2 (generated via the appropriate $PhHgCX_2Br$) and addition-elimination reactions with phenyl- and n-butyllithium to give $Me_3SiCH_2CH{=}C(R)F$ (R = Ph, n-Bu).

Introduction

In 1972 Mironov and his coworkers [2] reported the hot tube reaction of vinylmethylchlorosilanes, $CH_2{=}CHSiMe_{3-n}Cl_n$ (n = 0—3), with difluorochloromethane. At temperatures of 485—505°C the yield of the products sought, the respective 2,2-difluorocyclopropylsilanes, I, was optimum. Presumably I were formed by a two-step process (eq. 1 and 2). However, compounds of type I showed limited thermal stability and underwent rearrangement to the respec-

$$HCF_2Cl \rightarrow HCl + CF_2 \qquad (1)$$

$$CF_2 + CH_2{=}CHSiMe_{3-n}Cl_n \rightarrow$$



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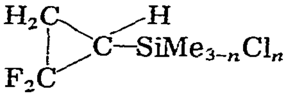
* Preliminary communication: ref. 1.

tive 3,3-difluoroallylsilane under the reaction conditions (eq. 3). The yields of



$$\rightarrow CF_2{=}CHCH_2SiMe_{3-n}Cl_n \qquad (3)$$

(II)

the rearrangement products were at a minimum at 485—505°C and increased with increasing temperature, until the tube coked up at 590—610°C and II were the only observed volatile products.

3,3-Difluoroallylsilanes of type II were reported to be stable to 600°C for short periods of time, i.e., they survived passage through a hot tube at that temperature in a stream of nitrogen. At higher temperature (~680°C) these silanes lost CF_2 to give the vinylsilane, $CH_2{=}CHSiMe_{3-n}Cl_n$, and tetrafluoroethylene. The chemistry of 3,3-difluoroallylsilanes of type II was the subject of a further brief study by this Russian group [3]. In the main, reactions were carried out at the reactive Si—Cl functionality in compounds of type II where $n = 1$, 2 and 3: reduction with $LiAlH_4$, alkylation with CH_3MgI, methanolysis, hydrolysis and fluorination with antimony trifluoride. In all these reactions the $CH_2CH{=}CF_2$ substituent survived unchanged. The C=C addition reactions also were reported (eq. 4, 5).

$$CH_3Cl_2SiCH_2CH{=}CF_2 \xrightarrow{Br_2} CH_3Cl_2SiCH_2CHBrCF_2Br \qquad (4)$$

$$CH_3Cl_2SiCH_2CH{=}CF_2 \xrightarrow{HI(g)} CH_3Cl_2SiCH_2CH_2CF_2I \qquad (5)$$

In view of their apparent high thermal stability and their potentially interesting chemistry at the 3,3-difluoroallyl substituent, these silanes seemed worthy of further investigation. However, it was not clear that the hot tube synthesis was the most practical one possible and, in fact, no useful, detailed synthesis of compounds of type II was provided in the cited papers. In any case, we were interested in the possibility of an alternate, directed synthesis of 3,3-difluoroallylsilanes.

We report here concerning a new route to 3,3-difluoroallyl derivatives of silicon which is based on organophosphorus methodology. Also described are some further reactions of 3,3-difluoroallylsilanes.

Results and discussion

3,3-Difluoroallyltrimethylsilane was prepared as shown in eq. 6—10:

$$Me_3SiCH_2Cl + NaI \xrightarrow{acetone} Me_3SiCH_2I + NaCl \qquad (6)$$

$$Ph_3PCH_3^+Br^- + NaNH_2 \xrightarrow{NH_3(l)} \xrightarrow{Et_2O} Ph_3P{=}CH_2 + NH_3 + NaBr \qquad (7)$$

$$Ph_3P{=}CH_2 + Me_3SiCH_2I \rightarrow Ph_3PCH_2CH_2SiMe_3^+I^- \qquad (8)$$

$$Ph_3PCH_2CH_2SiMe_3{}^+I^- + CH_3Li \rightarrow Ph_3P{=}CHCH_2SiMe_3 + CH_4 + LiI \quad (9)$$

$$2\ Ph_3P{=}CHCH_2SiMe_3 + HCF_2Cl \xrightarrow{Et_2O} Ph_3PCH_2CH_2SiMe_3{}^+Cl^- + Ph_3P + Me_3SiCH_2CH{=}CF_2 \quad (10)$$

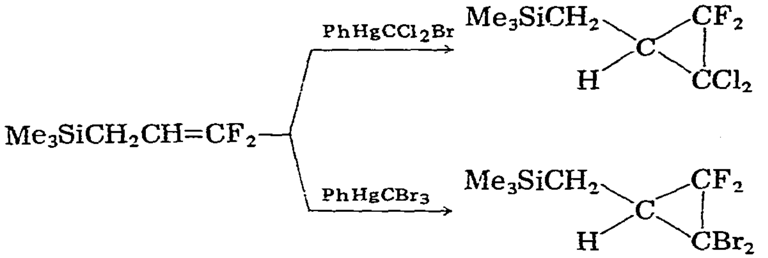
Equations 6 [4] and 7 [5] represent well-known chemistry. We have reported all details of the preparation of β-silylalkyltriphenylphosphonium iodides and their conversion to the Wittig reagents in a previous paper [6]. Full details also have been provided of the preparation of an analogous tin-substitutted phosphonium salt, β-trimethylstannylethyltriphenylphosphonium iodide, and its conversion to the ylide, $Ph_3P{=}CHCH_2SnMe_3$ [7] and of the application of the latter to the synthesis of $Me_3SnCH_2CH{=}CF_2$ [8]. Thus the methodology required for the preparation of 3,3-difluoroallylsilanes as shown in eq. 6—10 was well in hand. In fact, the chemistry of eq. 6—10 was much more easily effected in the case of the silicon compounds than in the case of the preparation of $Me_3SnCH_2CH{=}CF_2$. First of all, the required iodomethylsilicon compounds are much more readily prepared from commercially available chloromethyl-silicon compounds. Secondly, in the case of $Ph_3PCH_2CH_2SnMe_3{}^+I^-$, deprotonation had to be effected with lithium diisopropylamide since organolithium reagents such as phenyllithium attacked at tin as well as at the protons α to the phosphonium center. For successful utilization of the ylide, the amine formed in the deprotonation reaction first had to be removed from the reagent at reduced pressure. In contrast, methyllithium reacted solely as a deprotonating agent in the case of $Ph_3PCH_2CH_2SiMe_3{}^+I^-$. No complications due to competing attack at silicon were encountered.

The reaction shown in eq. 10 is based on chemistry developed by Wheaton and Burton [9] in which a phosphorus ylide first deprotonates HCF_2Cl to give difluorocarbene which then reacts with another mole of the ylide to produce the *gem*-difluoro-olefin and triphenylphosphine. This reaction proceeded very well with $Ph_3P{=}CHCH_2SiMe_3$, giving $Me_3SiCH_2CH{=}CF_2$ in 90% yield. At first sight, this reaction has the drawback that two moles of the β-silyl ylide (and thus of the β-silylalkylphosphonium salt) are required to produce one mole of $Me_3SiCH_2CH{=}CF_2$. However, one mole of the ylide is converted to the phosphonium chloride, $Ph_3PCH_2CH_2SiMe_3{}^+Cl^-$, which can be recycled. The triphenylphosphine also can be recovered and used to make more $Ph_3PCH_3{}^+Br^-$.

3,3-Difluoroallylsilanes with a reactive functionality on the silicon atom would be of special interest, since incorporation of the 3,3-difluoroallyl group into polysiloxane systems might possibly give silicones with interesting chemical and physical properties. For this reason we also prepared the phosphonium halides $Ph_3PCH_2CH_2SiMe_2H^+I^-$, $Ph_3PCH_2CH_2SiMe_2OSiMe_3{}^+I^-$ and $Ph_3PCH_2CH_2SiMe(OSiMe_3)_2{}^+I^-$ [6]. These salts could be converted to the respective 3,3-difluoroallylsilicon derivatives, $Me_2HSiCH_2CH{=}CF_2$, $Me_3SiOSiMe_2CH_2CH{=}CF_2$ and $(Me_3SiO)_2SiMeCH_2CH{=}CF_2$, in good yield. Also prepared by this procedure, using $Ph_3PCH(CH_3)CH_2SiMe_3{}^+I^-$ [6].as the starting material, was $Me_3SiCH_2C(CH_3){=}CF_2$. The ylide $Ph_3P{=}C(C_6H_5)CH_2SiMe_3$ apparently was not sufficiently basic to deprotonate difluorochloromethane, so $Me_3SiCH_2C(C_6H_5){=}CF_2$ could not be prepared by this procedure.

While 3,3-difluoroallylsilicon compounds are stable for short contact times at 600°C [2,3], the thermal stability of such compounds in the liquid phase for extended periods was of greater interest. An NMR tube experiment, using $Me_3SiCH_2CH{=}CF_2$ in benzene-d_6 solution, showed this compound to be quite stable. It survived successive heating periods of 15 h at 150°C, 6 h at 175°C and 21 h at 220°C without decomposition and only underwent substantial decomposition after it had been heated at 280°C for 16 h. In other similar experiments, solutions of $Me_3SiCH_2CH{=}CF_2$, $Me_2HSiCH_2CH{=}CF_2$ and Me_3SiO-$SiMe_2CH_2CH{=}CF_2$ in carbon tetrachloride were heated first at 130°C for 16 h and then at 200°C for 23 h. At 130°C, only $Me_2HSiCH_2CH{=}CF_2$ showed a small degree of decomposition, probably as a result of reaction of its Si—H function with the solvent. All three compounds decomposed in CCl_4 at 200°C.

Only a few reactions of $Me_3SiCH_2CH{=}CF_2$ have been investigated thus far. The C=C bond of this silane was found to be reactive toward phenyl(trihalomethyl)mercurial-derived dihalocarbene (eq. 11 and 12):



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(12)

The addition of organolithium reagents to the C=C bond of polyfluoro-olefins, followed by elimination of lithium fluoride, is a well-known reaction [10]. Phenyllithium added to $Me_3SiCH_2CH{=}CF_2$ (eq. 13), but the yield of the addition-elimination product, obtained as a 1 : 1 mixture of *cis* and *trans* isomers, was only 30%. The results obtained with n-butyllithium were even less satisfactory (eq. 14). Alternate modes of attack by these lithium reagents on 3,3-difluoroallyltrimethylsilane are possible, i.e., difluoroallyl displacement by

$$Me_3SiCH_2CH{=}CF_2 + PhLi \xrightarrow{Et_2O} Me_3SiCH_2CH{=}CFPh + LiF \quad (13)$$

$$Me_3SiCH_2CH{=}CF_2 + n\text{-}BuLi \xrightarrow{Et_2O/hexane} \underset{(20\%)}{Me_3SiCH_2CH{=}CFBu\text{-}n} \quad (14)$$

both RLi, α-deprotonation by n-butyllithium, so the low yields of the desired products are not surprising.

Other C=C bond additions to $Me_3SiCH_2CH{=}CF_2$ should be possible, but such studies are not within the scope of our present interests. We note that we have also been able to develop a route to the isomeric 1,1-difluoroallylsilanes, $R_3SiCF_2CH{=}CH_2$, based on the reactions of organochlorosilanes with *gem*-difluoroallyllithium [8,11].

Experimental

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of dry argon or nitrogen. All solvents were rigorously dried, diethyl ether by distillation from lithium aluminum hydride, tetrahydrofuran from sodium benzophenone ketyl.

Infrared spectra were recorded using a Perkin Elmer 457A infrared spectrophotometer, proton NMR spectra using a Varian Associates T60 spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Internal standards used were tetramethylsilane, chloroform and dichloromethane. Gas-liquid chromatography (GLC) was used in product analysis, yield determinations by the internal standard method and for the isolation of pure product samples for analysis and spectroscopy.

The preparation of the β-silylalkyltriphenylphosphonium iodides has been described in detail in a previous paper [6].

Preparation of 3,3-difluoroallyl-silicon compounds

(a) 3,3-Difluoroallyltrimethylsilane. A 200 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, a Dry Ice condenser, a pressure-equalizing addition funnel and a gas inlet tube, was flame-dried, flushed with argon while cooling and charged with 14.71 g (30.0 mmol) of $Ph_3PCH_2CH_2SiMe_3^+I^-$ and 50 ml of diethyl ether. The resulting slurry was cooled in an ice bath and then 30 mmol of methyllithium in 16.0 ml of diethyl ether was added, dropwise, with stirring, under argon. The reaction mixture turned red immediately. The resulting solution of $Ph_3P{=}CHCH_2SiMe_3$ was stirred at room temperature for 1 h. It then was cooled to 0°C again and 340 ml (gas volume, about 15 mmol) of difluorochloromethane was condensed into the reaction mixture. A white solid precipitated immediately and the red color of the ylide was discharged, giving an amber solution upon final addition of HCF_2Cl. The mixture was stirred for 4 h at room temperature and then was filtered. The filtrate was trap-to-trap distilled (room temperature, 0.05 mmHg) into a receiver cooled to —78°C. The distillate was distilled at atmospheric pressure to remove the ether. The liquid residue was analyzed by GLC (6 ft × 0.25 in, 10% DC-200 silicone oil on 80—100 mesh Chromosorb W at 80°C). It was determined that 13.6 mmol (90% yield) of $Me_3SiCH_2CH{=}CF_2$ was present. Pure samples (n_D^{20} 1.3841; lit. [2] n_D^{20} 1.3836) were isolated by GLC. IR (film) cm^{-1}: 3095w, 3040w, 2965s, 2900m, 2810w, 2640w, 1740s, 1628w, 1480w, 1415m, 1327s, 1252s, 1230s, 1170m, 1058s, 905s, 840—870s, 820s, 790w, 763m, 700m, 630m, 610w. ^1H NMR ($CCl_4/CHCl_3$): δ 0.04 (s, 9 H, Me_3Si), 1.11—1.31 (d of t, $^3J(HH)$ 9 Hz, $^4J(FH)$ 1.5 Hz, 2 H, $SiCH_2$), 3.68—4.44 ppm (12 line pattern, $^2J(HH)$ 9 Hz, $^3J(FH)(cis)$ 3 Hz, $^3J(FH)(trans)$ 24 Hz, 1 H, =CH) *.

The pot residue from the trap-to-trap distillation was recrystallized from

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* In support of these assignments is previously published work on compounds of type $ArCH{=}CF_2$ (Ar = C_6H_5, p-FC_6H_4, p-$O_2NC_6H_4$ and 2-furyl). Their proton NMR spectra showed the following spin-spin coupling constants for the $—CH{=}CF_2$ group: $J(FH)$ (*cis*): range 3.3—5.0 Hz; $J(FH)$ (*trans*): range 25—25.7 Hz [12].

ethanol to give 2.785 g (71%) of triphenylphosphine, m.p. 77—78°C, identified also by IR. The initial filtration left 7.97 g of white solid whose proton NMR spectrum was identical with that of the starting phosphonium salt.

In a larger-scale reaction, 150 mmol of methyllithium in 94 ml of diethyl ether was added, dropwise at 0°C, to a slurry of 73.5 g (150 mmol) of $Ph_3PCH_2CH_2SiMe_3{}^+I^-$. After the red ylide solution had been stirred at room temperature for 1.5 h, about 75 mmol (1.7 l gas volume) of HCF_2Cl was condens into the reaction mixture. The resulting dark brown mixture was filtered, and the filtrate was distilled at atmospheric pressure to give 9.72 g (86%) of $Me_3SiCH_2CH=CF_2$, b.p. 83—85°C.

(b) 3,3-Difluoroallyldimethylsilane. The same procedure was used in the reaction of 10 mmol each of methyllithium and $Ph_3PCH_2CH_2SiMe_2H^+I^-$ in diethyl ether medium. The resulting brownish ylide solution was stirred at room temperature for 1 h, cooled again to 0°C and treated with about 5 mmol of HCF_2Cl (113 ml gas volume). A solid formed immediately, and after the mixture had been stirred for 2 h, the supernatant liquid was colorless. Filtration was followed by trap-to-trap distillation (0.05 mmHg, slight heating) of the filtrate. The colorless distillate was concentrated at reduced pressure and analyzed by GLC (4 ft. SE-30 at room temperature). The product, $Me_2HSiCH_2CH=CF_2$, was present in 83% yield. Pure samples, n_D^{25} 1.3778, were isolated by GLC. Anal. Found: C, 44.52; H, 7.40; $C_5H_{10}F_2Si$ calcd.: C, 44.08; H, 7.40%. IR (CCl_4/CH_2Cl_2), cm^{-1}: 2128s (Si—H), 1742s (C=C), 1328s (=CF_2), 1250s (Me_2Si), 1230s (=CF_2) (principal bands). In support of these assignments, we note that ν(C=C) of $CH_2=CF_2$ is found at 1730 cm^{-1} [13], of $Me_3SnCH_2CH=CF_2$ at 1736 cm^{-1} [8]. The =CF_2 group has been reported to have characteristic absorptions at 1340 and 1200 cm^{-1} [14]. ^1H NMR (CCl_4/CH_2Cl_2): δ 0.08 (d, J 4.0 Hz, 6 H, Me_2Si), 1.28 (d with some fine splitting, J 8 Hz, 2 H, $SiCH_2$), 3.64—4.03 (m, 1 H, SiH) and 4.03 ppm (AXY_2 pattern, ^2J(HH) 8 Hz, ^3J(FH) (*cis*) 3 Hz, ^3J(FH) (*trans*) 24 Hz, 1 H, =CH).

(c) 3,3-Difluoroallylpentamethyldisiloxane. Lithium diisopropylamide was used to deprotonate the phosphonium salt rather than methyllithium since methyllithium is known to cleave the Si—O—Si linkage of hexamethyldisiloxane [15].

To a solution of 0.907 g (8.98 mmol) of diisopropylamine in 25 ml of dry diethyl ether was added dropwise at 0°C, under nitrogen, 8 mmol of n-butyllithium in 3.33 ml of hexane. The resulting solution was stirred at room temperature for 1 h.

A 300 ml, three-necked, round-bottomed flask equipped with a mechanical stirrer, a gas inlet tube and a rubber septum was charged with 4.8 g (8 mmol) of $Ph_3PCH_2CH_2SiMe_2OSiMe_3{}^+I^-$ and 40 ml of dry Et_2O. To this slurry was added the i-Pr_2NLi solution, dropwise with stirring, under nitrogen. The resulting red solution was stirred at room temperature for 1 h. Subsequently, the mechanical stirrer was replaced with a magnetic stirring assembly and the rubber septum with a ground glass stopper. The gas inlet tube was connected to the vacuum line and all volatiles were removed at 0.5 mm Hg. Forty ml of Et_2O was added to the dry residue to dissolve the ylide and the reaction flask was fitted with a mechanical stirrer and a Dry Ice condenser. About 5 mmol (about 110 ml gas volume) of HCF_2Cl was added at 0°C. The reaction mixture turned brown and a precipitate was formed. The mixture was stirred at room temperature for 3 h and worked up as in (a) and (b) above. GLC analysis (4 ft SE-30 at 100°C) showed that 3.92 mmol (98%) of $Me_3SiOSiMe_2CH_2CH{=}CF_2$ was present. Pure samples were isolated by GLC; n_D^{25} 1.3838. Anal. Found: C, 42.90; H, 8.11. $C_8H_{18}OF_2Si_2$ calcd.: C, 42.82; H, 8.08%. IR (CCl_4), cm^{-1}: 1745s (C=C), 1329s (=CF_2), 1258s (Me_3Si, Me_2Si), 1232s (=CF_2), 1070s (SiOSi). ^1H NMR (CCl_4/CH_2Cl_2): δ 0.02 (s, 9 H, Me_3Si), 0.03 (s, 6 H, Me_2Si), 1.22 (d of t, $^3J(HH)$ 8 Hz, $^4J(FH)$ 1.5 Hz, 2 H, $SiCH_2$), 4.03 ppm (12 line pattern, $^2J(HH)$ 8 Hz, $^3J(FH)$(*cis*) 3 Hz, $^3J(FH)$ (*trans*) 24 Hz, 1 H, =CH).

(d) 3,3-Difluoroallyl-bis(trimethylsiloxy)methylsilane. The lithium diisopropylamide route was used in the preparation of the ylide from 6.38 g (10.0 mmol) of $Ph_3PCH_2CH_2SiMe(OSiMe_3)_2{}^+I^-$ using the procedure described in (c). The ylide was redissolved in diethyl ether and 22 mmol of HCF_2Cl was added at 0°C under nitrogen. The dark red solution gradually faded to light amber and a dark oil separated. The mixture was stirred at room temperature for 10 h, and then the ether layer was decanted from the oil. Trap-to-trap distillation of volatiles was followed by concentration of the distillate and examination of the liquid residue by GLC (4 ft. 10% SE-30, 80°C). The desired product, $(Me_3SiO)_2MeSiCH_2CH{=}CF_2$, was present in 56% yield (2.80 mmol). Samples of pure product, n_D^{25} 1.3880, were collected by GLC. Anal. Found: C, 40.07; H, 8.05; $C_{10}H_{24}O_2F_2Si_3$ calcd.: C, 40.23; H, 8.10%. IR (liquid film), cm^{-1}: 1744s (C=C), 1328m (=CF_2), 1260s (Me_3Si, MeSi), 1233s (=CF_2), 1064vs (SiOSi). ^1H NMR ($CDCl_3/CHCl_3$): δ 0.05 (s, 3 H, $SiCH_3$), 0.10 (s, 18 H, Me_3Si), 1.14—1.42 (d of t, $^3J(HH)$ 8 Hz, $^4J(FH)$ 1.75 Hz, 2 H, $SiCH_2$), 3.69—4.50 (12 line pattern, $^2J(HH)$ 8 Hz, $^3J(FH)$ (*cis*) 3 Hz, $^3J(FH)$ (*trans*) 25 Hz, 1 H, =CH).

(e) 3,3-Difluoro-2-methylallyltrimethylsilane. Using the apparatus and procedure described in (a), 4.83 g (9.64 mmol) of $Ph_3PCH(CH_3)CH_2SiMe_3{}^+I^-$ in 25 ml of diethyl ether was treated with 10 mmol of methyllithium in 5.5 ml of ether at 0°C. The red-brown ylide solution was stirred at room temperature for 1 h and then 5 mmol (about 120 ml gas volume) of HCF_2Cl was added by the usual procedure. The reaction mixture was stirred at room temperature overnight, filtered, and the filtrate was trap-to-trap distilled at 0.02 mmHg. GLC examination of the distillate (6 ft. 10% Apiezon L at 70°C) showed the presence of 3.15 mmol (65%) of the desired product, pure samples of which (n_D^{25} 1.3919) were isolated by GLC. Anal. Found: C, 51.31; H, 8.59. $C_7H_{14}F_2Si$ calcd.: C, 51.18; H, 8.59%. IR (liquid film), cm^{-1}: 1753s (C=C). ^1H NMR ($CCl_4/CHCl_3$): δ 0.02 (s, 9 H, Me_3Si), 1.26 (t, $J(FH)$ 2.4 Hz, 2 H, $SiCH_2$), and 1.54 ppm (t, $J(FH)$ 3.2 Hz, 3 H, =CCH_3).

The salts in the filter cake were dried to give 2.47 g of $Ph_3PCH(CH_3)$-$CH_2SiMe_3{}^+Cl^-$. The residue from the trap-to-trap distillation was recrystallized from ethanol to give 0.91 g (3.47 mmol, 72%) of Ph_3P.

Dihalocarbene addition to 3,3-difluoroallyltrimethylsilane

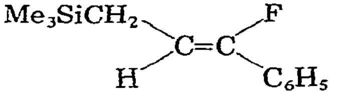
(a) Dichlorocarbene. A 100 ml one-necked, round-bottomed flask equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stir-bar was charged with 2.408 g (5.6 mmol) of $PhHgCCl_2Br$ [16], 0.874 g (5.83 mmol) of $Me_3SiCH_2CH{=}CF_2$ and 20 ml of dry benzene. The resulting solution was stirred and heated at reflux (ca. 80°C) under nitrogen for 90 min. The

reaction mixture was allowed to cool to room temperature and was filtered to remove phenylmercuric bromide. The filtrate was trap-to-trap distilled at 0.05 mmHg with slight heating into a receiver cooled at −78°C. GLC analysis (4 ft SE-30 at 110°C) of the distillate showed the presence of 4.31 mmol (77%) of 1,1-difluoro-2,2-dichloro-3-(trimethylsilylmethyl)cyclopropane, n_D^{25} 1.4297. Anal. Found: C, 36.24; H, 5.14. $C_7H_{12}F_2Cl_2Si$ calcd.: C, 36.06; H, 5.19%. ^1H NMR (CCl_4/CH_2Cl_2): δ 0.13 (s, 9 H, Me_3Si), 0.73—1.02 (m, 2 H, $SiCH_2$) and 1.67—2.32 ppm (m, 1 H, cyclopropyl H).

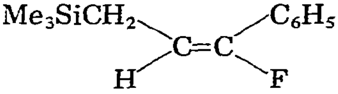
(b) Dibromocarbene. The same procedure was used in the reaction of 1.827 g (3.45 mmol) of $PhHgCBr_3$ [16] and 0.494 g (3.29 mmol) of $Me_3SiCH_2CH{=}CF_2$ in 5 ml of benzene at 80°C for 5 h. GLC analysis of the final trap-to-trap distillate (4 ft SE-30 at 130°C) showed the presence of 2.43 mmol (70%) of 1,1-difluoro-2,2-dibromo-3-(trimethylsilylmethyl)cyclopropane, n_D^{25} 1.4698. Anal. Found: C, 26.14; H, 3.82. $C_7H_{12}F_2Br_2Si$ calcd.: C, 26.10; H, 3.76%. ^1H NMR (CCl_4/CH_2Cl_2): δ 0.03 (s, 9 H, Me_3Si), 0.56—0.89 (m, 2 H, $SiCH_2$) and 1.63—2.31 (m, 1 H, cyclopropyl H).

Reaction of 3,3-difluoroallyltrimethylsilane with organolithium reagents

To a solution of 3.82 mmol of $Me_3SiCH_2CH{=}CF_2$ in 5 ml of dry diethyl ether (50 ml three-necked flask equipped with magnetic stirbar, nitrogen inlet tube and addition funnel) was added, dropwise with stirring, 3.84 mmol of freshly prepared phenyllithium in 6.7 ml of 4/1 Et_2O/benzene. The reaction mixture was stirred at room temperature for 17 h and the resulting cloudy solution then was trap-to-trap distilled at 0.05 mmHg (with heating) into a receiver cooled to −78°C. GLC examination of the distillate (6 ft Apiezon L at 140°C) showed the presence of 1.14 mmol (30%) of a 1/1 mixture of the *cis* and *trans* isomers of $Me_3SiCH_2CH{=}CFPh$. The isomers were separable by GLC and were individually characterized.



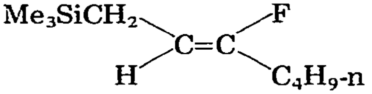
n_D^{25} 1.5138. Anal. Found: C, 69.33; H, 8.23. $C_{12}H_{17}FSi$ calcd.: C, 69.17; H, 8.23. ^1H NMR (CCl_4/CH_2Cl_2): δ 0.06 (s, 9 H, Me_3Si), 1.62 (d of d, J(HH) 8.5 Hz, J(FH) 1.5 Hz, 2 H, $SiCH_2$) and 5.35 ppm (d of t, J(FH) 36.3 Hz, 1 H, =CH).



n_D^{25} 1.5031. Anal. Found: C, 69.29; H, 8.32. ^1H NMR (CCl_4/CH_2Cl_2): δ 0.06 (s, 9 H, Me_3Si), 1.58 (d, J(HH) 8.0 Hz, 2 H, $SiCH_2$) and 5.36 (d of t, J(FH) 22.0 Hz, 1 H, =CH).

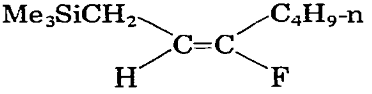
The isomer assignments are based on the magnitude of J(FH) in the vinylic system. In published examples, J(FH) (*trans*) is larger than J(FH) (*cis*) in $RCH{=}CHF$ compounds. For instance, in the *cis* and *trans* isomers of $PhCH{=}CHF$ and $n\text{-}C_6H_{13}CH{=}CHF$, Burton and Greenlimb reported J(FH) (*trans*) in the range of 40—44 Hz, J(FH) (*cis*) in the range 17.9—19.6 Hz [17]. The geminal coupling constants were in the range 79.5—85.4 Hz, thus excluding the alternate structure, $Me_3SiCH_2(Ph)C{=}CHF$, for our product.

A similar reaction was carried out with n-butyllithium. The lithium reagent, 4.41 mmol in hexane, was added to 4.41 mmol of $Me_3SiCH_2CH{=}CF_2$ in 5 ml of diethyl ether at −78°C and then 0.44 mmol of *N,N,N′,N′*-tetramethylethylenediamine was added by syringe. The mixture was allowed to warm to room temperature and then was stirred for 2 h. Trap-to-trap distillation of volatiles at 0.05 mmHg with heating was followed by GLC analysis of the distillate (6 ft Apiezon L at 120°C, 6 ft silver nitrate at 58°C). The two isomers of $Me_3SiCH_2CH=CF(n\text{-}Bu)$ were present in 20% combined yield. Pure samples of each were isolated by GLC.



(1 part)

^1H NMR ($CCl_4/CHCl_3$): δ −0.14 (s, 9 H, Me_3Si), 0.64—1.44 (m, 9 H, C_4H_9), 0.64—1.44 (m, 11 H, C_4H_9 and $SiCH_2$) and 4.33 (d of t, *J*(FH) 37 Hz, 1 H, =CH).



(3 parts)

^1H NMR ($CCl_4/CHCl_3$): δ −0.12 (s, 9 H, Me_3Si), 0.58—1.50 (m, 9 H, C_4H_9), 1.08 (d, *J*(HH) 9 Hz, 2 H, $SiCH_2$) and 4.88 ppm (d, of t, *J*(FH) 22 Hz, 1 H, =CH). The isomer mixture had n_D^{25} 1.4309.

Acknowledgement

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