THERMAL DECOMPOSITION OF SOME PERFLUOROALKYL GRIGNARD REAGENTS. SYNTHESIS OF *TRANS*-1-HALO- AND *TRANS*-1-ALKYLPERFLUORO-VINYL COMPOUNDS

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Summary

The thermal decomposition of perfluoroalkyl Grignard reagents (R_fMgX) , formed from halogen-metal exchange with alkyl Grignard reagents, provides a good synthetic route to *trans*-1-haloperfluorovinyl compounds.

The decomposition of R_fMgX (where X = Cl, Br, I) in the presence of RMgX generally leads to a mixture of *trans*-1-alkylperfluorovinyl and *trans*-1-haloperfluorovinyl compounds. However, the choice of RMgX with respect to both the alkyl group and halogen is critical as regards the formation of the *trans*-1-alkylperfluorovinyl compounds.

Several possible mechanisms are suggested to account for the experimental observations.

Introduction

Although many reports [1 - 19] in the literature deal with the preparation and synthetic applications of perfluoroalkyl Grignard reagents, only little attention has been given to the thermal decomposition of these compounds. It has been reported that the products from the reaction of trifluoromethyl iodide with Mg/Hg are tetrafluoroethylene and fluorocarbon polymers [3]. A radical mechanism was suggested for the decomposition of perfluoropropylmagnesium iodide in ether in order to explain the formation of certain by-products (C_3F_7H , CH_3CHO , $C_3F_7CH(OH)CH_3$, etc.) [3]. Significant studies by Tatlow and co-workers have shown that perfluorobicyclo(2,2,1)heptan-1-yl magnesium iodide (or bromide) has a greater thermal stability than non-bridgehead perfluoroalkyl Grignard reagents, and it has been suggested that this compound decomposes *via* transient bridgehead olefin or diradical formation [18, 19]. The decomposition of perfluoroisopropyl Grignard and lithium reagents gave perfluoropropene in high yield [7]. Our preliminary investigations [15] and work recently reported by Tamborski and co-workers [17] have shown that a *trans*-1bromoperfluorinated olefin is the major product from the thermal decomposition of certain perfluoroalkylmagnesium bromides in ether. This present report describes in greater detail the nature and scope of this novel route to some *trans*-substituted fluorinated olefins.

Results and discussion

When R_fMgX compounds ($R_f = n \cdot C_6 F_{13}$, $n \cdot C_8 F_{17}$, $n \cdot C_{10} F_{21}$) were thermally decomposed in ether or a pentane/ether solvent mixture which contained only a small amount of ether from the RMgX exchange agent, *trans*-1-haloperfluorinated terminal olefins [$R_fCF=CFX$; X = Cl, Br, I] were formed. Yields (Table 1) in the case of the chloro and bromo Grignard reagents were generally in the range 40 - 55%. Co-products of the decomposition included $R_fCF=CF_2$ (5 - 10%), R_fH (*ca.* 5%), an isomeric mixture of $R_fCF_2CF_2CF=CFR_f$ (15 - 25%) and several unidentified very minor highboiling products. No evidence was found for any of the *cis*-perfluorovinyl halides, even when the reaction was followed by low-temperature ¹⁹F NMR or by VPC analysis of hydrolyzed aliquots.

The exchange reaction between R_fI and RMgX has been employed to prepare the R_fMgX species. Such exchange reactions have been found to be rapid and quantitative at low temperatures with EtMgBr or PhMgBr [4 - 6, 16]. The exchange with non-fluorinated alkyl iodides has usually been thought to be an equilibrium process [20 - 23]:

 $RMgX + R'X \implies RX + R'MgX$

In the case of the reaction with R_fI , it was found that the position of the equilibrium was insensitive to the addition of excess RI, and to varying the nature of RMgX from MeMgX to EtMgX and from i-PrMgX to PhMgX. The methyl or ethyl Grignard reagents were generally employed since the fluorinated products were readily removed from the more volatile MeI or EtI. It should be noted that the exchange between an alkyl-lithium and alkyl iodide is an equilibrium process [24], and ESR and CIDNP experiments have demonstrated the presence of radicals in hydrocarbon solutions, but not generally in ethereal solvents [25].

Isolated yields of the *trans*-1-iodoperfluorovinyl compounds (*ca.* 20 - 30%, see Table 1) were lower than those obtained for the corresponding chloro and bromo compounds under identical reaction conditions. Exchange of RMgI (5% excess) with R_fI in ether as a solvent was incomplete since *ca.* 20% of the R_fI was recoverable. A 5% excess of RMgCl or RMgBr completely consumed the R_fI compound, while a 50 - 75% excess of RMgI was required in ether.

Preparation of some trans-R_fCF=CFX compounds and other fluorinated olefins

R _f I (mmol)	RMgX (mmol)	Solvent (cm ³)	Time at room tem- perature (h)	% Yield R _f CF=CFX ^a
$C_{10}F_{21}I$ (10.0)	EtMgCl (10.5)	Et ₂ O (100)	3	43 [nc]
$C_{10}F_{21}I$ (10.0)	MeMgCl ^b (20.0)	Et ₂ O (100)	2	35 C ₈ F ₁₇ CF=CFMe (26) [nc] C ₈ F ₁₇ CF=C(Me) ₂ (8) [nc]
$C_{10}F_{21}I$ (10.0)	MeMgCl ^b (20.0)	Et ₂ O (150)	2	21 C ₈ F ₁₇ CF=CFMe (7) C ₈ F ₁₇ CF=C(Me) ₂ (38)
$C_{10}F_{21}I$ (10.0)	EtMgBr ^c (10.5)	THF (75)	2	$C_8F_{17}CF=CF_2^d (71)^e$
$C_{10}F_{21}I$ (10.0)	EtMgBr (11.0)	Et ₂ O (60)	2	38 [nc]
$C_{10}F_{21}I$ (10.0)	EtMgBr (10.5)	Et ₂ O (75)	3	46
$C_{10}F_{21}I$ (50.0)	EtMgBr (55.0)	Pentane (250)	3	32 C ₈ F ₁₇ CF=CFEt (4) [nc]
C ₁₀ F ₂₁ I (20.0)	MeMgBr (21.0)	Et ₂ O (150)	3	53
$C_{10}F_{21}I$ (10.0)	MeMgBr (20.0)	Et ₂ O (100)	1	20 C ₈ F ₁₇ CF=CFMe (17) C ₈ F ₁₇ CF=C(Me) ₂ (38)
$C_{10}F_{21}I$ (10.0)	MeMgBr (40.0)	Et ₂ O (100)	1	5 C ₈ F ₁₇ CF=CFMe (20) C ₈ F ₁₇ CF=C(Me) ₂ (63)
$C_{10}F_{21}I$ (10.0)	EtMgI (10.5)	Et ₂ O (75)	18	21 [nc]
$C_{10}F_{21}I$ (10.0)	EtMgI (10.0)	Pentane (60)	3	29
$C_{10}F_{21}I$ (10.0)	EtMgI (10.5)	Pentane (125)	3	36
$C_{10}F_{21}I$ (10.0)	MeMgI (10.5)	Et ₂ O (75)	18	28
$C_{10}F_{21}I$ (10.0)	MeMgI (20.0)	Et ₂ O (75)	3	C ₈ F ₁₇ CF=CFMe (<i>ca.</i> 5) C ₈ F ₁₇ CF=CMe ₂ (16) C ₈ F ₁₇ CF=CFH (40) [nc]
C ₁₀ F ₂₁ I (10.0)	MeMgI (40.0)	Et ₂ O (100)	3	C ₈ F ₁₇ CF=CFMe (17) C ₈ F ₁₇ CF=C(Me) ₂ (52) C ₈ F ₁₇ CF=CFH (ca. 10)
$C_8F_{17}I$ (10.0)	MeMgCl (10.5)	Et ₂ O (100)	3	40 [nc]

TABLE 1 (continued)

R _f I (mmol)	RMgX (mmol)	Solvent (cm ³)	Time at room tem- perature (h)	% Yield R _f CF=CFX ^a
C ₈ F ₁₇ I (10.0)	MeMgCl ^b (20.0)	Et ₂ O (100)	2	32 C ₆ F ₁₃ CF=CFMe (30) [nc] C ₆ F ₁₃ CF=C(Me) ₂ (7) [nc]
$C_8F_{17}I$ (20.0)	EtMgCl (21.0)	Et ₂ O (150)	3	38
$C_8F_{17}I$ (10.0)	EtMgCl (40.0)	Et ₂ O (100)	2	11 C ₆ F ₁₃ CF=CFEt (45) [nc]
C ₈ F ₁₇ I (10.0)	EtMgCl, MgBr ₂ (10.5, 10.0)	Et ₂ O (125)	3	29 C ₆ F ₁₃ CF=CFBr (34)
$C_8F_{17}I$ (10.0)	i-PrMgCl (40.0)	Et ₂ O (100)	2	7 C ₆ F ₁₃ CF=CFPr-i (44) [nc]
C ₈ F ₁₇ I (10.0)	PhCH ₂ MgCl (40.0)	Et ₂ O (100)	2	8 C ₆ F ₁₃ CF=CFCH ₂ Ph (35) [nc
$C_8F_{17}I$ (10.0)	MeMgBr ^c (10.5)	THF (75)	3	$C_6F_{13}CF = CF_2^d (30)^e$
$C_8F_{17}I$ (10.0)	MeMgBr (10.5)	Et ₂ O (125)	3	50
C ₈ F ₁₇ I (10.0)	MeMgBr, MgBr ₂ (10.5, 10.0)	Et ₂ O (125)	3	65
C ₈ F ₁₇ I (10.0)	MeMgBr (20.0)	Et ₂ O (100)	1	26 C ₆ F ₁₃ CF=CFMe (8) C ₆ F ₁₃ CF=C(Me) ₂ (37)
$C_8F_{17}I$ (10.0)	MeMgBr (40.0)	Et ₂ O (100)	1	3 C ₆ F ₁₃ CF=CFMe (21) C ₆ F ₁₃ CF=C(Me) ₂ (61)
C ₈ F ₁₇ I (10.0)	$\begin{array}{l} MeMgBr^{f} + EtMgCl\\ (10.5) & (15.0)\\ + i \mbox{-} PrMgCl +\\ (15.0)\\ PhCH_2MgCl\\ (15.0) \end{array}$	Et ₂ O (100)	2	$C_6F_{13}CF=CFEt (25)$ $C_6F_{13}CF=CFPr-i (28)$ $C_6F_{13}CF=CFCH_2Ph (23)$
C ₈ F ₁₇ I (20.0)	EtMgBr (21.0)	Et ₂ O (150)	3	47
C ₈ F ₁₇ I (5.0)	EtMgBr (20.0)	Et ₂ O (50)	1	5 C ₆ F ₁₃ CF=CFH (50) [nc] C ₆ F ₁₃ CF=CFEt (8)
C ₈ F ₁₇ I (5.0)	i-PrMgBr (20.0)	Et ₂ O (50)	1	ca. 2 C ₆ F ₁₃ CF=CFH (53) C ₆ F ₁₃ CF=CFPr-i (9)
C ₈ F ₁₇ I (10.0)	PhMgBr (10.5)	Et ₂ O (125)	3	52

R _f I (mmol)	RMgX (mmol)	Solvent (cm ³)	Time at room tem- perature (h)	% Yield R _f CF=CFX ^a
C ₈ F ₁₇ I (20.0)	EtMgI (20.0)	Pentane (100)	3	28 [nc]
$C_8F_{17}I$ (10.0)	EtMgI (10.5)	Pentane (125)	3	49
$C_6F_{13}I$ (20.0)	EtMgBr (20.0)	Et ₂ O (75)	3	30 [nc]
$C_6F_{13}I$ (10.0)	EtMgBr (10.0)	Pentane (60)	3	26
$C_6F_{13}I$ (10.0)	PhMgBr (10.5)	Et ₂ O (125)	3	48
$C_6F_{13}I$ (10.0)	EtMgI (10.5)	Pentane (125)	3	41 [nc]
C ₆ F ₁₃ I (10.0)	EtMgI, MgI ₂ (10.5, 10.0)	Pentane, Et ₂ O (125, 50)	3	46
C ₆ F ₁₃ I (10.0)	EtMgI, MgI ₂ (10.5, 10.0)	Et ₂ O (125)	18	30

TABLE 1 (continued)

^a X = X of RMgX.

^b The product ratio from excess "MeMgCl" reactions was quite variable. MeMgCl in ether is known to deposit MgCl₂ and the amount of MgCl₂ which precipitated during the formation of MeMgCl differed in two separate preparations. Highest yields of $R_fCF=C(Me)_2$ were obtained from clear MeMgCl solutions used in high dilution.

^c RMgBr prepared in THF.

^d IR identical to that supplied by Dr. E. S. Lo for the authentic sample.

^eApproximate yield by VPC. Although we were unable to separate $C_6F_{13}CF=CF_2$

from THF by distillation, cooling (ca. -30 °C) produced a lower layer of the olefin.

 $^{\rm f}$ The RMgCl reagents were added at $-50\ ^{\circ}{\rm C}$ to the solution of ${\rm C_8F_{17}MgBr}.$

In the presence of some RMgI and R_fI arising from incomplete exchange, R_fMgI was found to be more thermally stable in ether than R_fMgBr or R_fMgCl . At room temperature, more than 18 h were required for complete decomposition of R_fMgI , whereas R_fMgCl and R_fMgBr were thermally stable to *ca*. --10 °C but decomposed rapidly above this temperature. The presence of R_fI may have some stabilizing effect on R_fMgI as has been suggested for R_fI in the presence of R_fLi [26]. An alternative suggestion is that elimination of MgFI may not be as favorable as that of MgFBr and MgFCl.

The corresponding R_fLi compounds are considerably less stable and decompose rapidly above *ca*. -75 °C to give the terminal perfluoro-olefin and *trans*-1-alkylperfluoro-olefin [26 - 29].

Several attempts were made to improve the yield of the *trans*-1-iodoperfluorovinyl compounds. Addition of excess RMgI to the ether solution resulted in a lower isolated yield of the vinyl iodide because of several competing reactions (mentioned later). Solvents of greater solvating power than ether were employed since it has been established that such solvents aid the halogen-metal exchanges involved with alkyl halides [21]. However, THF and triglyme gave very complex reaction mixtures as a result of the formation and decomposition of R_fMgI . The use of a large amount of pentane (or Skelly A) mixed with a small amount of the ether employed in the addition of the RMgX in ether significantly improved the yield of the vinyl iodides (Table 1). That the extent of the exchange was greater in this solvent system is indicated by the smaller amounts of unchanged initial R_fI (*ca.* 10%), and decomposition of R_fMgI was a much faster process than with the ether solvent alone.

Whereas the addition of MgI_2 to R_fMgI in ether did not significantly alter the yield of the *trans*-perfluorovinyl iodide, the amount of *trans*-vinyl bromide was increased by 10 - 15% when $MgBr_2$ was added to the ether solution prior to the decomposition of the R_fMgBr . It was found that a minimum addition of 75 cm³ of ether for 0.01 mol of R_fI was necessary to minimize the formation of high-boiling by-products.

Decomposition of $R_fCF_2CF_2MgBr$ in THF gave $R_fCF=CF_2$ and anisomeric mixture of $R_fCF_2CF_2CF=CFR_f$ together with numerous very minor high-boiling by-products. The VPC yield of $R_fCF=CF_2$ (*ca.* 30 - 70%) was apparently dependent on the experimental conditions. Surprisingly, no *trans*- $R_fCF=CFBr$ was formed. The increased solvation by THF [30] may decrease the electrophilic character of R_fMgBr and thereby make the mechanisms suggested later less favorable. In addition, THF may substantially alter the position of the Schlenk [31] equilibrium at lower temperatures in favor of an $(R_f)_2Mg\cdot MgBr_2$ species or some other. Such suggestions are in accord with the observation that the solvent is apparently vital in determining the position of the Schlenk equilibrium for alkyl Grignard reagents [32 - 35]. The results of low-temperature ¹⁹F NMR examination of the THF reaction mixtures were inconclusive (partly due to solubility problems which were not encountered in ether), but indicated the presence of more than the one species (Table 3) which is observed in ether.

Reactions employing excess RMgX

When R_fMgX was allowed to thermally decompose in the presence of excess RMgX, a *trans*-1-alkylperfluorovinyl compound was formed. The yield (Table 1) was highly dependent upon the particular RMgX reagent used. Methyl Grignards (X = Cl, Br, I) were the only RMgX species which gave a dialkyl-substituted fluoro-olefin. A large excess of MeMgX (see footnote b, Table 1) resulted in high isolated yields of the 1,1-dimethyl-perfluorovinyl compound. The lack of any apparent reaction between MeMgBr and $R_fCF=CFMe$ in ether precluded the preparation of $R_fCF=C(Me)_2$ by that means.

Trans-perfluorovinyl chlorides and bromides were also isolated from reactions involving excess MeMgCl or MeMgBr, but no evidence was found

TABLE 2

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Compound	B.p./ °C/mmHg	n ²⁰	$\frac{\mathrm{IR}[\nu(\mathrm{C=C})]}{(\mathrm{cm}^{-1})}$	Mass spectrum ^a [M ⁺ (% of base) base ^b]	Analysis (% C (calcd.)	Xd %	
C8F17CF=CFCI	92/60	1.3115	1718	516, 518 (2) 147, 149	23.19 (23.25)	6.77 (6.86)	
C ₈ F ₁₇ CF=CFBr	91/40	1.3234	1709	560, 562 (7) 191, 193	21.70 (21.41)	14.29 (14.24)	
C ₈ F ₁₇ CF=CFI ^e	101/40	1.3423	1689	608 (16) 239	19.67 (19.76)	20.50 (20.87)	
C ₆ F ₁₃ CF=CFCI	79/130	1.3082	1717	416, 418(2)147, 149	23.33(23.07)	8.01 (8.51)	
C ₆ F ₁₃ CF=CFBr	79/92	1.3220	1708	460, 462 (8) 191, 193	20.80 (20.84)	17.51 (17.34)	
C ₆ F ₁₃ CF=CFI	76/40	1.3461	1687	508 (21) 239	18.92 (18.92)	24.48 (24.98)	
C4F9CF=CFBr	59/130	1.3195	1706	360, 362 (8) 191, 193	19.68 (19.97)	22.16 (22.14)	
C4F9CF=CFI	70/130	1.3505	1683	408 (28) 239	17.79 (17.66)	30.87 (31.07)	
C ₈ F ₁₇ CF=CFMe	91/60	1.3080	1737	496 (3) 127	26.86 (26.63)	0.59 (0.61)	
C ₈ F ₁₇ CF=CFEt	95/60	1.3140	1732	510 (4) 141	28.03 (28.25)	1.03 (0.99)	
C ₈ F ₁₇ CF=CFH	78/40	(< 1.3)	1722	482 (1) 113	24.72 (24.91)	0.46 (0.21)	

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	mHg	nD ²⁰	$\operatorname{IR}[\nu(\operatorname{C=C})]$ (cm^{-1})	Mass spectrum ^a [M ⁺ (% of base) base ^b]	Analysis (% C (calcd.)	X ^d
C8F17CF=CMe2 84/2	20	1.3205	1712	492 (5) 123 ^f	29.55 (29.28)	1.31 (1.23)
C ₆ F ₁₃ CF=CFMe 70/6	60	1.3042	1739	396 (3) 127	27.33 (27.29)	0.85 (0.76)
C ₆ F ₁₃ CF=CFEt 74/6	60	1.3120	1733	410(4)141	29.20 (29.28)	1.29 (1.23)
C ₆ F ₁₃ CF=CFPr-i 82/6	60	1.3182	1726	$424\ (11)\ 409^{8}$	31.19 (31.15)	1.68 (1.66)
$C_6F_{13}CF=CFCH_2Ph$ 84/3	<i>ი</i> ე	1.3780	1732	472 (92) 153 ^h	38.42 (38.15)	1.49 (1.50)
C ₆ F ₁₃ CF=CMe ₂ 86/1	100	1.3195	1709	392 (5) 123 ^f	30.38 (30.63)	1.45 (1.54)

 a Compounds which contained bromine gave M^{\star} peaks in a 1:1 ratio, and compounds containing chlorine gave M^{\star} peaks in a 3:1 ratio as expected.

^b The base peak $(C_3F_4X^{\dagger})$ corresponded to the following fragmentation. $R_fCF_2^{\dagger}CF_2CF=CFX \rightarrow [CF_2CF=CFX]^{\dagger} + [CF_3CF_2]^{\dagger} + [CF_3CF_2]^{\dagger}$, etc.

^c Most compounds were too volatile for satisfactory fluorine analysis.

^d X refers to the particular halogen (Cl, Br, I) in the first eight compounds, and to hydrogen in the last nine compounds. ^e %F 59.15; calcd. 59.37.

 $\begin{array}{c} {}^{f} \left[{\rm CF}_{2} {\rm CF} {\rm = CMe}_{2} \right]^{\dagger}. \\ {}^{g} \left[{\rm M}^{\dagger} {\rm - Me} \right]. \\ {}^{h} \left[{\rm FC} {\rm = CF} {\rm CH}_{2} {\rm Ph} \right]^{\dagger}. \end{array}$

TABLE 3

Some NMR spectral data^a on trans-R_fCF=CFX compounds and other fluorinated olefins

Trans-R _f CF=CFX compound									
Chemic	al shifts ^b	(ppm)	(Coupling c	onstant	s (Hz)	<u> </u>		
CF3 ^c	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂	CF ₂ ^{*d}	, F _a	
-81.6	-126.9		-122 -123	2.7, 6F 5.5, 2F		-124	4.0 C / F _b		
$X = F_c$									
CF ₂ *	-118.4			$I(\mathbf{F}_{n}, \mathbf{F}_{n})$	= 1	16	$J(\mathbf{F}_{\mathbf{h}}, \mathbf{F}_{\mathbf{a}})$	= 40	
F,	-105.6		د	(-a, -b) $I(F_{a}, F_{a})$	=	51	$J(CF_{0}^{*}, F_{0})$	≅ 5.5	
F _b	-190.0			(CF ₂ *, F ₂) = :	27	2 , - c/		
F _c	- 89.1			. 2 . 4					
X = Cl									
CF_2 *	117.7			$I(F_a, F_b)$	= 13	34	J(CF ₂ CF ₂ , F	a) ≅ 5.4	
F _a			J	(CF ₂ *, F ₂) = :	27	<u> </u>	a,	
F _b	-160.3								
X = Br									
CF ₂ *	-117.5		J	$(\mathbf{F}_{a}, \mathbf{F}_{b})$	= 14	41	J(CF ₂ CF ₂ , F	_) ≅ 5.5	
F _a	-105.8		ز	(CF ₂ *, F.) = :	27.5		a,	
Γ _b	-153.8			. 2 / a	, ,				
X = I									
CF ₂ *	-116.8		j	(F_a, F_b)	= 1	51	$J(CF_2CF_2, F$	_a)≅ 5.5	
Fa	-106.2		J	(CF ₂ *, F _a) = :	26	· <u> </u>		
F _b	-145.2								
X = H									
CF ₂ *	-118.8		J	$(\mathbf{F}_{a}, \mathbf{F}_{b})$	= 13	35	$J(\mathbf{F}_a, \mathbf{H})$	= 71	
Fa	-164.4		J	(CF ₂ *, F _c) = 5	25	$J(\mathbf{F_{h}}, \mathbf{H})$	= 5.1	
Fb	-175.7				-				
H	7.37	7							
X = CH	3								
CF ₂ *	-117.3		J	(F_a, F_b)	= 13	33	$J(CH_3, F_b)$	= 6.0	
Fa	-131.0		J	(CH_3, F_a)	= :	16.9	$J(CH_3, CF_2*$) = 2.4	
F _b	-171.3								
CH ₃	2.13	3							

TABLE 3 (continued)

Trans-F	R _f CF=CFX cor	npound					
Chemic	al shifts ^b (ppn	n)	Coupling constants (Hz)				
X = CH	2 ₂ CH ₃						
CF_2^*	-117.4		$J(\mathbf{F}_{a}, \mathbf{F}_{b})$	= 133			
Fa	-139.1		$J(CF_2^*, F_a)$	\cong 27			
F _b	-172.5		$J(CH_2, F_a)$	= 21.5			
CH_2	2.49						
CH_3	1.21		$J(\mathrm{CH}_3,\mathrm{CH}_2)$	$\cong J(\mathrm{CH}_2,$	$(\mathbf{F_b}) \cong 7.2$		
CF ₃	CF ₂	CF ₂	CF ₂	CF ₂	CF_{2}^{*} F_{a}		
81.6	-126.9	-122.4	to123.4	-124.0	$\mathbf{F}_{\mathbf{b}}$		
$X = F_c$							
CF ₂ *	-118.2		$J(\mathbf{F}_{a}, \mathbf{F}_{b})$	= 117	$J(\mathbf{F}_{\mathbf{h}}, \mathbf{F}_{\mathbf{c}}) = 41$		
F _a	-105.6		$J(\mathrm{CF}_2^*, \mathrm{F}_a)$	= 27	$J(\mathrm{CF}_2^*, \mathrm{F}_c) \cong 5.3$		
Fb	-189.6		$J(F_a, F_c)$	= 52			
$\mathbf{F}_{\mathbf{c}}$	- 89.2						
X = Cl							
CF_2^*	-117.6		$J(\mathbf{F}_{a}, \mathbf{F}_{b})$	= 135	$J(\underline{\mathrm{CF}}_{2}\mathrm{CF}_{2}, \mathbf{F}_{a}) \cong 5.4$		
Fa	-107.4		$J(CF_2^*, F_a)$	= 27			
Fb	-159.7						
X = Br							
CF_2^*	-117.6		$J(\mathbf{F}_{\mathbf{a}}, \mathbf{F}_{\mathbf{b}})$	= 141	$J(\underline{CF}_2CF_2, F_a) \cong 5.5$		
F_a	-105.7		$J(CF_2^*, F_a)$	= 26			
F _b	-154.0						
X = I							
CF_2^*	-116.8		$J(\mathbf{F}_{a}, \mathbf{F}_{b})$	= 149	$J(\underline{CF_2}CF_2, F_a) \cong 5.5$		
Fa	106.8		$J(CF_2^*, F_a)$	= 26.5			
Fb	-144.9						
X = CH	, 3						
CF_2^*	-117.6		$J(\mathbf{F}_{a}, \mathbf{F}_{b})$	= 133	$J(CH_3, F_b) = 6.0$		
Fa	130.8		$J(\mathrm{CF}_2^*, \mathrm{F}_a)$	\cong 27	$J(CH_3, CF_2^*) = 2.4$		
Fb	-171.3		$J(CH_3, F_a)$	= 17.2			
CH ₃	2.15						

Trans-R _f CF=CFX compound							
Chemica	al shifts ^b (pp	m)	Coupling constants (Hz)				
X = CH	$_2CH_3$		<u> </u>				
CF_2^* F_a F_b CH_2 CH_3 $X = CH_1$	-117.5 -139.0 -172.2 2.53 1.25 $(CH_2)_2$		$J(F_a, F_b)$ $J(CF_2^*, F_a)$ $J(CH_2, F_a)$ $J(CH_3CH_2)$	= 133 ≈ 27 = 21.5 = 7.2 $\approx J(CH_2, 1)$	F _b)		
CF_2^* F_a F_b CH $(CH_3)_2$	$-117.3 \\ -149.6 \\ -172.9 \\ 2.98 \\ 1.22$		$J(F_a, F_b)$ $J(CF_2^*, F_a)$ $J(CH, F_a)$ $J(CH, CH_3)$	= 133 = 27 = 29 = 7.2			
$X = CH_2$	₂ Ph						
CF ₂ * F _a F _b CH ₂ Ph	-117.2 -135.5 -170.6 3.72 7.21		$J(F_{a}, F_{b}) \\ J(CF_{2}^{*}, F_{a}) \\ J(CH_{2}, F_{a}) \\ J(CH_{2}, F_{b}) \\ J(CH_{2}, CF_{2}^{*})$	= 134 ≈ 27 = 23.2 = 6.0 = 1.5			
CF ₃	CF ₂	CF ₂	CF ₂ * 1	a			
-81.7	126.9	124.8	С=С / Ц				
X = Br							
CF ₂ * F _a F _b	-117.4 -105.6 -153.7		$J(F_a, F_b)$ $J(CF_2^*, F_a)$	= 140 $J(\underline{CF}_2)$ = 26.5	$(\mathbf{F_2}, \mathbf{F_a}) \cong 5.5$		
X = I							
CF ₂ * F _a F _b	-117.0 -106.6 -144.8		$J(\mathbf{F}_{\mathbf{a}}, \mathbf{F}_{\mathbf{b}})$ $J(\mathbf{CF}_{2}^{*}, \mathbf{F}_{\mathbf{a}})$	$= 151 \qquad J(\underline{CF}_2)$ $= 27$	$(\mathbf{F}_2, \mathbf{F}_a) \cong 5.5$		
CF ₃ (CF	⁷ 2) ₆ CF ₂ * ∕C=C	$CH_3 (1.84)$	$(t)^{e}$				
CF2* F	-113.3 -128.3	0113 (1.04	J(CH ₃ , CF ₂ *) J(CH ₃ , F)	= 2.5 = 2.7			

TABLE 3 (continued)

Trans-R_fCF=CFX compound

Chem	ical shifts ^b	(ppm)	С	oupling	constant	s (Hz)		
CF ₃	(CF ₂) ₄ CF	72 [*] C=C / F	CH ₃ (1.8 / CH ₃ (1.9	$(3, t)^{e}$ 2, d) ^e				
CF2* F	-113.3 -128.2		J	(CH ₃ , CH (CH ₃ , F)	F ₂ *) = 2 = 2	.5 .7		
Some	perfluorina	ted Gr	ignard reag	gents (Et	₂ O, - 50	°C)		
CF ₃	CF_2	CF ₂	CF_2	CF_2	CF ₂	CF_2	CF ₂ -MgBr	
80.7	7 —126.2		121. - 122.	9,6F 8,2F		-127.8	-119.5	
CF ₃	CF_2	CF_2	CF ₂	CF_2	CF ₂ -I	MgBr		
80.8	8 -126.4	1 1	21.8, 2F 22.8, 2F	-127.7	7 —119.	5		

^a CCl₄/CFCl₃ solvent mixture.

^b Chemical shifts of the CF₃ and CF₂ groups (except for CF₂*) did not vary beyond experimental error (± 0.1 ppm) over a series of compounds.

^c Triplet (9.5 Hz). Other splittings were generally unresolved in CF₃ and CF_2 groups.

^d Though unresolved in $C_8F_{17}CF=CFX$ compounds, this CF_2 group appeared as a pseudo-sextet in $C_6F_{13}CF=CFX$ and $C_4F_9CF=CFX$ (X = Cl, Br, I, R) compounds due to overlap of a doublet (25 - 27 Hz, F_a) of doublet (12 - 14 Hz, F_b) of triplets (12 - 14 Hz, CF_2).

^e Reversed assignment is possible.

for a $R_f CF = CXR$ species. A small amount of the vinyl bromide was consumed by reaction with MeMgBr.

$$trans-R_{f}CF=CFX + MeMgX \xrightarrow{Et_{2}Q, 0 \ ^{\circ}C} trans-R_{f}CF=CFMgX + MeX$$
$$H^{+}/H_{2}O$$
$$trans-R_{f}CF=CFH \xleftarrow{H^{+}/H_{2}O}$$
$$(during work-up)$$

When X = Cl no reaction was observed, with X = Br a slow exchange occurred, whilst with X = I the exchange reaction was rapid. However, *trans*-perfluoro-vinyl iodides were not isolated from reactions which employed a large excess of MeMgI in the above exchange.

A three-fold excess of ethyl-, isopropyl- or benzyl-magnesium chlorides gave isolated yields of ca. 40% of the corresponding trans-1-alkylperfluoro-

vinyl compounds. Surprisingly, in these cases, use of RMgBr ($R \neq Me$) resulted in very little formation of *trans*- $R_fCF=CFR$.

Mechanistic implications

One mechanism which we considered for the formation of *trans*-R_fCF=CFX (or *trans*-R_fCF=CFR) compounds involved β -elimination of MgXF followed by nucleophilic attack on the resultant olefin by MgXF (or RMgX). Small amounts of the terminal perfluoro-olefin were always observed, and such olefins are very susceptible to nucleophilic substitution (predominantly of the fluorine *trans* to the perfluoroalkyl group)[36]. If this were the reaction path, however, one might expect the more polar and basic solvent THF to facilitate the reaction observed in ether or ether/ pentane solvents. This is clearly not the case. In addition, MgBr₂, MgI₂ or RMgX did not react with C₆F₁₃CF=CF₂ or C₈F₁₇CF=CF₂ under the same reaction conditions. (Some other fluoro-olefins are more reactive with certain Grignard reagents in ether [37 - 39].)

$$R_{f}CF=CF_{2} + RMgX \xrightarrow{Et_{2}O}_{20 °C, 3h} R_{f}CF=CFR \text{ (no reaction)}$$

$$R_{f}CF=CF_{2} + MgX_{2} \xrightarrow{Et_{2}O}_{R,T} R_{f}CF=CFX \text{ (no reaction)}$$

On allowing $C_{10}F_{21}MgBr$ to thermally decompose in the presence of an added equivalent of $C_6F_{13}CF=CF_2$, the major product was *trans*- $C_8F_{17}CF=$ CFBr while no $C_6F_{13}CF=CFBr$ was formed. Although the possibility of a mechanism involving an $R_fCF=CF_2$ ·MgXF complex cannot be excluded, this seems somewhat unlikely on the basis of the above evidence that $R_fCF=CF_2$ is formed as an intermediate.

Several other possible mechanisms are shown below:



Replacement of X by R corresponds to the possible mechanisms which might apply to reactions in the presence of excess RMgX.

The formation of 1,1-dimethylperfluorovinyl compounds could arise in the following manner:



The fact that compounds of the type $R_fCF=CXR$ are not prepared could be due to the increasingly unfavorable steric requirements, or a much greater tendency for $R_fCF_2CFXMgF$ (or R_fCF_2CX) once formed to yield $R_fCF=CFX$, and for $R_fCF_2CFMeMgF$ (or R_fCF_2CMe) to yield $R_fCF=CFMe$.

Presumably the steric requirements for attack of an ethyl Grignard upon an ethylated intermediate are too great to allow the formation of the 1,1-diethyl-substituted olefins.

Attempts to trap a carbene by the use of olefins (cyclohexene, tetramethylethylene and cis-but-2-ene) or triethylsilane were unsuccessful. Although fluorocarbenes have been successfully trapped by these means [40-42], failure to trap a carbene, however, does not rule out a carbene mechanism since X-MgF (or R-MgX) may be a better carbene trap than olefins or Et₃SiH. Carbene insertion into Mg-X bonds has been reported [43], and the order of reactivity of carbene insertion into metal-halogen bonds was M-I > M-Br > M-Cl \gg M-F [44]. No examples have been reported of carbene insertion into an M-F bond.

The mechanistic schemes presented above may be likened to those suggested by Franzen and Fikentscher[45] and Villieras [46,47] to account for the products they obtained from the reaction of RMgX or RLi reagents with CF_2Br_2 or CF_3Br . Of course, o-elimination was not possible with these halomethanes.

Hydrolysis of aliquots of ethereal solutions of $\rm R_fMgCl$ or $\rm R_fMgBr$ (even those to which MgBr₂ or excess RMgBr had been added) prior to thermal decomposition (ca. -15 "C) provided a nearly quantitative amount of $\rm R_fCF_2H$. This, coupled with the rapid rate of decomposition above – -10 °C, indicates that no stable intermediates are formed.

Experimental

Infrared spectra were obtained with a Beckman IR-12 spectrophotometer. Analytical VPC was performed on an F & M Model 500 Gas Chromatograph using 3 m X 6 mm copper columns packed with either 15% SE-30 or 15% QF-1. Preparative VPC was performed on a Hewlett-Packard Model 776 Gas Chromatograph using 3.6 m X 1.8 cm stainless-steel columns packed with 15% SE-30 or 15% QF-1 Chromosorb P, 60 - 80 mesh. Mass spectra were recorded on an Atlas CH-4 spectrometer at 70 eV.¹H NMR spectra were obtained using a Varian A-60 instrument with TMS as an internal standard, and ¹⁹F NMR spectra were measured with a Varian HA-100 instrument at 94.075 MHz using trichlorofluoromethane as the internal standard.

General procedure

Into an oven-dried, nitrogen-flushed flask was placed the perfluoroalkyl iodide and the required volume of LiAlH_4 -dried ether or THF (or sodiumdried pentane) solvent as indicated in Table 1. The solution was cooled to -78 °C and the alkyl Grignard reagent was added *via* a syringe. Either the cooling bath was retained and the reaction mixture was allowed to warm to room temperature over a 6 - 8 h period, or the bath was removed in which case the reaction mixture warmed to room temperature during 1 - 2 h (similar results were obtained by either procedure). After stirring at room temperature for the indicated time (Table 1), the reaction mixture was hydrolyzed with 3 moll⁻¹ HCl, washed with water and dried over an-hydrous MgSO₄. Distillation provided the crude products which were then obtained in a pure state by preparative VPC (Tables 2 and 3). The boiling points of R_fCF₂CF₂I and R_fCF=CFI were too close to allow any separation by distillation.

Magnesium bromide was prepared in ether by the reaction of ethylene bromide with magnesium. Magnesium iodide was obtained from the reaction of iodine with magnesium in ether at room temperature. The perfluoroalkyl iodides were purified by spinning-band distillation of a telomer iodide mixture of $C_6F_{13}I$, $C_8F_{17}I$ and $C_{10}F_{21}I$ obtained from the Thiokol Corporation.

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