SOME PERFLUOROALKYL GRIGNARD REAGENTS AND THEIR DERIVATIVES

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Summary

Some perfluoroalkyl Grignard reagents have been prepared in high yields through halogen-metal exchange reactions between perfluoroalkyl iodides (R_fI) and EtMgBr. Derivatization with Me_3SiCl or Me_2HSiCl gave satisfactory yields of the corresponding silylated products in THF. However, ether was a very poor solvent for reaction of R_fMgBr with these chlorosilanes. The exchange reaction between R_fI and EtMgBr was nearly quantitative in ether as evidenced by high yields of the 1-hydroperfluoroalkanes upon hydrolysis, but the major product from the attempted silylation in ether was a *trans*-vinyl bromide [1], *i. e.*



Spectral data are presented for several new compounds.

Introduction

Perfluoroalkyl Grignard derivatives of the type R_fMgBr have been prepared by a halogen--metal exchange reaction between R_fI and RMgBr in ether $[2 - 5]^*$. Previous work in our laboratories indicated that THF was a good solvent for the formation of silyl derivatives of R_fMgBr [6] and $BrMg(CF_2)_6MgBr$ [7] types generated through halogen-metal exchange. The present study deals with the extension of our earlier work.

Results and discussion

Reaction of $n-C_{10}F_{21}I$ or $n-(CF_3)_2CFO(CF_2)_nI$ (n = 2, 4, 6 and 8) with EtMgBr in THF followed by derivatization of the perfluoroalkyl Grignard reagents with chlorosilanes or *ca*. 3 mol l^{-1} HCl gave the corresponding perfluoroalkyl derivatives (Table 1).

^{*} See Note added in proof.

Derivatives of perfluo	roalkyl Grignard re	eagents				
Perfluoroalkyl derivative (% yield)	B. p./ °C (mmHg)	$^{n}_{D}^{20}$	IR/cm ⁻¹	¹ H NMR ^d /ð in ppm	Elemental found (cal C	analysis: cd.) H
n-C ₁₀ F ₂₁ SiMe ₃ (63.0)	73 - 74 (5)	1.3248	C—F: 1245, 1210, 1150 SiMe: 850, 765	SiMe ₃ : 0.30 (s)	26.32 (26.37)	1.40 (1.53)
n-C ₁₀ F ₂₁ SiMe ₂ H (57.1)	75 (10)	1.3200	Si-H:2175 C-F: 1250, 1205, 1150 SiMe: 845, 780	SiMe ₂ : 0.38 [d, J(Me, H) = 3.8 Hz] Si-H: 4.25 (b)	25.05 (24.93)	1.07 (1.22)
R(CF ₂) ₂ SiMe ₃ ^{a,b} (65.0)	122 - 123 (micro)	1.3180	C—F: 1245, 1195, 1135 SiMe: 850, 760	SiMe ₃ : 0.29 (s)	27.03 (26.82)	$2.37 \\ (2.54)$
R(CF ₂) ₄ SiMe ₃ ^{a,b} (58.4)	54 - 55 (35)	1.3184	C—F: 1100 - 1300 SiMe: 845, 765	SiMe2: 0.31 (s)		
R(CF ₂) ₄ SiMe ₂ H ^{a,b} (67.6)	60 - 61 (80)	1.3092	Si-H: 2170 C-F: 1245, 1195, 1150 SiMe: 840, 790	SiMe ₂ : 0.38 [d, J(Me, H) = 3.8 Hz] Si-H: 4.25 (b)	24.21 (24.33)	1.37 (1.59)
R(CF ₂) ₆ SiMe ₃ ^a (59.6)	68 - 69 (8)	1.3184	C—F: 1250, 1200, 1150 SiMe: 850, 765	SiMe ₂ : 0.31 (s)	26.05 (25.82)	1.37 (1.63)
R(CF ₂) ₆ SiMe ₂ H ^a (68.8)	52 - 53 (10)	1.3110	Si-H: 2175 C-F: 1100 - 1300 SiMe: 840, 785	SiMe ₂ : 0.39 [d, J(Me, H) = 3.7 Hz] Si-H: 4.20 (b)	24.43 (24.28)	1.10 (1.30)
R(CF ₂) ₈ SiMe ₃ ^a (62.3)	83 - 84 (10)	1.3188	C—F: 1250, 1200, 1155 SiMe: 855, 770	SiMe ₃ :0.30 (s)	25.80 (25.52)	1.43 (1.38)
R(CF ₂) ₆ H ^a (68.5)	124 - 125 (micro)	I	C—H: 2985 C—F: 1100 - 1300	$CF_2H: 6.08 [tt, J(CF_2, H) = 52 Hz, J(CF_2, H) = 51 Hz, J(CF_2CF_2, H) = 5 Hz]$		
$ m R(CF_2)_8H^a$ (63.1)	52 - 53 (50)	1	C—H: 2990 C—F: 1100 - 1300	$CF_{2}H: 6.00 [tt, J(CF_{2}, H) = 52 Hz, J(CF_{2}, E) = 5 Hz, J(CF_{2}CF_{2}, H) = 5 Hz$	22.50 (22.55)	0.31 (0.17)
n-C ₁₀ F ₂₁ H ^c (84.0)	33.5 - 34.5 (m. p.)	I	C—H: 2995 C—F: 1100 - 1300	$CF_{2}H: 5.85 [tt, J(CF_{2}, H) = 51.5 Hz, J(CF_{2}, H) = 51.5 Hz, J(CF_{2}CF_{2}, H) = 5 Hz]$		
${}^{a}R = (CF_{3})_{2}CFO. {}^{b}Pr_{1}$ d = doublet, t = triple:	epared earlier by and $b = broad$, $tt = tr$	n in situ tec iplet of trip	hnique [9]. ^c Ref. 8. ^d The foll dets.	owing abbreviations are used:	s = singlet,	

TABLE 1

The reaction conditions have a significant effect upon the yields of the perfluoroalkylsilanes. THF has been found to be a good medium. Long reaction time (6 - 8 h) at low temperature (-78 °C) was essential in promoting moderately high yields.

In contrast, derivatization of $n-C_{10}F_{21}MgBr$ with Me₂RSiCl in ether provided only *ca.* 5% yields of the silyl derivative, and none was observed in the corresponding $n-(CF_3)_2CFO(CF_2)_nMgBr$ reactions. The main product was a *trans*-vinyl bromide compound [1], *i. e.*

$$\begin{bmatrix} R_{f} \\ F \end{bmatrix} = C \begin{bmatrix} F \\ Br \end{bmatrix}$$

It appears that silvlation of R_fMgBr requires a medium of higher dielectric constant (*i. e.* THF) than is provided by ether. Differences in the thermal stability of the R_fMgBr reagents in ether and THF at low temperature were not sufficient to account for the observed results.

Other active trimethyl
silylating reagents may be effective in characterizing
 $R_f MgBr$ in ether as well as in THF.

Experimental

All reactions were carried out in an atmosphere of pre-purified nitrogen. Glassware was dried at 120 °C, assembled while hot and flushed with nitrogen. Ether and THF were dried by standard methods. Distillation of a mixture of telomer iodides (Thiokol Corp.) provided pure $n-C_{10}F_{21}I$. Perfluoro-(isopropoxy)alkyl iodides (Allied Chemical Corp.) were shaken with sodium thiosulfate and distilled before use.

IR spectra were taken as thin films. UV spectra were recorded in hexane on a Cary model 14R spectrometer. The UV spectra of the perfluoroalkyl iodides gave $\lambda_{max.}$ 272.0 ± 0.5 with (ϵ) 220 - 300 while silyl derivatives gave $\lambda_{max.}$ 232.5 ± 0.5 with (ϵ) 15 - 30. ¹H NMR (CCl₄/CFCl₃) spectra were recorded on a Varian HA-60 spectrometer. ¹⁹F NMR (CCl₄/CFCl₃) spectra were obtained with a Varian HR-100 spectrometer tuned to 94.075 MHz and peak center positions are reported in ppm upfield (-) from CFCl₃ internal standard. Preparative GC was performed on either a F and M model 500 or Hewlett-Packard model 776GC with 15% SE-30 on 60 - 80 mesh Chromosorb[®] P packed 3 m columns.

TABLE 2

10							
15F	NMR	spectral	data	of some	perfluoroalky	yl Grignard	derivatives

Compou Chemica	und ^a al shift in	ppm (—)								
CF ₃ (81.7)	CF ₂ (127.0)	CF ₂	CF ₂	CF_2	CF ₂	CF ₂	CF ₂	CF_2	CF ₂ (129.0)	SiMe ₃
		· <u> </u>	- <u>n</u> -	(122.5, (123.3,	10F) 2F)			(119.6)		
CF ₃ (81.7)	CF ₂ (126.9)	CF ₂	CF_2	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂ (120.7)	CF ₂ (127.2)	SiMe ₂ H
				(122.6, (123.4,	10F) 2F)					
(CF ₃) ₂	CFO (146.0)	CF_2	CF_2 (126.0)	$(CF_2)_2$ (122.8)	CF_{2} (119.6)	CF_2 (129.1)	SiMe ₃			
(81.5, 8	(110.0) F)		(120.0)	(122.0)	(110.0)	(120.1)				
(CF ₃) ₂	CFO (145.8)	CF ₂	CF_2	$(CF_2)_2$	CF_2	CF_{2}	SiMe ₂ H			
(81.2, 8	(140.8) F)		(120.0)	(122.2)	(120.0)	(127.1)				
(CF ₃) ₂	CFO (146.0)	CF₂ ∟	CF ₂ (125.9)	$({\rm CF}_2)_4$ (122.7)	CF ₂ (119.5)	CF ₂ (129.1)	SiMe ₃			
(81.5, 8	F)									
(CF ₃) ₂ (81.0)	CFO (146.0)	CF ₂ (82.7)	CF ₂ (130.5)	SiMe ₃						
$(CF_3)_2$ (81.2)	CFO (145.4)	CF ₂ ((80.7) (CF ₂ (125.1)	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂ (129.8)	CF ₂ H (137.7)	
(01.2)					(122.0, (123.7,	6F) 2F)				
$(CF_3)_2$ (81.2)	CFO (145.5)	CF_2 (80.8)	CF_2 (125.3)	CF ₂	CF ₂	$CF_2 CF_2H$ (130.0) (137.8	CF_2H (137.8)			
(01.2)	(110.0)	(00.0)	(120.0)	(122.7, (123.8,	2F) 2F)	(100.0)	(101.0)			
CF _{3.}	CF_2	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂	CF_2	CF_2H	
(01.4)	(120.3)			(121.8, (122.8, (123.2, (123	8F) 2F) 2F)			(129.4)	(130.2)	

^a Integrated intensities always indicated the expected number of fluorine nuclei for a given peak.

General preparation of perfluoroalkylsilanes

The perfluoroalkyl iodide (x mol) was treated with EtMgBr (1.1 x mol)in THF (75 cm³ per 0.01 mol) at -78 °C and stirred at this temperature for *ca.* 45 min. The chlorosilane (1.1x mol) was added and the reaction mixture was stirred at -78 °C for 6 - 8 h, slowly warmed to room temperature and the solvent was removed under reduced pressure. The pot residue was then extracted with hexane. Subsequent distillation on a spinning-band column afforded the desired perfluoroalkylsilanes (Tables 1 and 2).

Preparation of 1-hydroperfluoro-n-decane

The Grignard reagent from $n-C_{10}F_{21}I$ (6.46 g, 0.01 mol) and EtMgBr (0.01 mol) in ether (75 cm³) at -78 °C was hydrolyzed with 3 mol l⁻¹ HCl. After warming to room temperature, additional ether (*ca.* 50 cm³) was added. The ether solution was washed (3 × 25 cm³ H₂O), dried (MgSO₄) and distilled to give 4.36 g (84%) of $n-C_{10}F_{21}H$, m.p. 33.5 - 34.5 °C (cited [8]: 31 - 32 °C).

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Note added in proof

We have learned that a relevant article by D. D. Denson, C. F. Smith and C. Tamborski has recently appeared in J. Fluorine Chem., 3 (1974) 247.