

SOME PERFLUOROALKYL GRIGNARD REAGENTS AND THEIR DERIVATIVES

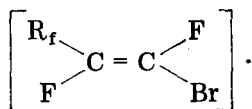
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Summary

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.

TABLE 1

Derivatives of perfluoroalkyl Grignard reagents

Perfluoroalkyl derivative (% yield)	B. p./ °C (mmHg)	n_D^{20}	IR/cm ⁻¹	¹ H NMR ^d , δ in ppm		Elemental analysis: found (calcd.)	
				C	H	C	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	SiMe ₂ : 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)	—	C-H: 2985 C-F: 1100 - 1300	CF ₂ H: 6.08 (tt, J(CF ₂ , H) = 52 Hz, J(CF ₂ CF ₂ , H) = 5 Hz)			
R(CF ₂) ₈ H ^a (63.1)	52 - 53 (50)	—	C-H: 2990 C-F: 1100 - 1300	CF ₂ H: 6.00 (tt, J(CF ₂ , H) = 52 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.)	—	C-H: 2995 C-F: 1100 - 1300	CF ₂ H: 5.85 (tt, J(CF ₂ , H) = 51.5 Hz, J(CF ₂ CF ₂ , H) = 5 Hz)			

^aR = (CF₂)₃CFO. ^bPrepared earlier by an *in situ* technique [9]. ^cRef. 8. ^dThe following abbreviations are used: s = singlet, d = doublet, t = triplet, b = broad, tt = triplet of triplets.

TABLE 2

¹⁹F NMR spectral data of some perfluoroalkyl Grignard derivatives

Compound ^a											
Chemical 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 (119.6)	CF ₂ (129.0)	SiMe ₃
				(122.5, 10F)							
				(123.3, 2F)							
CF ₃ (81.7)	CF ₂ (126.9)	CF ₂	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, 10F)							
				(123.4, 2F)							
(CF ₃) ₂ (81.5, 8F)	CFO (146.0)	CF ₂	CF ₂	(CF ₂) ₂ (122.8)	CF ₂ (119.6)	CF ₂ (129.1)	SiMe ₃				
(CF ₃) ₂ (81.2, 8F)	CFO (145.8)	CF ₂	CF ₂	(CF ₂) ₂ (122.2)	CF ₂ (120.0)	CF ₂ (127.1)	SiMe ₂ H				
(CF ₃) ₂ (81.5, 8F)	CFO (146.0)	CF ₂	CF ₂	(CF ₂) ₄ (122.7)	CF ₂ (119.5)	CF ₂ (129.1)	SiMe ₃				
(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)		
				(122.0, 6F)							
				(123.7, 2F)							
(CF ₃) ₂ (81.2)	CFO (145.5)	CF ₂ (80.8)	CF ₂ (125.3)	CF ₂	CF ₂	CF ₂	CF ₂ H (137.8)				
				(122.7, 2F)		(130.0)					
				(123.8, 2F)							
CF ₃ (81.4)	CF ₂ (126.3)	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂ (129.4)	CF ₂ H (138.2)		
				(121.8, 8F)							
				(122.8, 2F)							
				(123.2, 2F)							

^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 (1.1 x 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 $n\text{-C}_{10}\text{F}_{21}\text{I}$ (6.46 g, 0.01 mol) and EtMgBr (0.01 mol) in ether (75 cm^3) at -78°C was hydrolyzed with $3\text{ mol l}^{-1}\text{ HCl}$. After warming to room temperature, additional ether (*ca.* 50 cm^3) was added. The ether solution was washed ($3 \times 25\text{ cm}^3\text{ H}_2\text{O}$), dried (MgSO_4) and distilled to give 4.36 g (84%) of $n\text{-C}_{10}\text{F}_{21}\text{H}$, m.p. $33.5 - 34.5^\circ\text{C}$ (cited [8]: $31 - 32^\circ\text{C}$).

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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.