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gem-DIFLUOROALLYLLITHIUM: PREPARATION BY THE TRANSMETALATION PROCEDURE AND SOME REACTIONS *

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Summary

3,3-Difluoroallyltrimethyltin has been prepared by the reaction of β-trimethylstannylethylidenetriphenylphosphorane with chlorodifluoromethane. This tin compound reacts with n-butyllithium in tetrahydrofuran at —95°C to generate *gem*-difluoroallyllithium. The latter, however, is not stable in solution at that temperature. If generated in situ in the presence of a triorganochlorosilane, products of the type $R_3SiCF_2CH{=}CH_2$ are obtained in good yield. Addition to the C=O bond of 3-pentanone to give $(C_2H_5)_2C(OH)CF_2CH{=}CH_2$ was achieved by the method of alternate, incremental additions.

Introduction

Recently, we have prepared *gem*-dichloroallyllithium and have studied its reactions with aldehydes, ketones and esters [2] and with organic halides, as well as with halides of silicon, germanium, tin and mercury [3]. The regioselectivity of the additions of *gem*-dichloroallyllithium to the C=O bonds of aldehydes and ketones received detailed attention. It appeared that electronic effects in the carbonyl compound were of paramount importance in determining the regioselectivity in such reactions under the conditions used. For this reason it became of interest to examine the chemistry of the as yet unknown *gem*-difluoroallyllithium in which the substituents are the most electronegative halogen. In this reagent, I, the polarity difference between the α and γ termini is greater than in *gem*-dichloroallyllithium so that any special electronic effects noted in the chemistry of the latter reagent might be more pronounced in its difluoro analog.

gem-Dichloroallyllithium can be prepared in almost quantitative yield by the

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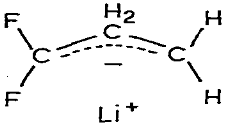
* Preliminary communication: ref. 1.



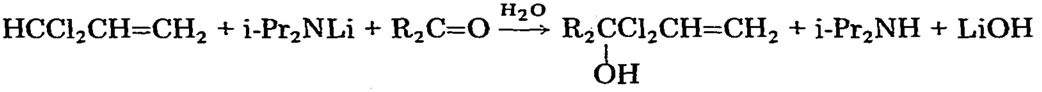
(I)

transmetalation reaction (eq. 1) [2,3] or, much less effectively by lithium—halogen exchange (eq. 2) [3]. It also has been prepared in situ by lithium—hydrogen

$$Ph_3PbCH_2CH{=}CCl_2 + n\text{-}BuLi \xrightarrow{THF/-95^\circ C} Li(CCl_3CHCH_2) + n\text{-}BuPbPh_3 \qquad (1)$$

$$CCl_3CH{=}CH_2 + n\text{-}BuLi \xrightarrow{THF/-95^\circ C} Li(CCl_2CHCH_2) + n\text{-}BuCl \qquad (2)$$

exchange (eq. 3) [4]. Of these possible procedures, we chose the transmetalation

 (3)

$$HCCl_2CH{=}CH_2 + i\text{-}Pr_2NLi + R_2C{=}O \xrightarrow{H_2O} R_2\underset{\displaystyle OH}{C}Cl_2CH{=}CH_2 + i\text{-}Pr_2NH + LiOH \qquad (3)$$

reaction for initial examination for applicability to the synthesis of *gem*-difluoroallyllithium.

Results and discussion

Utilization of the transmetalation reaction in the synthesis of *gem*-difluoroallyllithium required the availability of a difluoroallyl derivative of a heavy metal such as tin, lead or mercury. Presumably, a 1,1-difluoroallyl compound, $MCF_2CH{=}CH_2$, or a 3,3-difluoroallyl compound, $MCH_2CH{=}CF_2$, would serve for this purpose.

In recent research we had developed β-trimethylsilyl [5] and β-trimethylstannylethylidenetriphenylphosphorane [6] reagents and had utilized them in Wittig syntheses of allylic silicon and tin compounds (Scheme 1). Allylic tin compounds are excellent starting materials for the preparation of allylic lithium reagents by the transmetalation reaction [7—9], and we found that $Ph_3P{=}CHCH_2SnMe_3$ could be used for the synthesis of 3,3-difluoroallyltrimethyltin, a potential *gem*-difluoroallyllithium precursor (eq. 6). This procedure for the preparation

$$2\,Ph_3P{=}CHCH_2SnMe_3 + HCF_2Cl \rightarrow$$
$$Me_3SnCH_2CH{=}CF_2 + [Ph_3PCH_2CH_2SnMe_3]^+Cl^- + Ph_3P \qquad (6)$$
$$(74\%)$$

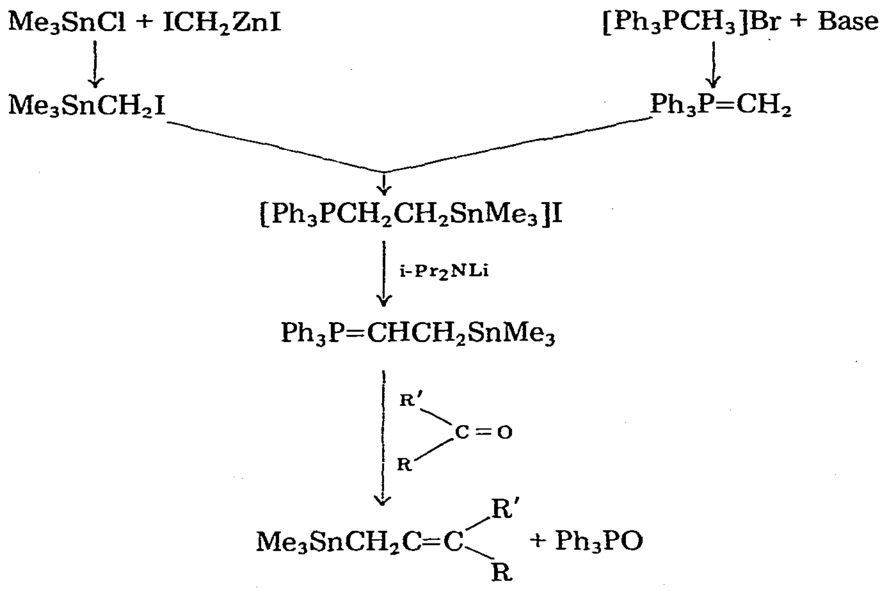
of terminal difluoroolefins had been developed by Wheaton and Burton [10]. It proceeds following eq. 7, 8.

$$Ph_3P{=}CHR + HCF_2Cl \rightarrow [Ph_3PCH_2R]^+Cl^- + CF_2 \qquad (7)$$

$$Ph_3P{=}CHR + CF_2 \rightarrow RCH{=}CF_2 + Ph_3P \qquad (8)$$

The deprotonation of β-trimethylstannylethyltriphenylphosphonium iodide to the ylide had to be effected using lithium diisopropylamide. Phenyllithium

SCHEME 1



was not sufficiently selective in its attack on this salt, attacking at tin (to form phenyltrimethyltin in 20% yield) as well as at the α protons. Only a 45% yield of $Me_3SnCH_2CH=CF_2$ was obtained.

3,3-Difluoroallyltrimethyltin is a stable liquid which can be distilled at 129—131°C at atmospheric pressure. It is chemically robust, and the difluoroallyl group appears to be strongly bonded. For instance, treatment of an acetone solution of $Me_3SnCH_2CH=CF_2$ with mercuric chloride resulted in CH_3- Sn cleavage, not in scission of the difluoroallyl group. A comparable reaction of $Me_3SnCH_2CH=CH_2$ resulted in cleavage of the allyl group [11].

The availability of 3,3-difluoroallyltrimethyltin permitted an investigation of the synthesis and reactivity of *gem*-dilfuoroallyllithium. It was expected that this reagent would be even less stable than *gem*-dichloroallyllithium with respect to decomposition by way of lithium halide elimination, and, therefore, all experiments aimed at its generation, detection and utilization were carried out at low (—95°C or lower) temperature. Attempts to prepare *gem*-difluoroallyllithium in a separate step prior to its utilization were not successful. Apparently the reagent is only marginally stable, if at all, at even these low temperatures. Thus, when the n-BuLi/$Me_3SnCH_2CH=CF_2$ reaction mixture was kept at —95°C for 1 h (after initial mixing of the reactants at that temperature) and then was treated with trimethylchlorosilane, no organosilicon product, $Me_3SiCH_2CH=CF_2$ or $Me_3SiCF_2CH=CH_2$, was formed. However, a yield of n-butyltrimethyltin above 90% indicated that the transmetalation had taken place in substantial yield (eq. 9). Other reactions in which the transmetalation step was carried out at —130°C and in which the resulting solution was kept from 25 min to 3.5 h at —130°C before addition of a carbonyl substrate also gave no difluoroallylated product. At that temperature the transmetalation reaction was far from complete, and substantial quantities of $Me_3SnCH_2CH{=}CF_2$ were recovered.

Although *gem*-difluoroallyllithium appears to be too unstable to maintain in solution after its preparation and to utilize in a two-step procedure, it could be very effectively applied to the synthesis of difluoroallyl derivatives of silicon by the in situ technique. For instance, when n-butyllithium was added slowly to a mixture containing $Me_3SnCH_2CH{=}CF_2$ and an excess of phenyldimethylchlorosilane in THF at −95° C, $PhMe_2SiCF_2CH{=}CH_2$ was produced in 75% yield. Similar reactions with trimethylchlorosilane and tri-n-propylchlorosilane gave Me_3SiCF_2-$CH{=}CH_2$ in 64% yield and n-$Pr_3SiCF_2CH{=}CH_2$ in 86% yield. The success of these reactions is due to the relatively low reactivity of trialkylchlorosilanes toward n-butyllithium, especially at low temperatures [12]. The reaction of n-butyllithium with 3,3-difluoroallyltrimethyltin (eq. 9) is faster than its reaction with trimethylchlorosilane, and the reagent thus formed then is intercepted by the chlorosilane present in solution before it can decompose (eq. 10).

$$Li(CF_2CHCH_2) + Me_3SiCl \rightarrow Me_3SiCF_2CH{=}CH_2 + LiCl \qquad (10)$$

Only one of the two possible isomeric *gem*-difluoroallylsilanes was formed in each case: $R_2SiCF_2CH{=}CH_2$, not $R_3SiCH_2CH{=}CF_2$. 3,3-Difluoroallyltrimethylsilane, prepared by the ylide route using $Ph_3P{=}CHCH_2SiMe_3$ [1,13] was available for comparison with the 1,1-difluoro isomer obtained via $Li(CF_2CHCH_2)$. Their physical and spectroscopic properties, especially their proton NMR spectra were quite different.

The in situ procedure is only applicable if the reaction of n-butyllithium with the reactant which provides the group for the new organolithium reagent ($Me_3SnCH_2CH{=}CF_2$ in the present case) is faster than its reaction with the substrate. It was found not to be applicable to *gem*-difluoroallyllithium addition to aldehydes and ketones since the C=O function was an effective competitor for n-butyllithium. When the latter was added to a mixture of $Me_3SnCH_2CH{=}CF_2$ and benzaldehyde in THF/dimethyl ether at −130°C, only the product of n-butyllithium addition to benzaldehyde was obtained. When the in situ procedure was used in such a reaction with 3-pentanone (in THF at −95°C), the major product, after hydrolytic work-up, was n-$C_4H_9(C_2H_5)_2COH$. A minor product (~10% yield) was tentatively identified (by comparison of its GLC retention time with that of an authentic sample; see below) as the desired $(C_2H_5)_2C(OH)CF_2CH{=}CH_2$.

However, *gem*-difluoroallyllithium can be brought into reaction with a ketone by the method of alternate, incremental additions. In this procedure, a given quantity of $Me_3SnCH_2CH{=}CF_2$, in THF solution at −95°C, was treated with a small portion of n-butyllithium in hexane (ca. 1/5 to 1/6 molar proportion of the $Me_3SnCH_2CH{=}CF_2$ used) and then, very quickly, with the same (as n-BuLi) molar quantity of the ketone. Then another portion of n-butyllithium and immediately thereafter, another of the ketone followed. This alternating addition of n-butyllithium and ketone continued until the amount of $Me_3SnCH_2CH{=}CF_2$ was exceeded by a factor of four. This procedure gave $(C_2H_5)_2C(OH)CF_2CH{=}CH_2$ in 52% yield following hydrolytic work-up. In a similar reaction, in which the reaction mixture was treated with trimethylchlorosilane instead if with water, the trimethylsilyl ether, $(C_2H_5)_2C(OSiMe_3)$-

$CF_2CH{=}CH_2$, was obtained in 75% yield. When benzaldehyde was the carbonyl compound used, this procedure gave a difluoroallylation product after Me_3SiCl work-up, $PhCH(OSiMe_3)CF_2CH{=}CH_2$, in only 13% yield. There was no evidence for the formation of the isomeric product, $PhCH(OSiMe_3)CH_2CH{=}CF_2$.

In its reaction with triorganochlorosilanes and 3-pentanone *gem*-difluoroallyllithium parallels the regioselectivity of *gem*-dichloroallyllithium [2,3]. In its reaction with benzaldehyde it differs from *gem*-dichloroallyllithium, which had been found to give exclusively $PhCH(OH)CH_2CH{=}CCl_2$. However, in view of the poor yield of product in the $Li(CF_2CHCH_2)/PhCHO$ reaction, we do not consider our result significant. A reaction with a much better material balance is required. However, this hint that there may be some differences between the regioselectivities of $Li(CF_2CHCH_2)$ and $Li(CCl_2CHCH_2)$ is of interest, but to pursue the matter further, a better route to *gem*-difluoroallyllithium will be needed.

The product of the reaction of *gem*-dichloroallyllithium and trimethylchlorosilane was $Me_3SiCCl_2CH{=}CH_2$. Our evidence, based on comparative reactions with trimethylchlorogermane and trimethyltin chloride, suggested strongly that this was the product of kinetic control. Accordingly, we suggest that $Me_3SiCF_2CH{=}CH_2$, which was produced in the $Li(CF_2CHCH_2)/Me_3SiCl$ reaction, also is the product of kinetic control. The 1,1-difluoroallylsilanes are of potential interest with respect to their chemical reactivity, but here also a better route to *gem*-difluoroallyllithium is needed before this potential can be explored.

Experimental

General comments

All reactions involving organolithium reagents were carried out in flame-dried glassware under an atmosphere of dry nitrogen or argon, in rigorously dried solvents. The temperatures cited are the stem temperatures observed and are probably 5—10°C higher than the values reported. The pentane thermometers used were of the total immersion type and found to read −71°C (bulb immersion) vs. −77°C (total immersion) in a dry-ice/acetone bath. Since most of the procedures described involved only bulb immersion, the temperatures probably are somewhat high.

Infrared spectra were recorded using a Perkin—Elmer Model 457A grating 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 and for isolation of pure product samples for analysis and spectroscopy.

Starting materials

Iodomethyltrimethyltin was prepared as described in a previous paper from these laboratories [14] and then was converted to the phosphonium salt, $[Ph_3PCH_2CH_2SnMe_3]^+I^-$, by reaction with $Ph_3P{=}CH_2$. Deprotonation of the phosphonium salt with lithium diisopropylamide gave a solution of $Ph_3P{=}CHCH_2SnMe_3$ in THF [6]. n-Butyllithium was purchased from Alfa Division, Ventron Corp. Chlorosilanes were obtained from Petrarch Systems, Inc.

Preparation of 3,3-difluoroallyltrimethyltin

A one-liter, three-necked, round-bottomed flask equipped with a mechanical stirrer, an argon inlet tube and no-air stopper was flame-dried while being flushed with argon; the inert gas stream was continued while the apparatus was allowed to cool. The flask then was charged with 36 ml (ca. 0.26 mol) of diisopropylamine and 200 ml of dry THF. This solution was cooled to 0°C while 0.23 mol of n-butyllithium in 98 ml of hexane was added dropwise from an addition funnel. The resulting mixture was stirred at room temperature for 30 min. Another 400 ml was then added and the solution was cooled to 0°C again while 133.4 g of crude β-trimethylstannylethyltriphenylphosphonium iodide (0.196 mol of $[Ph_3PCH_2CH_2SnMe_3]^+I^-$ containing 0.036 mol of $[Ph_3PCH_3]^+I^-$; cf. ref. 6) was added by means of a solids addition funnel, slowly in small portions. The solution immediately turned cranberry-red. Stirring was continued for 1.5 h. A deep red-orange solution resulted. The mechanical stirrer was replaced with a magnetic stir-bar and while the solution was stirred, the volatile components were trap-to-trap distilled (50°C at 0.02 mmHg) into a receiver cooled to −196°C. Heating was continued for 14 h to ensure removal of volatiles. The dark red solid residue was dissolved in 600 ml of diethyl ether and the reaction flask was again fitted with a mechanical stirrer, a gas inlet tube and a dry ice condenser. The ylide solution was cooled to 0°C while 6.75 ml (liquid) (ca. 0.116 mol) of chlorodifluoromethane (Matheson) was condensed into the reaction mixture over a period of 15 min. White solid precipitated immediately and the color of the solution gradually changed to dark amber. The mixture was stirred at room temperature for 4 h and then was filtered (Schlenk apparatus) through a medium frit. The filtrate was trap-to-trap distilled in vacuo into a receiver cooled with liquid nitrogen. The distillate was concentrated (Widmer column) at atmospheric pressure under argon. Fractional distillation of the residue afforded 17.33 g (74%) of $Me_3SnCH_2CH{=}CF_2$, b.p. 129−131°C at atmospheric pressure, n_D^{25} 1.4465. (Found: C, 29.88; H, 5.07. $C_6H_{12}F_2Sn$ calcd.: C, 29.92; H, 5.02%). IR (film) (cm^{-1}): 3080w, 2980m, 2920m, 1736s, 1327s, 1230s, 1140s, 1050s, 885s, 830m, 775s (broad), 530s and 510m. (The absorption at 1736 cm^{-1} is close to the 1730 cm^{-1} C=C stretching frequency of $CH_2{=}CF_2$ [15]). ^1H NMR ($CDCl_3/CHCl_3$): δ 0.14 (s, $^2J(SnH)$ 54 Hz, 9 H, Me_3Sn), 1.43 (d of t, $^3J(HH)$ 9.2 Hz, $^4J(FH)$ 3.5 Hz, $^2J(SnH)$ 57 Hz, 2 H, CH_2Sn) and 4.26 ppm (12 line pattern, $^3J(HH)$ 9.2 Hz, $^3J(FH,$ *trans*) 24.5 Hz, $^3J(FH,$ *cis*) 3.5 Hz, 1 H, =CH).

Recrystallization from ethanol of the trap-to-trap distillation residue afforded 24 g (79%) of pure triphenylphosphine, m.p. 78—80°C.

The solid in the Schlenk filter was washed with diethyl ether and dried at 0.02 mmHg to give 69 g of impure $[Ph_3PCH_2CH_2SnMe_3]^+Cl^-$.

In another experiment in which the diisopropylamine was not removed prior to the addition of chlorodifluoromethane the yield of $Me_3SnCH_2CH{=}CF_2$ was only 53%.

Another reaction was carried out using phenyllithium as the deprotonation agent. The apparatus described above was charged with 93.6 g of crude $[Ph_3PCH_2CH_2SnMe_3]^+I^-$ (containing 143 mmol of this salt and 25 mmol of methyltriphenylphosphonium iodide) and 400 ml of diethyl ether. The mixture was cooled to 0°C and then 0.168 mol of phenyllithium in 200 ml of diethyl ether was added dropwise with stirring under argon. The resulting red-orange solution was stirred at 0°C for 1 h. Subsequently 5.8 ml (ca. 85 mmol) of $CHClF_2$ was condensed into the reagent solution. A solid precipitated and a dark amber solution was formed. The reaction mixture was stirred at room temperature for 15 h, filtered, trap-to-trap distilled and the distillate was concentrated at atmospheric pressure under argon. GLC analysis (10% DC-200 on Chromosorb W, temperature program 70—180°C at 5° per min) of the concentrated distillate showed the presence of 32 mmol (45%) of $Me_3SnCH_2CH{=}CF_2$ and 29 mmol (20%, based on the $[Ph_3PCH_2CH_2SnMe_3]^+I^-$ used) of Me_3SnPh. Fractional distillation gave 6.63 g (38%) of pure 3,3-difluoroallyltrimethyltin, b.p. 128—130°C, A sample of phenyltrimethyltin was obtained from the pot residue by preparative GLC; it was identified by comparison of its IR and NMR spectra with those of an authentic sample. The trap-to-trap distillation residue was recrystallized from ethanol to give 15.1 g (69%) of pure triphenylphosphine, m.p. 77—79°C. The residue in the Schlenk filter yielded 44.6 g of impure $[Ph_3PCH_2CH_2SnMe_3]^+$-Cl^-.

In situ generation of gem-difluoroallyllithium in the presence of chlorosilanes

(a) Trimethylchlorosilane. A 250 ml, three-necked Morton (creased) flask equipped with a mechanical stirrer, a no-air stopper and a Claisen adapter fitted with a pentane thermometer and an argon inlet tube (the "standard apparatus") was flame-dried under argon and charged with 25 ml of dry THF, 1.655 g (6.87 mmol) of $Me_3SnCH_2CH{=}CF_2$ and 1.8 ml (ca. 13 mmol) of trimethylchlorosilane. The reaction mixture was cooled to —95°C and then 7.68 mmol of n-butyllithium in 3.2 ml of hexane was added dropwise over a 45 min period. A colorless solution resulted. After the mixture had been stirred at —95°C for another 45 min, it was allowed to warm to room temperature during the course of 2 h and then was trap-to-trap distilled in vacuo into a receiver cooled to —78°C. An aliquot of the distillate was concentrated at atmospheric pressure and the residue was examined by GLC (10% DC 200 on Chromosorb W, temperature program from 60—160°C at 10° per min). Three compounds were collected and identified; n-butyltrimethylsilane and n-butyltrimethyltin, both known compounds which were identified by comparison of their NMR and IR spectra with those of authentic samples, and 1,1-difluoroallyltrimethylsilane, $Me_3SiCF_2CH{=}CH_2$, n_D^{25} 1.3861. (Found: C, 48.18; H, 8.28. $C_6H_{12}F_2Si$ calcd.: C, 47.96; H, 8.05%). IR (film) (cm^{-1}): 3100w, 2965m, 2900w, 1633w (ν(C=C)), 1414m, 1255s, 1150m, 1070s, 1035s, 986s, 945s, 855s, 762s, 715m, 705m and 635m. NMR (C_6D_5/C_6H_6): δ 0.14 (s, 9 H, $SiMe_3$) and 4.81—6.34 ppm (complex m, 3 H, $CH{=}CH_2$).

A GLC yield determination gave the following results (in order of elution on a DC-200 column): $Me_3SiCF_2CH{=}CH_2$, 4.38 mmol (64%); n-$BuSiMe_3$, 1.02 mmol; $Me_3SnCH_2CH{=}CF_2$, 0.14 mmol (5%) and n-$BuSnMe_3$, 6.44 mmol (94%).

(b) Phenyldimethylchlorosilane. The standard apparatus was charged with 1.412 g (5.912 mmol) of $Me_3SnCH_2CH{=}CF_2$, 3.90 ml (ca. 23 mmol) of $PhMe_2SiCl$ and 25 ml of dry THF. The reaction mixture was cooled to —95°C and then 11.8 mmol of n-butyllithium in 4.75 ml of hexane was added dropwise over a period of 1 h. The reaction mixture was allowed to warm slowly to

room temperature over a 2 h period and then was trap-to-trap distilled. The distillate was concentrated at atmospheric pressure and the residue analyzed by GLC (10% DX-200 at 160°C). Phenyldimethyl-n-butylsilane and n-butyltrimethyltin were present in addition to the desired product, 1.1-difluoroallyldimethylphenylsilane, $PhMe_2SiCF_2CH{=}CH_2$, n_D^{25} 1.4861. (Found: C, 62.24; H, 6.62; $C_{11}H_{14}F_2Si$ calcd.: C, 62.22; H, 6.65%). IR (film) (cm^{-1}): ν(C=C) 1635w. NMR (CCl_4/CH_2Cl_2): δ 0.43 (s, 6 H, Me_2Si), 5.08—6.28 (complex m, 3 H, $CH{=}CH_2$) and 7.23—7.63 ppm (broad s, 5 H). The following yields were determined by GLC: 5.64 mmol (95%) of n-$BuSnMe_3$; 4.46 mmol of $PhMe_2SiCF_2CH{=}CH_2$ (75% yield); 5.64 mmol of n-$BuSiMe_2Ph$. No $Me_3SnCH_2CH{=}CF_2$ was present.

(c) Tri-n-propylchlorosilane. Essentially the same procedure was used in the addition of 12.4 mmol of n-butyllithium in hexane to 6.19 mmol of $Me_3SnCH_2CH{=}CF_2$ and 25 mmol of n-Pr_3SiCl in 25 ml of THF at —95°C. A similar work-up gave a concentrate which contained (by GLC); $(n\text{-}C_3H_7)_3SiCF_2CH{=}CH_2$, (5.32 mmol, 86%), n_D^{25} 1.4317; tri-n-propyl-n-butylsilane (2.50 mmol) and n-butyltrimethyltin.

1,1-Difluoroallyltri-n-propylsilane was analyzed and characterized spectroscopically. (Found: C, 61.80; H, 10.40. $C_{12}H_{24}F_2Si$ calcd.: C, 61.49; H, 10.32%). IR (film) (cm^{-1}): ν(C=C) 1635w. NMR ($CCl_4/CHCl_3$): δ 0.51—1.74 (complex m, 21 H, n-Pr_3Si), and 5.14—6.34 ppm (complex m, 3 H, $CH{=}CH_2$).

(d) Dimethyldichlorosilane. A similar reaction in which 7.52 mmol of n-butyllithium in hexane was added to a solution of 7.514 mmol of $Me_3SnCH_2CH{=}CF_2$ and 3.8 mmol of Me_2SiCl_2 in 30 ml of THF was not successful, giving as the only organosilicon product (14% yield) $Me_2(n\text{-}C_4H_9)SiCF_2CH{=}CH_2$, n_D^{25} 1.4152. (Found: C, 56.16; H, 9.47. $C_9H_{18}F_2Si$ calcd.: C, 56.20; H, 9.43%). NMR ($CCl_4/CHCl_3$): δ 0.09 (s, 6 H, Me_2Si), 0.46—1.54 (complex m, maxima at 0.90 and 2.25 ppm, 9 H, C_4H_9) and 5.12—5.91 (complex m, 3 H, $CH{=}CH_2$). A recovery of 28% of $Me_3SnCH_2CH{=}CF_2$ was realized and n-$BuSnMe_3$ was obtained in 62% yield. Apparently Me_2SiCl_2 (in contrast to the R_3SiCl compounds) can compete with $Me_3SnCH_2CH{=}CF_2$ for n-butyllithium.

In situ generation of gem-difluoroallyllithium in the presence of carbonyl compounds.

The standard apparatus was charged with 1.425 g (5.92 mmol) of $Me_3SnCH_2CH{=}CF_2$, 0.798 g (9.27 mmol) of 3-pentanone and 25 ml of THF and then was cooled to —95°C. Subsequently 9.3 mmol of n-butyllithium in 3.9 ml of hexane was added dropwise under argon over a period of 10 min. The reaction mixture was stirred for another 10 min. at −95°C and then was allowed to warm to —78°C. At that temperature 2 ml (ca. 16 mmol) of trimethylchlorosilane was added. The resulting mixture was allowed to warm to room temperature over a period of 2 h. Subsequently the solvents were removed at atmospheric pressure. Trap-to-trap distillation of the residue was followed by GLC analysis of the distillate (10% DC-200, temperature programmed 70—200°). The following were present: n-butyltrimethyltin (0.8 mmol, 14%), 3,3-difluoroallyltrimethyltin (4.95 mmol, 84% recovery), a minor product identified as $(C_2H_5)_2C(OSiMe_3)CF_2CH{=}CH_2$ on the basis of its GLC retention time (tentative identification; an authentic sample was available) (ca. 0.6 mmol, 10%) and $(C_2H_5)_2C(OSiMe_3)C_4H_9\text{-}n$ (7.7 mmol), n_D^{25} 1.4225.

Similar reactions with benzaldehyde and with pivaldehyde failed to give any products derived from *gem*-difluoroallyllithium.

Reaction of gem-difluoroallyllithium with carbonyl compounds by the method of alternate, incremental additions

The standard apparatus was charged with 1.481 g (6.15 mmol) of $Me_3SnCH_2CH{=}CF_2$ and 25 ml of THF. This solution was cooled to −95°C (under argon) and then 1 mmol of n-butyllithium in 0.40 ml of hexane was added, with stirring, over a period of 15 s. The reaction mixture was stirred for another 30 s and then 0.105 ml (ca. 1 mmol) of 3-pentanone was added. The resulting mixture was stirred at −95°C for 3 min. Subsequently, the above method of addition of n-butyllithium followed by 3-pentanone was repeated identically at 3 min intervals until 25 mmol of each reagent had been added. After the final addition, the reaction mixture was stirred at −95°C for 1 h and then 5.0 ml (ca. 40 mmol) of trimethylchlorosilane was added. The mixture was allowed to warm to room temperature over a period of 2 h and stirred at room temperature overnight. The solvents were distilled off at atmospheric pressure and the residue was trap-to-trap distilled in vacuo into a receiver at −78°C. GLC analysis of the distillate (10% DC-200 on Chromosorb W at 120°C) showed the presence of the following: 5.91 mmol (96%) of n-butyltrimethyltin; $(C_2H_5)_2C(OSiMe_3)$-C_4H_9-n; 4.61 mmol (75%) of $(C_2H_5)_2C(OSiMe_3)CF_2CH{=}CH_2$, n_D^{25} 1.4140. (Found: C, 56.00; H, 9.37. $C_{11}H_{22}F_2OSi$ calcd.: C, 55.89; H, 9.38%). IR (film) (cm^{-1}): $\nu(C{=}C)$ 1648w. NMR ($CCl_4/CHCl_3$): δ 0.11 (s, 9 H, Me_3Si), 0.87 (broad t, *J* 7 Hz, 6 H, CH_3 of Et), 1.62 (broad q, *J* 7 Hz, 4 H, CH_2 of Et) and 5.27−6.26 ppm (complex m, 3 H, $CH{=}CH_2$).

This reaction was repeated at −92°C by treating 1.663 g (6.9 mmol) of $Me_3SnCH_2CH{=}CF_2$ in 25 ml of THF with 22 mmol of each of n-butyllithium in hexane and 3-pentanone in THF (as above, 2.2 mmol increments of each). After the final addition, the reaction mixture was stirred for 5 min. at −92°C and then 10 ml of 1 *N* HCl was added. Subsequently, 50 ml of diethyl ether was added and the resulting mixture was treated with three 75 ml portions of water. The organic phase was dried ($MgSO_4$), concentrated and analyzed by GLC (10% Carbowax on 80—100 mesh Chromosorb W, 70—150°C temperature program). The following were present: $Me_3SnCH_2CH{=}CF_2$ (2.70 mmol, 39% recovery), n-$C_4H_9SnMe_3$ (4.07 mmol, 59%), $(C_2H_5)_2(n\text{-}C_4H_9)COH$ and $(C_2H_5)_2C(OH)CF_2CH{=}CH_2$ (2.11 mmol, 52%, based on n-$C_4H_9SnMe_3$), n_D^{25} 1.4160. The latter was characterized. (Found: C, 58.77; H, 8.74. $C_8H_{14}F_2O$ calcd.: C, 58.52; H, 8.59%). IR (film) (cm^{-1}): $\nu(C{=}C)$ 1645w. NMR ($CCl_4/CHCl_3$): δ 0.91 (t, *J* 7.5 Hz, 5 H, CH_3 of Et), 1.59 (q, *J* 7.5 Hz, 4 H, CH_2 of Et), 1.67 (s, 1 H, OH), and 5.72—6.49 ppm (complex m, 3 H, $CH{=}CH_2$).

In another experiment a solution of 1.439 g (5.98 mmol) of $Me_3SnCH_2CH{=}CF_2$ in 25 ml of THF at −95°C was treated with 21 mmol each of n-butyllithium and benzaldehyde by the method of alternate, incremental additions. (The reaction mixture, which was light green during the course of the addition, unaccountably turned purple after 21 mmol of each reactant had been added.) The mixture then was treated with 3.5 ml (ca. 28 mmol) of trimethylchlorosilane, allowed to warm to room temperature and stirred overnight. The solvents were distilled off at atmospheric pressure and the residue was trap-to-trap distilled at 0.01 mmHg into a receiver at −78°C. GLC analysis of the distillate (10% DC-200 at 100 and 170°C) showed the following to be present: $Me_3SnCH_2CH{=}CF_2$ (0.6 mmol, 10% recovery), $n\text{-}C_4H_9SnMe_3$ (5.31 mmol, 89%), $PhCH(OSiMe_3)C_4H_9\text{-}n$, and $PhCH(OSiMe_3)CF_2CH{=}CH_2$ (0.79 mmol, 13%). A sample of the latter, n_D^{25} 1.4820, was collected by preparative GLC. (Found: C, 60.83; H, 7.10. $C_{13}H_{18}F_2OSi$ calcd.: C, 60.90; H, 7.08%). IR (CCl_4) (cm^{-1}): ν(C=C) 1645w. NMR (CCl_4/CH_2Cl_2): δ 0.14 (s, 9 H, Me_3Si), 4.79 (t, ^3J(HF) 8.5 Hz, 1 H, $PhC\underline{H}$), 5.17—6.29 (complex m, 3 H, $CH{=}CH_2$) and 7.29 ppm (broad s, 5 H).

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