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REACTION OF (BROMODIFLUOROMETHYL)PHENYLDIMETHYLSILANE WITH ORGANOMETALLIC REAGENTS

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Summary

A new fluorine-containing organosilicon compound, (bromodifluoromethyl)-phenyldimethylsilane (II), was synthesized by the *N*-bromosuccinimide (NBS) bromination of (difluoromethyl)phenyldimethylsilane (I), which was prepared from phenyldimethylsilyllithium and chlorodifluoromethane. Compound II reacted with dimethyl sulfoxide to give dimethyl sulfide and phenyldimethylfluorosilane in quantitative yield. The reaction of II with nucleophiles, such as sodium ethoxide, Grignard or lithium reagents, afforded products arising from cleavage of the carbon—silicon bond. In contrast, the reaction of II with Grignard reagents in the presence of appropriate catalysts (Group VIII transition metal salts or complexes) afforded the homo-coupling product of II, 1,2-bis-(phenyldimethylsilyl)-1,1,2,2-tetrafluoroethane (IV), in excellent yield. The silver(I) salt-catalyzed reaction of II with ethylmagnesium bromide gave the cross-coupling product, (1,1-difluoropropyl)phenyldimethylsilane (V) as well as III and IV. When cuprous bromide was employed as catalyst, the reaction of II with ethylmagnesium bromide afforded 1-phenyldimethylsilyl-1-propene (VI) and 3-phenyldimethylsilyl-2-pentene (VII) as main products.

Introduction

There have been many reports on the reaction of (dihalomethyl)silicon compounds with lithium reagents (eq. 1) [1], which afforded organosilicon-substituted dihalomethyllithium reagents. However, the reaction of (difluoromethyl)-silane derivatives still remains unexamined. The halogen—metal exchange reaction is commonly used for the preparation of poly- or per-fluoroalkyl Grignard or lithium reagents in organofluorine chemistry (eq. 2) [2]. It also has been shown that the perfluoroalkyl—silicon bond is easily cleaved by Grignard or lithium reagents (eq. 3) [2]. Accordingly, it was of interest to examine which

$$R_fCF_2X + RM \rightarrow R_fCF_2M + RX \qquad (2)$$

$$R_fCF_2SiMe_2H + RM \rightarrow R_fCF_2M + RSiMe_2H \quad (3)$$

($R_f = C_nF_{2n+1}$, X = Br or I, M = Li or MgY, R = alkyl or phenyl)

bond, C—X or C—Si, is cleaved by the attack of nucleophiles in (bromodifluoromethyl)silane derivatives.

We report here the synthesis of new fluorine-containing organosilicon compounds, (difluoromethyl)- and (bromodifluoromethyl)-phenyldimethylsilane, and their reactions with organometallic reagents in the presence or absence of transition metal catalysts.

Results and discussion

(Difluoromethyl)phenyldimethylsilane (I) was prepared by the reaction of phenyldimethylsilyllithium with chlorodifluoromethane in tetrahydrofuran in 35% yield based on the chlorosilane used. The silane I reacted with *N*-bromosuccinimide in carbon tetrachloride to give (bromodifluoromethyl)phenyldimethylsilane (II) in 74% yield. To our knowledge, this is the first example of the bromination of a C—H bond bearing a geminal silyl group or fluorine atom(s) by NBS, although radical halogenation of the R_3SiCH_2—H [3], R_3SiCX_2—H (X = Cl, Br) [1c] and RCF_2—H [4] bonds is well-known.

$$PhMe_2SiCl \xrightarrow[THF]{Li} [PhMe_2SiLi] \xrightarrow{ClCF_2H} \underset{(I)}{PhMe_2SiCF_2H} \xrightarrow{NBS} \underset{(II)}{PhMe_2SiCF_2Br} \quad (4)$$

Both difluoromethylsilane derivatives I and II are stable at ambient temperature. Compound II readily reacts with dimethyl sulfoxide even at 0°C to afford phenyldimethylfluorosilane and dimethyl sulfide in quantitative yield. The formation of these products can be understood in terms of a mechanism involving fluorobromocarbene. No reaction took place on mixing compound I and DMSO.

$$PhMe_2SiCF_2Br \rightarrow PhMe_2SiF + [BrFC:] \xrightarrow{DMSO} Me_2S + [BrFC{=}O] \quad (5)$$

Our attempt to prepare (phenyldimethylsilyl)difluoromethyllithium by the reaction of I with LDA was unsuccessful, and I was recovered unchanged *. Neither *n*-butyllithium, Grignard reagents, nor sodium ethoxide reacted with I. On the other hand, II reacted with sodium ethoxide in ethanol to give phenyldimethylethoxysilane (IIIa) (90%) and phenyldimethylfluorosilane ** (10%). The reaction of II with Grignard or lithium reagents in ether or THF gave similar products (IIIb and IIIc). Thus nucleophilic substitution took place selectively at silicon with displacement of the bromodifluoromethyl anion (eq. 6).

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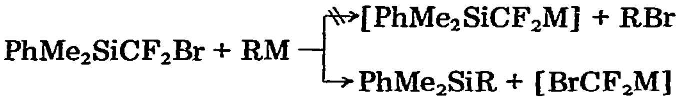
* The reaction was carried out in ether at —75°C using one equivalent of LDA.

** The formation of this compound may suggest the generation of fluorobromocarbene from II.



$$PhMe_2SiCF_2Br + RM \begin{cases} \nrightarrow [PhMe_2SiCF_2M] + RBr \\ \rightarrow PhMe_2SiR + [BrCF_2M] \end{cases} \quad (6)$$

R = OEt, M = Na (IIIa R = OEt;
R = Et, M = MgBr IIIb R = Et;
R = Ph, M = MgBr IIIc R = Ph)
R = Ph, M = Li

This reaction with Grignard reagent proceeded so slowly at temperatures below 0° C that an excess of Grignard reagent and some heating was necessary to obtain the cleavage product in reasonable yield. In contrast with the results descrived above, the presence of catalytic amounts of Group VIII transition metal chlorides, such as $NiCl_2$, $PdCl_2$, $CoCl_2$ and $FeCl_3$, resulted in a different reaction. As Table 1 shows, an unexpected homo-coupling product, 1,2-bis-(phenyldimethylsilyl)-1,1,2,2-tetrafluoroethane (IV), was obtained in 83—95% yield when the reaction was carried out with II, ethylmagnesium bromide and the catalyst at —75° C—room temperature. Similar treatment of II with n-butyl, n-octyl and phenyl Grignard reagents in the presence of catalytic amounts of

TABLE 1

REACTION OF (BROMODIFLUOROMETHYL)PHENYLDIMETHYLSILANE (II) WITH GRIGNARD REAGENTS IN THE PRESENCE OF METAL SALTS AND COMPLEXES [a]

RMgBr	Catalyst	(mol%) [b]	Solvent	Yield [c] (%)					Recovered II (%)
				IV	V	VI	VII	III	
Et	none		ether [d]	0	0	3	2	47	25
Et	none		THF [d]	0	0	0	0	69	6
Et	$NiCl_2$	(0.9)	ether	95	2	0	0	0	0
Et	$PdCl_2$	(1.3)	ether	94	3	0	0	0	0
Et	$CoCl_2$	(0.9)	ether	95	1	0	0	0	0
Et	$FeCl_3$	(2.7)	ether	83	0	1	6	3	0
Et	$PtCl_2$	(4.4)	ether	3	0	0	0	7	75
Et	$Ni(acac)_2$	(1.0)	ether	29	21	5	16	0	0
Et	$NiCl_2(PEt_3)_2$	(1.0)	ether	61	11	2	9	2	0
Et	$NiCl_2$(dppp) [e]	(1.0)	ether	70	14	2	7	0	0
Et	$NiCl_2$(dppp) [e]	(1.0)	THF	71	9	2	5	3	0
Et	$PdCl_2(PPh_3)_2$	(1.0)	ether	66	10	3	5	5	0
Et	$Pd(PPh_3)_4$	(1.2)	ether	67	9	3	4	0	0
Et	$Pd(PPh_3)_4$	(1.1)	THF	5	0	0	0	35	40
Et	$Pt(PPh_3)_4$	(0.9)	ether	0	0	0	0	13	71
Bu	$NiCl_2$	(2.1)	ether	98	0	0	0	0	0
Oc [f]	$NiCl_2$	(2.1)	ether	88 [g]	0	0	0	0	0
Ph	none		THF [h]	0	0	—	—	50	30
Ph [i]	none		ether	0	0	—	—	32	38
Ph	$NiCl_2$	(2.9)	ether	67 [j]	0	—	—	0	0
Ph	$Ni(acac)_2$	(0.8)	ether	67 [k]	0	—	—	0	0
Ph	$NiCl_2$(dppp) [e]	(0.9)	ether	69 [l]	0	—	—	0	0

[a] All reactions were carried out by mixing 0.5 mmol of II and 1.0 mmol of RMgBr in a solvent for 30 min at —75° C and then 1 h at room temperature. [b] Based on II used. [c] Yields were determined by GLC. [d] Refluxed for 30 min. [e] dppp = 1,3-bis(diphenylphosphino)propane. [f] n-Octylmagnesium bromide (0.5 mmol) was used. [g] 1-Octene (48%), n-octane (50%) and n-hexadecane (trace) were also obtained. [h] Reaction was run at room temperature. [i] Phenyllithium (1.0 mmol) was used. [j] Biphenyl (81%) was also obtained. [k] Biphenyl (70%) was also obtained. [l] Biphenyl (74%) was also obtained.

nickel(II) chloride also gave IV in satisfactory yield. It is noteworthy that the homo-coupling product (IV) was formed exclusively even when nickel(II) complexes such as $Ni(acac)_2$ and $NiCl_2(dppp)$ were employed in the reaction with phenylmagnesium bromide, since these complexes are the well-known catalysts for the cross-coupling reaction of Grignard reagents with aryl and alkenyl halides [5]. In all cases described above, virtually no cross-coupling product (V) was formed. A remarkable change was observed on using $Ni(acac)_2$ as catalyst for the reaction with ethylmagnesium bromide. The products in this case were 1-phenyldimethylsilyl-1-propene (VI) (5%), 3-phenyldimethylsilyl-2-pentene (VII) (16%) and (1,1-difluoropropyl)phenyldimethylsilane (V) (21%), in addition to IV (29%). When nickel or palladium complexes such as $NiCl_2(PEt_3)_2$, $NiCl_2(dppp)$, $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ were employed as the catalyst, the reaction resulted in the formation of V (9—14%), VI (2—3%), VII (4—9%) and IV (61—70%). Products VI and VII may arise from the further reaction of pre-formed cross-coupling product (V) and Grignard reagent promoted by the metal complex catalyst. Although $NiCl_2(dppp)$ was active both in ether and in THF, $Pd(PPh_3)_4$ was inactive in THF. Platinum salts and complexes such as $PtCl_2$ and $Pt(PPh_3)_4$ showed no catalytic activity in the present reaction. As for the fate of the Grignard reagents, 1-octene (48%), n-octane (50%) and n-hexadecane (trace) were produced on using n-octylmagnesium bromide, and biphenyl (70—81%) was formed on using phenylmagnesium bromide. These results are consistent with those obtained by Tamura and Kochi [6], who carried out the reaction of Grignard reagents with stoichiometric amounts of metal salts. Thus, it is clearly indicated that the Grignard reagents only act as reducing agent in these reactions.

As to the mechanism of this homo-coupling reaction, a free radical process can be excluded because of the absence of the products arising from hydrogen abstraction, disproportionation or cross-coupling *. Although a detailed understaning of the mechanism must await further investigation, we can deduce a probable catalytic cycle for the reaction based on the available data, which involves (a) the reduction of a metal salt (A) to a low valent metal complex (B) by a Grignard reagent [8] followed by (b) the oxidative addition [9] of II to B, (c) the disproportionation of the oxidative adduct (C) giving a dialkyl metal (D) and metal(II) halide (A) [10] and (d) the reductive elimination of the homo-coupling product as shown in Scheme 1 (Q = solvent or ligand; R_f = CF_2SiMe_2Ph). The oxidative addition of perfluoroalkyl halides to low valent transition metal complexes is well-known as an easy process leading to perfluoroalkyl-transition metal complexes [9]. In contrast with this, alkyl halides have been shown to react with Ni^0 to form Ni^I species in most cases by a radical process [11], which does not involve any alkyl-nickel complexes. In order to clarify the role of the fluorine atoms in the present unique homo-coupling, we carried out reactions of (bromomethyl)phenyldimethylsilane (VIII) with Grignard reagents in the presence of nickel catalysts for comparison purposes. The reaction gave phenyltrimethylsilane (IX) in good yield and no

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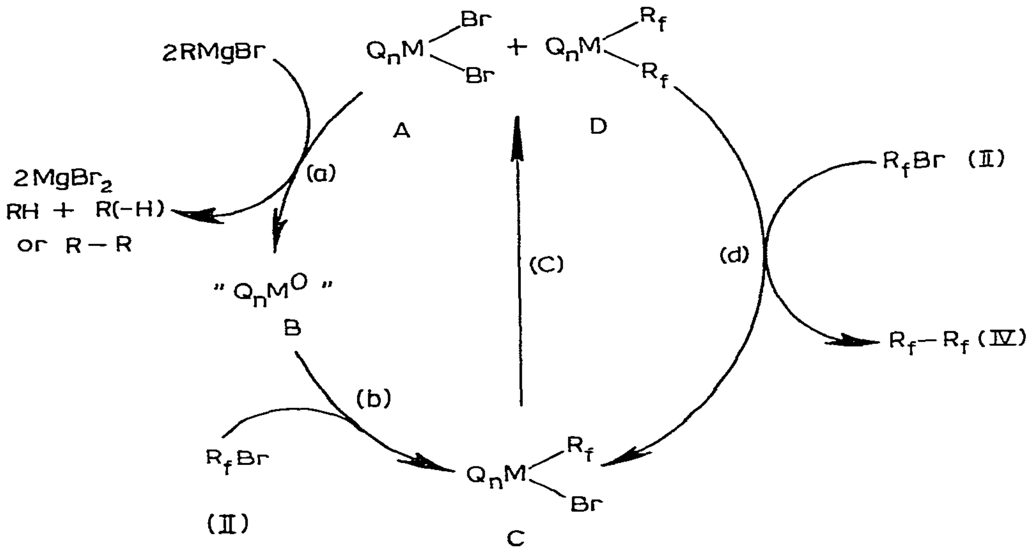
* It is known that trifluoromethyl radical generated by the photolysis of trifluoromethyl iodide gives little homo-coupling product, CF_3—CF_3, and the hydrogen abstraction product, CF_3H, is formed in moderate yield [7].

SCHEME 1



SCHEME 2

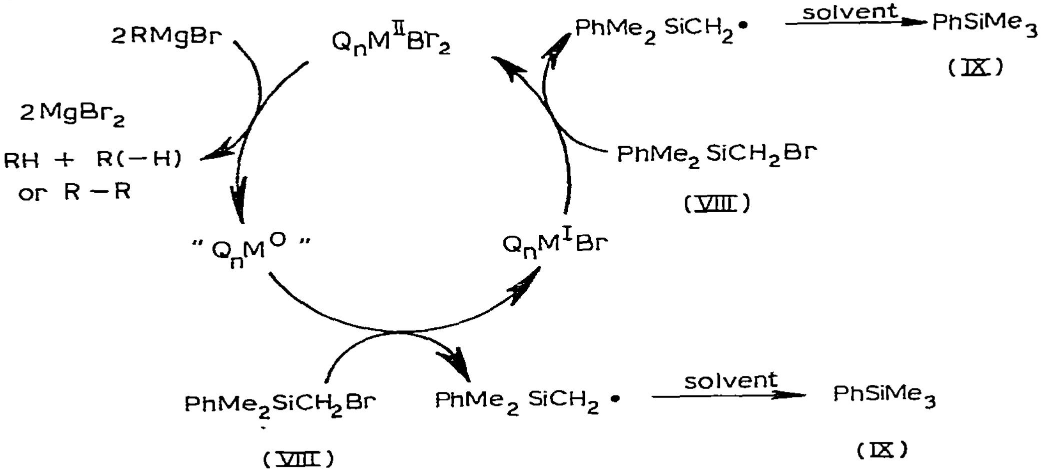


TABLE 2

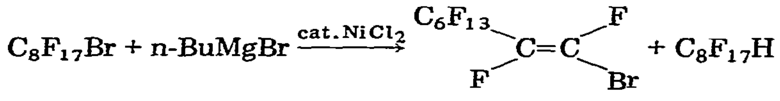
REACTION OF (BROMOMETHYL)PHENYLDIMETHYLSILANE (VIII) WITH GRIGNARD REAGENTS IN THE PRESENCE OF NICKEL CATALYSTS [a]

RMgBr	Catalyst	(mol%) [b]	Yield [c] (%) of $PhSiMe_3$	Recovered VIII (%)
Et	none		1	94
Et	$NiCl_2$	(1.1)	74	0
Et	$NiCl_2$(dppp) [d]	(0.8)	59	29
Bu	$NiCl_2$	(1.2)	91	4
Oc [e]	$NiCl_2$	(1.2)	61 [f]	26
Ph	$NiCl_2$	(1.1)	85 [g]	4

[a] All reactions were carried out by mixing 0.5 mmol of VIII and 1.0 mmol of RMgBr in ether for 30 min at —75°C and then for 1 h at room temperature. [b] Based on VIII used. [c] Yields were determined by GLC. [d] dppp = 1,3-bis(diphenylphosphino)propane. [e] n-Octylmagnesium bromide (0.5 mmol) was used. [f] 1-Octene (45%), n-octane (45%) and n-hexadecane (6%) were also obtained. [g] Biphenyl (66%) was also obtained.

reaction took place in the absence of catalyst (Table 2). Thus, the two fluorine atoms play a crucial role in steps (b) and (c) in Scheme 1 in the present reaction.

Our attempt to obtain a homo-coupling product in the reaction of perfluorooctyl bromide (X) under the same reaction conditions was unsuccessful, i.e., only compounds arising from the decomposition,of perfluorooctylmagnesium bromide were obtained (eq. 7) [12]. This result indicates that the rate of the bromine—metal exchange reaction of perfluoroalkyl bromide with the Grignard reagent is faster than that of the oxidative addition to low valent transition metal complex.



$$\mathrm{C_8F_{17}Br + n\text{-}BuMgBr \xrightarrow{cat.NiCl_2} (C_6F_{13})FC{=}CF(Br) + C_8F_{17}H} \qquad (7)$$

(XI) (XII)

When a silver(I) salt was employed as catalyst for the reaction of II with ethylmagnesium bromide in ether, cross-coupling product (V) was obtained in moderate yield in addition to III and IV (Table 3). An increase of the amount of catalyst resulted in little change in the yield and the ratio of the products. The occurrence of the random coupling may suggest a radical mechanism for the silver(I) salt-catalyzed reaction. However, the silver(I)-catalyzed reaction in THF gave III and IV as major products. When cuprous bromide was employed as catalyst, the reaction of II with ethylmagnesium bromide in THF afforded vinylsilanes VI and VII as main products without any homo-coupling product (IV). A similar reaction in ether resulted in the formation of IV (29%), VI (15%) and VII (16%) accompanied with small amounts of V and III. Vinylsilanes VI and VII may arise from the further reaction of once-formed cross-coupling product (V) with ethylcopper species.

$$\mathrm{PhMe_2SiCF_2Br + EtMgBr} \begin{cases} \xrightarrow{\text{cat. AgI}} \mathrm{PhMe_2SiCF_2Et + III + IV} \\ \qquad\qquad \mathrm{(V)} \\ \xrightarrow[\text{cat. CuI}]{} \mathrm{PhMe_2SiCH{=}CHMe + PhMe_2Si(Et)C{=}CHMe} \\ \qquad\qquad \mathrm{(VI)} \quad + \text{others} \quad \mathrm{(VII)} \end{cases} \qquad (8)$$

TABLE 3

REACTION OF (BROMODIFLUOROMETHYL)PHENYLDIMETHYLSILANE (II) WITH ETHYLMAGNESIUM BROMIDE IN THE PRESENCE OF SILVER(I) AND COPPER(I) SALTS [a]

Catalyst	(mol%) [b]	Solvent	Yield [c] (%)					Recovered II (%)
			IV	V	VI	VII	III	
AgBr	(1.0)	ether	46	39	0	1	10	0
AgBr	(8.0)	ether	40	44	0	0	7	0
AgBr	(44)	ether	40	47	0	0	8	0
AgBr	(1.3)	THF	59	9	1	0	22	0
AgCl	(1.0)	ether	43	21	0	1	9	15
AgI	(1.2)	ether	85	8	0	1	5	0
$AgNO_3$	(1.1)	ether	74	17	0	0	5	0
CuBr	(6.1)	ether	29	6	15	16	5	0
CuBr	(4.3)	THF	0	2	15	17	7	32

[a] All reactions were carried out by mixing 0.5 mmol of II and 1.0 mmol of EtMgBr in a solvent for 30 min at —75° C and then for 1 h at room temperature. [b] Based on II used. [c] Yields were determined by GLC.

Experimental

NMR spectra [chemical shifts in parts per million (ppm) from internal tetramethylsilane for ^1H and from trifluoroacetic acid (external reference) for ^{19}F; δ is positive for downfield shifts in all cases] were recorded for the proton on a Varian EM-390 and for the fluorine on a Varian XL-100-15A as solutions in deuteriochloroform. Mass spectra were recorded on a Hitachi RMU-6MG spectrometer at 70 eV. Exact mass spectrum was measured on a JEOL Model JMS-D300 equipped with a JMA-2000 data processing system. IR spectra were measured on a Hitachi EPI-G3 spectrometer. GLC analyses were carried out with Shimadzu GC-7A instrument, using a glass column (1.2 m × 0.3 mm) packed with Silicone SE-30 (30%), DC-550 (30%), Apiezon Grease L (30%) and PEG-6000 (20%) on Uniport B. Ether was dried by distillation from sodium wire. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride. (Bromomethyl)phenyldimethylsilane was prepared according to the literature method [13]. Perfluorooctyl bromide was used as purchased from PCR Research Chemicals, Inc.

Preparation of (difluoromethyl)phenyldimethylsilane (I)

A 500 ml three-necked flask fitted with a gas inlet tube and a dry ice-cooled reflux condenser was charged with 100 ml of dry THF and cooled with a dry ice/ethanol bath under nitrogen, and 22 g (0.25 mol) of difluorochloromethane was introduced from a cylinder through the gas inlet tube with stirring. The gas inlet tube was replaced by a pressure-equalizing dropping funnel containing phenyldimethylsilyllithium in 150 ml of THF (prepared from 5.5 g (0.79 g-atom) of lithium pieces and 40 g (0.24 mol) of phenyldimethylchlorosilane). After the phenyldimethylsilyllithium solution had been added dropwise over 1 h, stirring was continued for another 1 h, and then the reaction mixture was allowed to warm slowly to room temperature. The reaction mixture was poured into water and extracted with n-hexane for several times. The extracts were dried over anhydrous sodium sulfate and distilled under reduced pressure to give 15.7 g (35% yield) of (difluoromethyl)phenyldimethylsilane (I) as a colorless oil: b.p. 90°C/18 Torr. ^1H NMR: δ 0.46 (t, $J = 0.5$ Hz, 6 H), 5.94 (t, $J = 46.4$ Hz, 1 H), and 7.3—7.6 (m, 5 H). ^{19}F NMR: δ —59.3 (bd, $J = 46.4$ Hz). IR (neat): 1430, 1325, 1270, 1260, 1120, 1080, 1070, 1000, 985, 845, 820, 795, 740, 715, 700, 470 and 415 cm^{-1}. Mass spectrum, *m/e* (% rel. inten.): 186(1), 139(14), 137(19), 136(55), 135(100), 107(33), 105(20), 91(12), 77(15), 53(12), 51(10), 47(19) and 43(43). (Found: C, 57.74; H, 6.58. $C_9H_{12}F_2Si$ calcd.: C, 58.03; H, 6.49%.)

Preparation of (bromodifluoromethyl)phenyldimethylsilane (II)

To a suspension of 6.5 g (36.5 mmol) of *N*-bromosuccinimide in 30 ml of carbon tetrachloride was added 6.5 g (34.9 mmol) of (difluoromethyl)phenyldimethylsilane (I) and the mixture was heated at reflux for 48 h with stirring. Then, the reaction mixture was filtered, and the filtrate was washed with water, dried over anhydrous $CaCl_2$, and distilled under reduced pressure to give 6.8 g (74% yield) of (bromodifluoromethyl)phenyldimethylsilane (II) as a colorless oil: b.p. 115°C/27 Torr. ^1H NMR: δ 0.59 (bs, 6 H) and 7.3—7.7 (m, 5 H). ^{19}F

NMR: δ 22.7 (bs). IR (neat): 1430, 1270, 1265, 1120, 1040, 835, 790, 770, 735, 710, 695, 655 and 470 cm^{-1}. Mass spectrum, *m/e* (% rel. inten.): 216(3), 214(3), 201(19), 199(19), 170(12), 157(31), 156(10), 155(81), 154(19), 140(13), 139(100), 137(20), 135(59), 91(37), 63(18), 47(32) and 44(63). (Found: C, 40.95; H, 4.18. $C_9H_{11}BrF_2Si$ calcd.: C, 40.86; H, 4.18%.)

Reaction of II with dimethyl sulfoxide

To 0.4 ml of dimethyl sulfoxide was added 26.5 mg (0.10 mmol) of II at 0°C. After the reaction mixture had been shaken for a few minutes, GLC analysis showed quantitative formation of phenyldimethylfluorosilane and dimethylsulfide. The products were identified by comparing their retention times with those of authentic samples. The ^{19}F NMR spectrum of the reaction mixture showed a signal ascribed to phenyldimethylfluorosilane at δ —80.0 (septet, J = 7.4 Hz, 1 F). The spectrum also showed an unidentified signal at δ —91.4 (bs, 1 F), which could be due from decomposition of carbonyl bromide fluoride.

Reaction of II with sodium ethoxide

To a solution of 10 mg (0.15 mmol) of sodium ethoxide in 0.4 ml of ethanol was added 26.5 mg (0.10 mmol) of II. An exothermic reaction occurred which was complete within a few minutes. GLC analysis showed the formation of phenyldimethylethoxysilane (90% yield) and phenyldimethylfluorosilane (10% yield), which were identified by the comparison of their GLC retention times with those of authentic samples.

Reaction of II, VIII and X with Grignard reagents in the presence of a transition metal catalyst

The following procedure is typical. To a solution of 0.6 mg (4.6×10^{-3} mmol) of nickel(II) chloride and 133 mg (0.50 mmol) of II in 1 ml of dry ether was added 2.1 ml of ethylmagnesium bromide in ether (4.8 *N*, 1.0 mmol) at —75°C under argon with stirring. After the addition, the reaction mixture was stirred at —75°C for 30 min and then slowly warmed to room temperature. The mixture was stirred for another 1 h at room temperature, and then hydrolyzed with dilute hydrochloric acid. The organic layer was separated, and dried over anhydrous sodium sulfate. Yields of the products were determined by GLC analysis. All the products were isolated by preparative GLC. Ethylphenyldimethylsilane (IIIb), diphenyldimethylsilane (IIIc), phenyltrimethylsilane (IX), 1-bromoperfluoro-1-octene (XI), and 1-*H*-perfluorooctane (XII) were identified by comparing their spectral data and GLC retention times with those of authentic samples. Products IV, V, VI and VII were determined to be 1,2-bis-(phenyldimethylsilyl)-1,1,2,2-tetrafluoroethane, (1,1-difluoropropyl)phenyldimethylsilane, 1-phenyldimethylsilyl-1-propene, and 3-phenyldimethylsilyl-2-pentene, respectively, on the basis of their spectral data and elemental analyses.

1,2-Bis(phenyldimethylsilyl)-1,1,2,2-tetrafluoroethane (IV). m.p. 76—77°C. ^{1}H NMR: δ 0.46 (t, J = 0.7 Hz, 12 H) and 7.3—7.6 (m, 10 H). ^{19}F NMR: δ —39.7 (bs). IR (KBr): 1430, 1260, 1120, 1110, 1065, 1025, 850, 840, 795, 735, 705, 700, 655, 540 and 465 cm^{-1}. Mass spectrum, *m/e* (% rel. inten.): 271(3), 154(20), 149(28), 139(95), 136(23), 135(100), 120(30), 115(22), 101(75), 91(32), 81(37), 77(31), 47(22) and 43(28). (Found: C, 58.34; H, 6.06. $C_{18}H_{22}F_4Si_2$ calcd.: C, 58.35; H, 5.98%.)

(1,1-Difluoropropyl)phenyldimethylsilane (V). ^{1}H NMR: δ 0.38 (bs, 6 H), 0.84 (t, J = 7.2 Hz, 3 H), 1.71 (t, of q, J = 21.6, 7.2 Hz, 2 H) and 7.3—7.7 (m, 5 H). ^{19}F NMR: δ —35.5 (bt, J = 21.6 Hz). IR (neat): 1470, 1430, 1265, 1160, 1145, 1115, 1005, 930, 840, 815, 785, 740, 710, 700, 655 and 470 cm^{-1}. Mass spectrum *m/e* (% rel. inten.): 185(2), 139(23), 135(100), 47(14) and 43(14). (Found: C, 61.46; H, 7.40. $C_{11}H_{16}F_2Si$ calcd.: C, 61.64; H, 7.52%.)

1-Phenyldimethylsilyl-1-propene (VI). ^{1}H NMR: δ 0.29 (s, 6 H), 1.81 (d, J = 6 Hz, 3 H), 5.95 (d, J = 18 Hz, 1 H), 6.12 (dd, J = 18, 6 Hz, 1 H) and 7.2—7.6 (m, 5 H). IR (neat): 1620, 1430, 1255, 1110, 985, 840, 820, 785, 730 and 700 cm^{-1}. Mass spectrum, *m/e* (% rel. inten.): 176(8), 162(12), 161(72), 136(15), 135(100), 121(93), 105(15), 73(39), 71(13), 59(14), 57(28) and 43(37). Exact mass for $C_{11}H_{16}Si$: measured *m/e* 176.1020; calcd. 176.1021.

3-Phenyldimethylsilyl-2-pentene (VII). ^{1}H NMR: δ 0.34 (s, 6 H), 0.84 (t, J = 7.5 Hz, 3 H), 1.68 (d, J = 7 Hz, 3 H), 2.12 (q, J = 7.5 Hz, 2 H), 5.88 (q, J = 7 Hz, 1 H) and 7.2—7.7 (m, 5 H). IR (neat): 1620, 1430, 1255, 1110, 835, 820, 775, 735 and 705 cm^{-1}. Mass spectrum, *m/e* (% rel. inten.): 204(9), 189(32), 136(14), 135(100), 121(49), 73(12), 59(12) and 43(21). (Found: C, 76.49; H, 10.00. $C_{13}H_{20}Si$ calcd.: C, 76.40; H, 9.96%.)

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