

SYNTHESIS OF PERFLUOROALIPHATIC GRIGNARD REAGENTS*

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SUMMARY

Perfluoroaliphatic mono- and di-Grignard reagents (R_fMgX , $XMgR_fMgX$) have been conveniently synthesized in excellent yields (90–100%) through metal-halogen exchange reactions. The degree of exchange has been found to be subject to a number of experimental parameters, *e.g.* the nature of the solvent (tetrahydrofuran vis-à-vis diethyl ether), the type of halide displaced, the organomagnesium exchange reagent and the stoichiometry. These organomagnesium reagents have sufficient thermal stability at low temperatures (-70°) to be useful as intermediates for the synthesis of a variety of compounds. Various perfluoroaliphatic Grignard reagents have been reacted with H_3O^+ , CO_2 , $(CF_3)_2CO$ and cyclohexanone to yield R_fH , R_fCO_2H , $R_f(CF_3)_2OH$ and 1-cyclo- $C_6H_{10}(OH)R_f$ compounds, respectively. The selection of the proper reaction conditions, *i.e.* solvent, temperature and reaction time, has been found to be extremely important in the preparation of derivatives of the various perfluoroaliphatic Grignard reagents.

INTRODUCTION

Although many attempts have been made to prepare perfluoroaliphatic Grignard reagents, only limited success has been achieved¹. Most attempted syntheses employing "standard" Grignard preparation techniques (*e.g.* reaction of a perfluorinated alkyl halide with elemental magnesium) lead to extremely low yields of the desired Grignard reagent, due primarily to the formation of large amounts of decomposition products as well as to the slow rates of reaction

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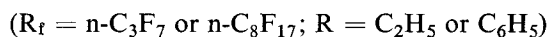
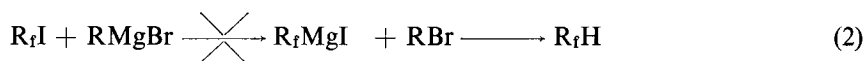
between the perfluorinated alkyl halide and magnesium. Haszeldine and McBee achieved some success with trifluoromethylmagnesium iodide, obtaining yields of derivatives within the range 14–57%^{2,3}. However, these results could not be reproduced satisfactorily. Indeed, in general, if one were to rely on normal preparative techniques, perfluorinated aliphatic Grignard reagents would have to be excluded from adoption as useful synthetic intermediates.

Unlike many of the other perfluorinated alkyl halides studied, *n*-perfluoropropyl iodide does react readily with elemental magnesium affording the desired Grignard reagent in reasonable yield^{4,5}. Because of the ready accessibility of *n*-heptafluoropropylmagnesium iodide, it has been the subject of numerous investigations^{6–10}. The Grignard reagent prepared directly from the alkyl halide and magnesium exhibits good thermal stability at temperatures below -40° ^{4,5,10}. Knunyants and co-workers have also successfully synthesized trifluorovinylmagnesium iodide from the reaction of iodotrifluoroethylene with magnesium¹¹. The Grignard reagent formed gave reasonably good yields of derivatives.

Pierce, Meiners and McBee were the first to employ a metal–halogen exchange reaction as an approach to the preparation of *n*-heptafluoropropylmagnesium bromide⁷. They found that *n*-heptafluoropropyl iodide would exchange readily with phenylmagnesium bromide at -70° in diethyl ether. Employing this technique, they were able to prepare a number of derivatives of the intermediate Grignard reagent in relatively good yields⁶. Heptafluoro-2-iodopropane was found to react in analogous fashion affording heptafluoroisopropylmagnesium bromide in high yield¹². Other workers have utilized this technique in the synthesis of trifluorovinylmagnesium bromide¹³.

We wish to report further extensions of the metal–halogen exchange reaction which have facilitated the syntheses of a number of perfluoroaliphatic Grignard reagents in near quantitative yields (Table 1). These intermediate Grignard reagents react with a variety of substrates in high yield, making the synthetic utility of the metal–halogen exchange reaction readily apparent. The effects of solvent, temperature, Grignard exchange reagent and perfluoroalkyl halide on the metal–halogen exchange reaction are discussed. Reactions used to characterize the Grignard reagents are also presented.

The scope of the metal–halogen exchange reaction toward normal perfluoroalkyl halides appears to be quite versatile. For example, the reaction of *n*-perfluorooctyl iodide with either phenyl- or ethylmagnesium bromide in diethyl ether at -70° is nearly quantitative and as rapid as the analogous reaction of *n*-heptafluoropropyl iodide. The progress of the reaction may be easily monitored by quenching the reaction at -70° with dilute aqueous acid and analyzing the solution for ethyl or phenyl iodide and the corresponding hydrofluoroalkane by GLC techniques. The isolation of the corresponding alkyl iodides (equation (1)) rather than the alkyl bromides (equation (2)) seems to negate an earlier supposition that a radical-transfer mechanism is involved¹⁴.



RESULTS AND DISCUSSION

We have found that all the variables, *e.g.* solvent, temperature, perfluoroalkyl halide, *etc.*, are very much inter-related and an explanation of all the results obtained requires the participation of more than one variable in a given system.

Effect of solvent

Earlier work by Haszeldine demonstrated the necessity for a basic solvent in the synthesis of perfluorinated Grignard reagents¹⁰. His study indicated that hydrocarbon ethers were to be preferred as solvents, and he employed tetrahydrofuran as the solvent in investigations of the reaction of *n*-heptafluoropropyl iodide with magnesium. The results obtained in the present study indicate that the previous conclusions concerning the choice of solvent were presumably based more on the rate of reaction between the perfluoroaliphatic iodide and magnesium rather than on the thermal stability of the resulting Grignard reagent formed. From his study, Haszeldine concluded that the increased basicity exhibited by the cyclic ether helped to stabilize the Grignard reagent somewhat better than either diethyl ether or di-*n*-butyl ether. Our present studies of the metal-halogen exchange reaction between perfluoroalkyl iodides and ethyl- or phenyl-magnesium bromide have shown that the possibility of a slow rate of reaction is not a limiting factor in the reaction between the iodide and Grignard exchange reagent. Rather, the exchange proceeds quite rapidly in both diethyl ether and tetrahydrofuran (THF). In fact, the exchange reaction appears to proceed at a slightly faster rate in diethyl ether relative to THF as far as *n*-perfluoro-octyl iodide is concerned, a result which is not entirely understood at this time. The results presented in Table 1 show that for most of the iodides examined the exchange has proceeded nearly quantitatively to completion within 15 min in diethyl ether as a solvent. When the exchange is carried out in THF, the exchange is only 76–93% complete within the same time period. The extent of the exchange reaction is dependent on the nature of the Grignard reagent employed rather than on the perfluoroalkyl iodide. When the reaction time is increased (20 h), the exchange in THF does go to completion, but because of the limited stability of the Grignard reagent in THF at -70° some of the Grignard reagent decomposes. Further studies on the stability of the Grignard reagent are at present in progress and will be published at a later date.

Some of the difficulties observed in THF may be accounted for in terms of a Schlenk-type equilibrium. Presumably this equilibrium is rapidly established

TABLE 1
SYNTHESIS OF PERFLUOROALIPHATIC GRIGNARD REAGENTS^a

R ₁ X	C ₂ H ₅ MgBr						C ₆ H ₅ MgBr								
	Et ₂ O			THF			Et ₂ O			THF					
	Time	R ₁ X	R ₁ H	Time	R ₁ X	R ₁ H	Time	RX	R ₁ X	R ₁ H	Time	RX	R ₁ X	R ₁ H	
C ₃ F ₇ I	15	94	0	—	15	—	20	—	15	99	0	—	15	90	10
C ₃ F ₇ I	15	99	0	100	15	77	13	77	15	99	0	100	15	93	7
I[CF ₂] ₃ I	60	97	0	—	60	—	—	—	60	98	0	—	15	53	12
I[CF ₂] ₆ I	30	100	0	—	15	—	—	—	15	100	0	—	—	—	—
C ₃ F ₇ Br	15	0	100	0	15	—	—	—	60	0	100	0	60	37	63
Br[CF ₂] ₆ Br ^b	15	0	100	0	15	90[0] ^c	0	90[0] ^c	15	2	94	—	120	55	5[90] ^e
Br[CF ₂] ₆ Br ^d	15	97	0	—	15	5[90] ^c	0	5[90] ^c	30	77	—	—	30	77	0 ^e
F ₂ C=CFI	15	98	0	—	15	—	7	—	15	93	—	—	15	100	—

^a All reactions were run at -70°, except those indicated.

^b Two moles of RMgX per mole of Br[CF₂]₆Br. Exchange of MeMgI and dibromide in diethyl ether gave no exchange. With H₂C=CHCH₂MgI in diethyl ether, 42% exchange was obtained after 2 h at -70°.

^c % H[CF₂]₆H, % Br[CF₂]₆H].

^d One mole of RMgX per mole of Br[CF₂]₆Br.

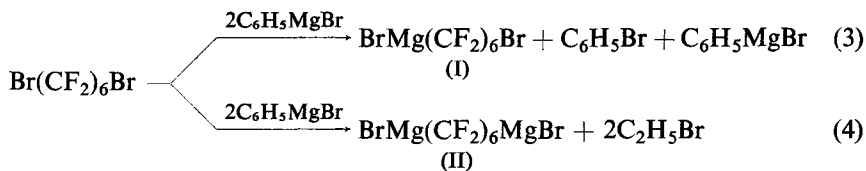
^e 0 = 0% H(CF₂)₆H.

and can be shifted to the right by using excess Grignard reagent. Experiments employing a slight excess (5–10%) of either phenyl- or ethyl-magnesium bromide (1–2 h) resulted in quantitative exchange based on the amount of alkyl iodide formed. However, the excess phenyl or ethyl Grignard reagent often interfered with the subsequent reactions of the perfluorinated alkyl Grignard reagent.

Effects of Grignard exchange reagent

McBee and co-workers reported earlier that in the exchange reaction of n-heptafluoropropyl iodide with various alkyl Grignard reagents in diethyl ether phenylmagnesium bromide was by far the superior reagent of those studied⁶. Although phenylmagnesium bromide is quite good, we have found that the efficiency of ethylmagnesium bromide is also comparable. In diethyl ether, the exchange between ethylmagnesium bromide and perfluoroaliphatic iodides affords quantitative yields of ethyl iodide (Table 1). However, in THF, a somewhat lower yield is obtained for the same reactions. In fact, the choice of the Grignard exchange reagent should be based not only on the perfluoroalkyl halide to be reacted, but also on the solvent system employed as well as on the ease of isolating the final perfluorinated product from the exchange product (RX). All of these variables are critical. Thus, for example, the exchange reaction between, 1,6-dibromododecafluorohexane (1 mol) and phenylmagnesium bromide (2 mol) in THF only goes to 50% conversion, but when ethylmagnesium bromide (2 mol) is employed the exchange is quantitative (Table 1). Previous data on n-perfluoro-octyl iodide (76% exchange, Table 1) suggest that ethylmagnesium bromide is a poor choice for affecting a complete exchange in THF.

Subsequent studies have shown that the reaction of 1,6-dibromododecafluorohexane (1 mol) with phenylmagnesium bromide (2 mol) in THF leads initially to the formation of the mono-Grignard reagent $\text{Br}(\text{CF}_2)_6\text{MgBr}$ (I) (see Table 1) (equation(3)) and even the presence of excess phenylmagnesium bromide does not cause the reaction to proceed to the di-Grignard reagent (II) (equation (4)).



This observation regarding the formation of the mono-Grignard reagent is not entirely unique. We have previously noted a similar behavior when 1 mol of hexabromobenzene was treated with 2 mol of phenyl- or ethyl-magnesium bromide¹⁵.

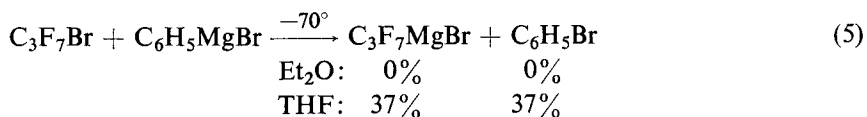
It is interesting to note that when a 1:1 molar ratio of 1,6-dibromododecafluorohexane to ethylmagnesium bromide in THF is employed both the mono-Grignard reagent (I) and the di-Grignard reagent (II) are formed in a 90:5 ratio.

Alternatively, when a 1:1 molar ratio of 1,6-dibromododecafluorohexane to phenylmagnesium bromide is used only the expected mono-Grignard reagent (I) is formed (Table 1).

Effect of halogen

The previously reported effect of halogen observed in metal-halogen exchanges appears to apply equally well to the exchange reactions presented in Table 1^{3,16}.

An exchange reaction was attempted with n-heptafluoropropyl bromide and phenylmagnesium bromide in diethyl ether at -70° but no exchange was observed. In THF, however, moderate yields of the exchange product (37%) were detected. The rates of exchange were extremely slow principally due to the halogen effect (equation (5)).



The magnitude of the halogen effect in the perfluoroaliphatic case is well illustrated by the following results of competition reactions (Table 2) of the type:



These experiments were accomplished using one equivalent of n-heptafluoropropyl iodide, one equivalent of n-heptafluoropropyl bromide and one equivalent of the Grignard exchange reagent.

TABLE 2

R	Solvent	% Yield	
		RBr	RI
C ₂ H ₅	Et ₂ O	0	100
C ₆ H ₅	Et ₂ O	0	94
C ₆ H ₅	THF	20	80

All experiments were run in the solvents indicated at -70° for 30 min. Quenching was accomplished at -70° using dilute aqueous acid. The solutions were warmed to room temperature, extracted with diethyl ether, dried and analyzed by GLC.

A similar halogen effect was also observed in the case of α,ω -perfluoroaliphatic dibromides and di-iodides. In diethyl ether, 1,6-dibromododecafluorohexane shows no reaction with methyl-, ethyl-, or phenyl-magnesium bromide. Even when an extremely facile exchange reagent, such as allylmagnesium bromide,

was employed, the exchange yield was poor (42%, Table 1). On the other hand, 1,8-di-iodo-octadecafluoro-octane and 1,3-di-iodoperfluoropropane behave as expected, undergoing rapid exchange with ethyl- or phenyl-magnesium bromide in diethyl ether and affording quantitative yields of exchange product (Table 1).

In the final analysis, although a marked halogen effect is present in most instances it can usually be overcome by employing a relatively facile exchange reagent (*e.g.* C_2H_5MgBr) in a more basic solvent (*e.g.* THF).

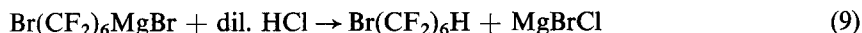
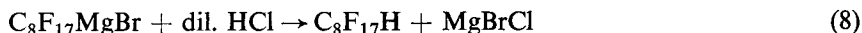
Characterization of perfluoroaliphatic Grignard reagents

The results obtained in Table 1 are somewhat tenuous and for this reason the presence of the perfluoroalkyl Grignard reagents were further confirmed by reactions with suitable substrates under a variety of conditions. This technique has already been established by McBee and Pierce^{4,6}.

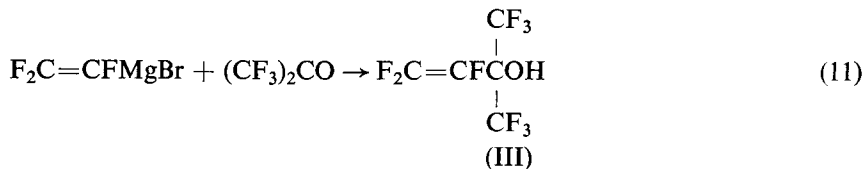
The selection of the substrate is critical and often the same substrate cannot be used in different solvents. These various shortcomings in the preparation of derivatives necessitated the utilization of a number of substrates. For example, cyclohexanone, which had been previously used as a suitable reagent for the preparation of derivatives in the perfluoropropyl⁶ Grignard system, was the reagent of choice for reactions with perfluoro-octylmagnesium bromide in diethyl ether. The reaction of perfluoroaliphatic Grignard reagents with cyclohexanone in diethyl ether afforded good yields of the corresponding cyclohexanols even at -70° (equation (7)).



The reaction of a Grignard reagent with dilute aqueous acid is a well-established method for replacing the $-MgX$ moiety with a hydrogen atom. The reaction with perfluoroaliphatic Grignard reagents is similar to the normal hydrocarbon reaction. The reaction between dilute aqueous acid and a perfluoroaliphatic Grignard reagent is extremely rapid even at temperatures as low as -70° and the use of this technique allows the confirmation of an intermediate Grignard reagent by the isolation and characterization of the resultant monohydro- and dihydro-fluorocarbons, R_fH and HR_fH , respectively (equations (8)–(10)).

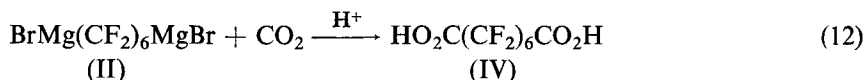


The reaction of trifluorovinylmagnesium bromide with hexafluoroacetone proceeds rapidly to the formation of the desired alcohol (III) (equation (11)).



Tarrant *et al.* have previously reported a preparation of the alcohol (III) *via* an organolithium reagent¹⁷.

In the case of the di-Grignard reagent (II), the carbonation reaction was fairly straightforward resulting in the formation of perfluorosuberic acid (IV) in 81% yield (equation (12)).



This carbonation reaction was carried out in THF at -70° for 18 h.

Carbonation of perfluoro-octylmagnesium bromide, however, afforded a complex mixture of products; some of these have not, as yet, been fully characterized. The desired perfluorononanoic acid, $\text{C}_8\text{F}_{17}\text{CO}_2\text{H}$, was obtained in very poor yield (5–10%). Continuing studies in this area will be reported at a later date.

EXPERIMENTAL

General comments

Reactions involving organometallic reagents were carried out under dry nitrogen employing the usual precautions for the rigorous exclusion of moisture and air. All chemicals used were commercially available except *n*-perfluoro-octyl iodide which was obtained from Thiokol Chemical Corporation and 1,6-dibromododecafluorohexane which was obtained from Dow Corning Corporation. Tetrahydrofuran (THF) was dried by refluxing over metallic sodium followed by distillation from calcium hydride prior to use. Dimethylacetamide (DMAC) was distilled from calcium hydride prior to use. Anhydrous diethyl ether (Mallinckrodt) was used without further purification. All other solvents used were analytical grade. Melting points were determined with a "Mel-Temp" or "Buchi" apparatus, and are uncorrected. NMR spectra were recorded on a Varian A56/60 spectrometer in CCl_4 solution. Chemical shifts are expressed in ppm using tetramethylsilane (TMS) as the internal standard for ^1H and fluorotrichloromethane as the internal standard for ^{19}F NMR spectra. GLC analyses were performed on an F&M Model 700 instrument using a 1.8 m column containing 10% SE-30 on Chromosorb W and a 3.6 m column containing 10% Apiezon L on Chromosorb W. Mass spectral analyses were performed on a CEC-21-110B mass spectrometer. All products, where possible, were characterized by GLC retention time with known

calibrated samples, and by mass spectral and NMR analyses. Yields of all products were determined by GLC analysis using appropriate hydrocarbon internal standards (*e.g.* *n*-decane, *n*-dodecane, *etc.*). Empirical response factors were determined separately using standard solutions.

Preparation of perfluoroaliphatic mono- and di-Grignard reagents

For the metal-halogen exchange reactions, the general procedure outlined by Pierce, Meiners and McBee was followed⁷.

The perfluoroalkyl halide to be reacted (1 equiv.) was introduced into the flask along with the selected solvent (Et₂O or THF) and an internal standard (*n*-C₁₂H₂₆). For the most part, synthesis of the Grignard reagent was carried out at a 0.08 mol l⁻¹ concentration. The above mixture was then cooled to -70° in a Dry Ice/acetone bath and treated with RMgX (1 equiv. for mono-Grignard synthesis and 2 equiv. for di-Grignard synthesis) at such a rate that the temperature remained below -60°. The white slurry that resulted was stirred for the time specified in Table 1 at -70° and then used as such for further reaction. In the case of hydrolysis, the Grignard reagent was hydrolyzed at -70° with dil. HCl (6 *N*) and then allowed to warm to room temperature. The mixture was extracted with diethyl ether (3 ×), and the combined ethereal extracts were dried over anhydrous MgSO₄. GLC analysis of the ethereal fraction revealed the degree of exchange as measured from the amount of RX and R_fH present (Table 1). In cases where the R_fH products (*i.e.* CF₃H, C₃F₇H) were gases, no attempt was made to isolate the hydrolyzed product. With the perfluoro-octyl Grignard hydrolyzed in diethyl ether, GLC analysis revealed 1*H*-perfluoro-octane (100%) as the sole product. Subsequent distillation of the ethereal layer gave an analytical sample of 1*H*-perfluoro-octane, b.p. 109–110°, as a colorless liquid. (Found: C, 22.10; H, 0.29; F, 77.11%. C₈HF₁₇ requires C, 22.87; H, 0.24; F, 76.89%).

The mass spectrum exhibited peaks at 350 (M-CF₃H), 313 (M-CF₅), 69 (CF₃) and 51 (CF₂H). ¹⁹F NMR spectroscopy gave the following data: a triplet at 81 (3F, CF₃); a multiplet at 125 (2F, CF₃CF₂); a multiplet at 121 (8F, -CF₂-); a multiplet at 128 (2F, CF₂CF₂H); and a pronounced doublet at 136 (CF₂H), *J*(H-F) = 55 Hz.

Preparation of 1-n-C₃F₇(cyclo-C₆H₁₀OH)

A precooled (-70°) solution of *n*-heptafluoropropylmagnesium bromide (48 mmol), prepared from phenylmagnesium bromide (48 mmol) in anhydrous diethyl ether (600 ml), was treated with anhydrous cyclohexanone (50 mmol, 4.9 g) ensuring that the temperature was always maintained below -65°. The reaction mixture was stirred at -70° for 30 min, warmed slowly to room temperature (30 min), hydrolyzed with 6 *N* HCl (100 ml) and the ethereal layer decanted. The residual aqueous acid layer was extracted with diethyl ether (2 × 50 ml). The

combined ethereal fractions were dried (anhydrous MgSO_4) and the solvent removed *in vacuo*. The resulting oil was purified on a silica gel column, employing standard column chromatography techniques. Elution with pentane to remove the phenyl iodide and unreacted cyclohexanone was followed by elution with a 50/50 solution of diethyl ether and pentane which afforded the desired material. The alcohol-containing fractions were combined and concentrated, yielding a low melting solid. The solid was dried under vacuum (1 mmHg) for 30 min at 25° , yielding 10.1 g (74.9%) of a 99% pure material, 1-heptafluoropropylcyclohexanol, m.p. $43\text{--}44^\circ$.

The mass spectrum exhibited peaks at 249 (M-F), 99 (cyclo- $\text{C}_6\text{H}_{10}\text{OH}$), 81 (C_2F_3) and 69 (CF_3). ^{19}F NMR spectroscopy gave the following data: a triplet at 80 (3F, CF_3) and a multiplet at 122 (4F, $(-\text{CF}_2-)_2$). ^1H NMR spectroscopy gave a multiplet at 1.70 ($-\text{CH}_2-$) with the OH hidden in the above region.

Preparation of 1-n-C₈F₁₇(cyclo-C₆H₁₀OH)

The Grignard reagent (4 mmol), prepared from phenylmagnesium bromide in diethyl ether (-70°), was treated with an excess of cyclohexanone (8 mmol, 0.79 ml). The mixture was stirred at this temperature for 15 min and then allowed to warm slowly (1 h) to room temperature. The reaction mixture was hydrolyzed (6 N HCl) and the diethyl ether layer decanted. The acid layer was extracted with diethyl ether (2×25 ml) and the combined ethereal fractions were dried (anhydrous MgSO_4). GLC-mass spectral analysis showed the major components to be phenyl iodide (98%), 1H-perfluoro-octane (10%) and 1-n- C_8F_{17} (cyclo- $\text{C}_6\text{H}_{10}\text{OH}$) (86%). The mixture was concentrated to a slurry, dissolved in pentane and eluted on a silica gel column with a pentane-diethyl ether mixture, starting with 100 ml of pentane and changing the ratio of solvents by 10 ml every 100 ml added until 100 ml of diethyl ether was obtained. The appropriate fractions were collected and concentrated to a white solid, which sublimed ($68\text{--}70^\circ/0.20\text{--}0.25$ mmHg) gave the desired alcohol in good yield (81%), m.p. $57\text{--}58^\circ$. (Found: C, 32.49; H, 2.13%. $\text{C}_{14}\text{H}_{11}\text{F}_{17}\text{O}$ requires C, 32.45; H, 2.14%.)

The mass spectrum exhibited peaks at 518 (M), 499 (M-F), 481 (M-F, H_2O), 479 (M-F₂H) and 99 (cyclo- $\text{C}_6\text{H}_{10}\text{OH}$). ^{19}F NMR spectroscopy gave the following data: a triplet at 82 (3F, CF_3); a multiplet at 126 (2F, CF_3CF_2); a broad multiplet at 122 (8F, $-\text{CF}_2-$); a multiplet at 123 (2F, $\text{CF}_2\text{CF}_2\text{-cyclo}$); and a multiplet at 119 (2F, $\text{CF}_2\text{-cyclo}$). ^1H NMR spectroscopy gave a broad multiplet at 1.70 ($-\text{CH}_2-$) and a sharp singlet at 1.50 (OH) hidden in the above region. For this reason, proton integration was not possible.

Preparation of F₂C=CFC(CF₃)₂OH

Trifluorovinylmagnesium bromide (150 mmol) was prepared in diethyl ether (500 ml) at -70° by allowing trifluorovinyl iodide (150 mmol, 31.2 g) to react with ethylmagnesium bromide (150 mmol, 46.5 ml) for 30 min. Hexafluoroacetone

(150 mmol, 24.9 g) was introduced and the resulting mixture allowed to stir at -70° for an additional 2 h. The mixture was then allowed to warm slowly to room temperature, the solvent removed at reduced pressure and the resulting solid treated with excess 6 *N* HCl. Separation of the organic layer afforded 24 g (98%) of the crude alcohol. The crude material was dissolved in 150 ml of 10% sodium hydroxide solution, boiled for 5 min and the basic solution acidified to pH 4 with concentrated HCl. The organic layer separated easily and was distilled from P_2O_5 to give 19.2 g (55%) of analytically pure $F_2C=CFC(CF_3)_2OH$, b.p. $85-86^{\circ}/760$ mmHg (lit.¹⁷, $83-85^{\circ}$).

Mass spectral analysis demonstrated the existence of a molecular ion at 248 (M). Further fragmentation gave peaks at 209 (M-HF₂), 179 (M-CF₃), 159 (M-CF₃, HF) and 109 (F₂C=CFCO). ¹⁹F NMR spectroscopy gave a multiplet at 77.3 (6F, CF₃) and a characteristic ABX pattern for the remaining three fluorines at 90.6, 107.6 and 185.3. ¹H NMR spectroscopy gave a singlet at 3.13 (OH).

Preparation of HO₂C(CF₂)₆CO₂H

A precooled (-70°) solution of the di-Grignard reagent (30 mmol), prepared from 1,6-dibromododecafluorohexane and ethylmagnesium bromide in THF, was treated with gaseous carbon dioxide for 22 h. The resulting heterogeneous mixture was allowed to warm slowly to room temperature (1.5 h). The solvent was removed *in vacuo* giving a white solid which, when dissolved in 50% aqueous H₂SO₄ and subjected to continuous liquid-liquid extraction with diethyl ether, afforded the desired diacid etherate. This material was dried at $60^{\circ}/10^{-2}$ mmHg for 1 h yielding perfluorosuberic acid in 81% yield, m.p. $142-143^{\circ}$. An analytical sample was prepared by recrystallization from toluene followed by sublimation, m.p. 144° (lit.¹⁸, $143-144^{\circ}$).

The mass spectrum contained peaks at 345 (M-CO₂H), 326 (M-F, CO₂H) and 45 (CO₂H). ¹⁹F NMR spectroscopy gave the following data: a multiplet at 119 (4F, CF₂CO₂H); a multiplet at 121 (4F, CF₂CF₂CO₂H); and a multiplet at 123 (4F, -CF₂-).

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