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REACTIONS OF BIS(PENTAFLUOROPHENYL)METHYLSILANE WITH ORGANOLITHIUM AND GRIGNARD REAGENTS

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Summary

Bis(pentafluorophenyl)methylsilane (I) reacts with primary alkyllithium and Grignard reagents to give high yields of the pentafluorophenylmetallic species.

$$\underset{\text{(I)}}{(C_6F_5)_2SiMeH} + 2\ RM \rightarrow 2\ C_6F_5M + R_2SiMeH$$

R = Me, n-Bu; M = Li

R = Me, Et; M = MgX

The influence of steric factors upon the course of the reactions with a series of RLi and RMgX compounds including PhMgBr, i-PrMgBr and t-BuLi are considered.

Introduction

Previous work has shown that (perhaloaryl)diphenylsilanes [1, 2], (perhaloaryl)dimethylsilanes [3—5] and bis(perhaloaryl)methylsilanes [6] are cleaved by alkyllithium compounds forming a perhaloaryllithium compound and the corresponding silane resulting from nucleophilic attack on silicon. (Pentafluorophenyl)trimethylsilane reacts differently with n-BuLi giving 1-(trimethylsilyl)-4-n-butyltetrafluorobenzene [7]. Grignard reagents in ether solution were found to be generally unreactive with (perhaloaryl)dimethylsilanes [4].

Results and discussion

Grignard reactions

Cleavage of one pentafluorophenyl group from silicon proceeded readily with a variety of Grignard reagents at 0° in THF or Et_2O/THF solvent mixture (Table 1).

TABLE 1

CLEAVAGE OF PENTAFLUOROPHENYL-SUBSTITUTED SILANES WITH GRIGNARD REAGENTS AND ORGANOLITHIUM COMPOUNDS

Silane[a] (mmoles)	RM (mmoles)	Solvent/ temp/time	Derivatizing Agent	Products (% yield)[b]
(I)(5.0)	MeMgCl (10.0)	THF/0°/3h	$ClSiMe_3$	(IV) (67), (II) (30)
(I)(5.0)	MeMgCl (10.0)	THF/0°/10h	$ClSiMe_3$	(IV) (73), (II) (24)
(I)(5.0)	MeMgCl (10.0)	Et_2O (80) THF/0°/3h	$ClSiMe_3$	(IV) (66), (II) (29)
(I)(5.0)	MeMgBr (10.0) (10.0)	THF/0°/10h	$ClSiMe_3$	(IV) (62), (II) (37)
(I)(5.0)	EtMgBr (10.0)	THF/0°/20 min	$ClSiMe_3$	(IV) (43)
(I)(10.0)	EtMgBr (20.0)	THF/0°/6h	$ClSiMe_3$	(IV) (67)
(I)(5.0)	i-PrMgCl (10.0)	THF/0°/3h	$ClSiMe_3$	(IV) (48), (V) (42)
(I)(5.0)	i-PrMgCl (10.0)	THF/0°/16h	$ClSiMe_3$	(IV) (48), (V) (42)
(I)(5.0)	i-PrMgCl (10.0)	THF/0°/6h	CO_2	(III) (18)[c]
(I)(5.0)	PhMgBr (10.0)	THF/0°/3h	$ClSiMe_3$	(IV) (51), (IV)[d] (40—45)
(I)(5.0)	MeLi (10.0)	Et_2O/—50°/1h	CO_2	(III) (92)[c]
(I)(30.0)	n-BuLi (60.0)	Et_2O/—78°/1h	$ClSiMe_3$	(IV) (76)[c]
(I)(5.0)	n-BuLi (10.0)	Et_2O/—70°/1h	CO_2	(III) (86)[c]
(I)(20.0)	t-BuLi (40.0)	Et_2O/—78°/30 min	$ClSiMe_3$	(IV) (21)[e], (VII) (24)[e] (VIII) (41)[e]
(VIII)(2.5)	MeLi (5.0)	Et_2O/—50°/1h	CO_2	(IX) (86)[c]
(II)(10.0)	MeMgCl (10.0)	THF/0°/10h	$ClSiMe_3$	(IV) (72)
(II)(10.0)	EtMgBr (10.0)	THF/0°/10h	$ClSiMe_3$	(IV) (37)
(II)(5.0)	i-PrMgCl (5.0)	THF/0°/10h	$ClSiMe_3$	(IV) (0), (II) (98)
(II)(10.0)	PhMgBr (10.0)	THF/0°/10h	$ClSiMe_3$	(IV) (10—15)
(II)(10.0)	MeLi (10.0)	Et_2O/—50°/1h	CO_2	(III) (91)[c]
(II)(10.0)	n-BuLi (10.0)	Et_2O/—70°/1h	CO_2	(III) (80)[f]

[a] (I) = $(C_6F_5)_2SiMeH$; (II) = $C_6F_5SiMe_2H$; (III) = $C_6F_5CO_2H$; (IV) = $C_6F_5SiMe_3$; (V) = $C_6F_5Si(i\text{-}Pr)MeH$; (VI) = $C_6F_5Si(Ph)MeH$; (VII) = $p\text{-}t\text{-}BuC_6F_4Si(t\text{-}Bu)MeH$; (VIII) = $(p\text{-}t\text{-}BuC_5F_4)_2SiMeH$; (IX) = $p\text{-}t\text{-}BuC_6F_4\text{-}CO_2H$. [b] GLC yield based on starting compound RM. Samples of (II) and (IV) were isolated and found to have identical IR and ^1H NMR spectra to those reported [2, 14]. [c] Isolated yield based on RM compound. [d] (VI); B.p., 93°/0.8 mm, n_D^{25} 1.5048. ^1H NMR: δ 0.76 ppm (doublet of triplets, $J(CH_3, H) = 4.2$ Hz, $J(o\text{-}F, CH_3) = 1.2$ Hz, 3 H), δ 5.08 (multiplet, 1 H), 7.40 ppm (multiplet, 5 H). IR: 2175 cm^{-1} (Si—H); 1644, 1518, 1466 cm^{-1} (C_6F_5). Molecular ion: m/e 288 (mol. wt. 288). Found: C, 54.43 H, 3.28; F, 32.64. $C_{13}H_9F_5Si$ calcd.: C, 54.16; H. 3.15; F, 32.95%.) [e] Isolated yield based on starting silane. [f] Ref. 4.

$$(C_6F_5)_2SiMeH + RMgX \rightarrow C_6F_5MgX + C_6F_5Si(R)MeH$$

$$C_6F_5Si(R)MeH + RMgX \rightarrow C_6F_5MgX + R_2SiMeH$$

Cleavage of the remaining pentafluorophenyl group was much more difficult, and was not observed in the case of i-PrMgCl. Ease of cleavage of (pentafluorophenyl)-dimethylsilane [(II), Table 1] by Grignard reagents was shown to be in the order MeMgCl > EtMgBr ≫ PhMgBr. This order may be indicative of the importance of steric hindrance in the cleavage of the Si—C bond.

Organolithium reactions

Cleavage of both pentafluorophenyl groups in compound (I) was effected rapidly under mild conditions with MeLi or n-BuLi (Table 1). However, nucleophilic displacement of *para*-fluorines occurred predominantly when compound (I) reacted with t-BuLi. In view of the trend observed with Grignard cleavages it is reasonable to assume that the steric bulk of the t-BuLi lessens its ability to cleave the Si—C bond and shifts attack mainly to the relatively more accessible *para*-fluorine atoms.

$$(C_6F_5)_2SiMeH + 2\ \text{t-BuLi} \rightarrow \underset{41\%}{(p\text{-t-BuC}_6F_4)_2SiMeH} + \underset{24\%}{p\text{-t-BuC}_6F_4Si(\text{t-Bu})MeH} + \underset{21\%}{C_6F_5Li} + LiF$$

When bis(p-tert-butyltetrafluorophenyl)methylsilane was reacted with MeLi, there was obtained upon derivatization with CO_2 an 86% yield of p-tert-butyltetrafluorobenzoic acid. To our knowledge there have been no tert-butyltetrafluorophenyl derivatives reported. Cleavage reactions of this type may have some synthetic value.

There was no evidence for any hydride displacement from silicon as occurs when many silicon hydrides are treated with Grignard reagents or organolithium compounds [8—10]. In cases where (pentafluorophenyl)trimethylsilane could be the product resulting from hydride displacement its absence was shown by GLC analysis prior to derivatization with $ClSiMe_3$. The pentafluorophenyl group, as expected, proved to be a much better leaving group than hydride.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen in oven-dried glassware which was assembled while hot and flushed with dry nitrogen prior to addition of the reagents. In the reactions listed in Table 1, Grignard or organolithium reagents were added by syringe to the stirred solution of the silane. Ether and THF were distilled from $LiAlH_4$. The molarities of alkyllithium and Grignard reagents were determined by the double-titration methods [11, 12]. GLC analyses were performed on an F and M model 500 Gas Chromatograph using either 10% DC-200 or LAC-446 liquid phase on Chromosorb W in 4′ × 1/4″ columns. ^1H NMR and ^{19}F NMR spectra were taken on about 20% solutions in CCl_4. ^{19}F NMR chemical shifts are reported in ppm upfield (—) from trichlorofluoromethane internal reference.

Preparation of bis(pentafluorophenyl)methylsilane(I)

To C_6F_5Li (0.20 mole) in 400 ml Et_2O was added 11.5 g (0.10 mole) Cl_2 SiMeH at —60°. After 3 h of warming to 0°, the reaction mixture was filtered (—30°). Ether was removed under reduced pressure. Distillation of the liquid residue gave compound (I), b.p. 106°/4 mm, n_D^{20} 1.4626 (31.8 g, 84%). Lit. [13, 14]: b.p. 94°/2 mm, n_D^{20} 1.4634; b.p. 70°/0.15 mm, n_D^{25} 1.4614.) The ^1H NMR spectrum, which has not been previously described, exhibited peaks at δ 0.94 ppm [doublet of pentets, $J(H, CH_3) = 4.2$ Hz, $J(o\text{-F}, CH_3) = 1.2$ Hz, 3 H], and δ 5.46 ppm [octet, $J(H, CH_3) \approx J(o\text{-F}, H) = 4.2$ Hz, 1 H].

Preparation of (pentafluorophenyl)isopropylmethylsilane(V)

To 1.89 g (0.01 mole) of compound (I) in 23.3 ml Et_2O at 0° was added 23.3 ml of 0.43 *N* (0.01 mole) i-PrMgCl in THF. After 3 h the reaction mixture was hydrolyzed with 5 ml of 0.1 *N* HCl. The Et_2O solution was washed with H_2O, dried over anhydrous $MgSO_4$ and distilled to give (pentafluorophenyl)isopropylmethylsilane, b.p. 92—93°/25 mm, n_D^{25} 1.4389 (1.93 g, 76%). The ^1H NMR spectrum showed peaks at δ 0.44 [doublet of triplets, $J(H, CH_3) = 4.2$ Hz, $J(o\text{-}F, CH_3) = 1.2$ Hz, 3 H], 1.12 (unsymmetrical broad peak, 7 H), and 4.42 ppm (multiplet, 1 H). IR: 2170 cm^{-1} (Si—H); 1647, 1524 and 1475 cm^{-1} (C_6F_5). Molecular ion; *m/e* 254 (mol. wt. 254). (Found: C, 47.38; H, 4.25; F, 37.06. $C_{10}H_{11}F_5Si$ calcd.: C, 47.24; H, 4.36; F, 37.36%.)

Reaction of tert-butyllithium with bis(pentafluorophenyl)methylsilane (I)

To 7.56 g (0.02 mole) of compound (I) in 150 ml of Et_2O at —78° was slowly added 36.7 ml of 1.09 *N* (0.04 mole) t-BuLi. After 1/2 h 4.34 g (0.04 mole) of $ClSiMe_3$ was added, and the mixture allowed to warm to room temperature. Distillation provided $C_6F_5SiMe_3$, b.p. 56—57°/9 mm (1.03 g, 21%). (Lit. [15], b.p. 60°/14 mm).

Also obtained was (*p*-tert-butyltetrafluorophenyl)tert-butylmethylsilane, b.p. 56—58°/0.08 mm, m.p. 34—35° (1.46 g, 24%). The ^1H NMR spectrum showed peaks at δ 0.43 [doublet of triplets, $J(H, CH_3) = 4.0$ Hz, $J(o\text{-}F, CH_3) = 1.2$ Hz, 3 H], 1.04 (singlet, 9 H), 1.53 [triplet, $J(p\text{-}(CH_3)_3C, o\text{-}F) = 2.2$ Hz, 9 H], 4.34 ppm ppm [sextet, $J(H, CH_3) \simeq J(H, o\text{-}F) = 4.0$ Hz, 1 H]. The ^{19}F NMR indicated *para* orientation of the tert-butyl group by exhibiting an A_2B_2 pattern at —126.8 (2 F) and —138.0 ppm (2 F). IR: 2165 cm^{-1} (Si—H); 1643, 1520, 1467 and 1439 cm^{-1} (C_6F_4). Molecular ion: *m/e* 306 (mol. wt. 306). (Found: C, 58.58; H, 6.99; F, 24.45. $C_{15}H_{22}F_4Si$ calcd: C, 58.80; H, 7.24; F, 24.80%.)

Also isolated was bis(*p*-tert-butyltetrafluorophenyl)methylsilane (VIII), b.p. 123—125°/0.01 mm, m.p. 97—98.5° (3.7 g, 41%). The ^1H NMR spectrum showed peaks at δ 0.83 [doublet of pentets, $J(H, CH_3) = 4.0$ Hz, $J(o\text{-}F, CH_3) = 1.2$ Hz, 3 H], 1.52 (triplet, $J(p\text{-}(CH_3)_3C, o\text{-}F) = 2.2$ Hz, 18 H), and 5.23 ppm [octet, $J(H, CH_3) \approx J(H, o\text{-}F) = 4.0$ Hz, 1 H]. The ^{19}F NMR indicated *para* orientation of the tert-butyl groups by an A_2B_2 pattern at —128.5 (4 F) and —137.7 ppm (4 F) IR: 2190 cm^{-1} (Si—H); 1642, and broad band between 1410 and 1500 cm^{-1} (C_6F_4) Molecular ion: *m/e* 454 (mol. wt. 454). (Found: C, 55.45; H, 4.86; F, 32.99. $C_{21}H_{22}F_8Si$ calcd. C, 55.50; H, 4.88; F, 33.44%.)

Reaction of bis(p-tert-butyltetrafluorophenyl)methylsilane (VIII) with methyllithium

To 1.13 g (0.0025 mole) of bis(*p*-tert-butyltetrafluorophenyl)methylsilane in 30 ml of Et_2O at —50° was added 0.005 mole MeLi. At the end of 1 h the reaction mixture was poured over a large excess of freshly crushed dry ice. After warming to room temperature, about 30 ml of 1 *M* HCl was added. The ether layer was separated, washed with H_2O and extracted with $NaHCO_3$ solution. After acidification there was obtained *p*-tert-butyltetrafluorobenzoic acid, m.p. 126—127° (1.08 g, 86%). The ^1H NMR exhibited peaks at δ 1.53 [triplet, $J(H, o\text{-}F) = 2.2$ Hz, 9 H], and 12.2 ppm (broad singlet, 1 H). The ^{19}F NMR showed an A_2B_2 pattern at —137.4 (2 F) and —138.7 ppm (2 F). IR: 3300—2500 cm^{-1}

(COOH); 1716 cm^{-1} (C=O); 1642, 1453 cm^{-1} (C_6F_4). Molecular ion: *m/e* 250 (mol. wt. 250). (Found: C, 52.73; H, 4.08; F, 29.98. $C_{11}H_{10}F_4O_2$ calcd.: C, 52.81; H, 4.03; F, 30.37%.)

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