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SYNTHESIS AND REACTIONS OF PERFLUORO-n-OCTYLMAGNESIUM BROMIDE

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SUMMARY

Perfluoro-n-octylmagnesium bromide has been conveniently synthesized through the metal–halogen exchange reaction between perfluoro-n-octyl iodide and ethyl- or phenyl-magnesium bromide. The thermal stability of the Grignard reagent and the products of the thermal decomposition have been estimated in diethyl ether and tetrahydrofuran. Reactions of the Grignard reagent with various substrates such as water, acetone, hexafluoroacetone, trimethylchlorosilane and carbon dioxide indicate the synthetic utility of n-octylmagnesium bromide.

INTRODUCTION

In a recent publication[1] we reported the synthesis of several perfluorinated mono- and di-Grignard reagents utilizing the metal–halogen exchange reaction [equation (1)] originally reported by Pierce, Meiners and McBee[2].

$$R_fX + RMgBr \rightarrow RX + R_fMgX \qquad (1)$$

$$(R_fX = C_3F_7Br,\ C_8F_{17}I,\ Br(CF_2)_6Br,\ I(CF_2)_8I;\ R = C_2H_5,\ C_6H_5)$$

We have found, as have other workers[3–7], that a low reaction temperature is perhaps the most stringent restriction placed on perfluoroaliphatic Grignard reagents. A prior knowledge of the stability of perfluoroalkyl Grignard reagents at different temperatures is fundamental to their subsequent utilization as organometallic intermediates. The successful utilization of these organometallics in syntheses depends on selecting a reaction temperature at which the rate of reaction with a substrate is much greater than the rate of thermal decomposition.

We have expanded our continuing studies on perfluoroaliphatic Grignard reagents to the synthesis of longer-chain perfluoroaliphatic Grignard reagents and have undertaken an investigation of the thermal stability and decomposition of n-$C_8F_{17}MgBr$ (I). In addition, reactions with various substrates have also been performed in order to indicate synthetic utility.

DISCUSSION

No detailed studies of the thermal stability of perfluoroalkyl Grignard reagents have been reported. Haszeldine[7], however, previously indicated that n-C_3F_7MgBr has a reasonable stability at −40 °C in diethyl ether, dibutyl ether and tetrahydropyran. It was further suggested that the decomposition of the Grignard reagent during its formation or subsequent storage yielded $CF_3CF{=}CF_2$, C_3F_7H, traces of C_6F_{14} and fluorinated tars.

We have found that the thermal stability of (I) is a function of time, temperature and solvent. Although we have not carried out an extensive detailed study of these variables, sufficiently diverse conditions have been examined to provide some guide lines to the stability and subsequent utility of (I). The reaction products of the thermal stability studies were conveniently determined by hydrolyzing the Grignard reagent and examining the products by GLC (gas–liquid chromatography) techniques. The hydrolysis reaction [equation (2)] is rapid and quantitative even at low temperatures.

$$\underset{\text{(I)}}{\text{n-}C_8F_{17}MgBr} + \text{dil. } HCl \rightarrow MgBrCl + \text{n-}C_8F_{17}H \qquad (2)$$

The difference between the theoretical and actual yield of n-$C_8F_{17}H$ as determined by GLC analysis provides a measure of the thermal stability of the Grignard reagent. Table 1 lists the results obtained for the thermal stability of (I) under different conditions. It can be seen that in diethyl ether as a solvent the Grignard reagent is more stable than in tetrahydrofuran. Similarly, low temperature (−70 °C) also has a stabilizing effect.

TABLE 1

STABILITY OF PERFLUORO-n-OCTYLMAGNESIUM BROMIDE
n-$C_8F_{17}I$ + C_6H_5MgBr → n-$C_8F_{17}MgBr$ + C_6H_5I

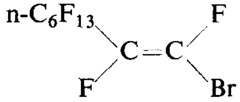
Solvent	Time	Temperature /°C	Yield of $C_8F_{17}H$(%)	Yield of C_6H_5I(%)
Et_2O	15 min	−70	100	99
Et_2O	20 h	−70	97	100
Et_2O	4 h	−40	61	—
THF	15 min	−70	88	93
THF	20 h	−70	59	100
THF	4 h	−40	14	—

In an attempt to understand the mode of decomposition of the Grignard better, a partial identification of the major products of the decomposition has been performed. From previous work reported by Haszeldine[7,8] for n-C_3F_7MgI and more recently by Lo[9,10] on n-$C_8F_{17}MgI$ at high temperature, the initial product of the decomposition was indicated as the terminal olefin $CF_3CF{=}CF_2$ and $C_6F_{13}CF{=}CF_2$, respectively [equation (3)].

$$R_fCF_2CF_2MgBr \rightarrow R_fCF{=}CF_2 + MgBrF \qquad (3)$$

Although from our studies we believe that the initial decomposition product is the terminal olefin, the overall decomposition of (I) is more complex than the pathway previously reported for perfluoroaliphatic Grignard reagents[7-10]. Our studies indicate that initially (I) decomposes to the expected olefin n-$C_6F_{13}CF{=}CF_2$; however, subsequently, the decomposition differs considerably and the products are a function of the solvent system. For example, in diethyl ether as the solvent, it is believed that the olefin n-$C_6F_{13}CF{=}CF_2$ undergoes nucleophilic attack by a bromide ion at the double bond resulting in the formation of an unstable carbanion which converts exclusively to the *trans* isomer of 1-bromoperfluoro-octene by loss of a fluoride ion [equation (4)].

$$n\text{-}C_6F_{13}CF{=}CF_2 + Br^- \longrightarrow [n\text{-}C_6F_{13}\bar{C}FCF_2Br] \xrightarrow{-F^-}$$



(4)

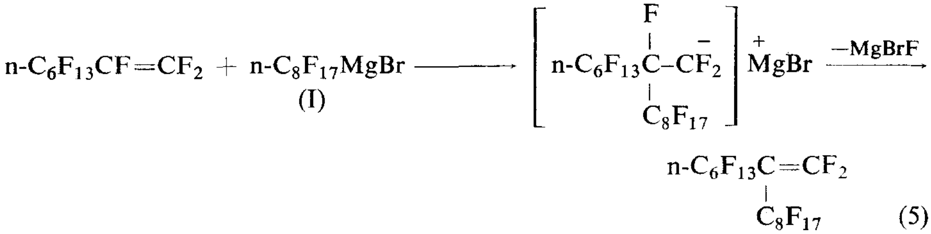
(II)
[52%]

In addition to the bromo-olefin, which was the major decomposition product, there were other smaller quantities of n-$C_8F_{17}H$, n-$C_6F_{13}CF{=}CF_2$ and a mixture of two $C_{16}F_{32}$ isomers.

The decomposition of (I) in tetrahydrofuran, however, follows a somewhat different path. The reason for this may possibly lie in the lower solubility of MgBrF salts in tetrahydrofuran as compared to diethyl ether at low temperatures. In tetrahydrofuran, none of the bromo-olefin (II) was formed. In addition to small quantities of n-$C_8F_{17}H$ and n-$C_6F_{13}CF{=}CF_2$, the major products were a mixture of two $C_{16}F_{32}$ isomers.

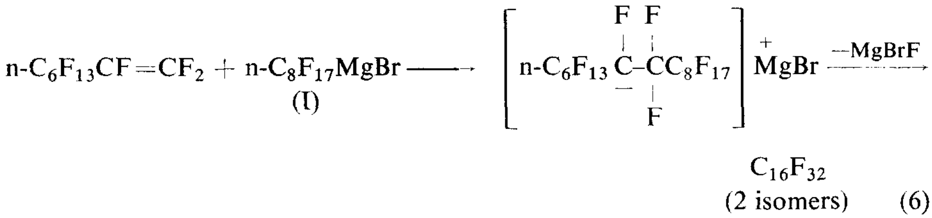
Without a complete analysis of these isomers, one can only suggest a possible mode of formation. It seems quite reasonable to suggest that such a mixture of products could arise from the reaction between the initially formed n-$C_6F_{13}CF{=}CF_2$ and undecomposed (I) by one of two paths [equations (5) and (6)].

Path A



$$n\text{-}C_6F_{13}CF{=}CF_2 + \underset{(I)}{n\text{-}C_8F_{17}MgBr} \longrightarrow \left[n\text{-}C_6F_{13}\overset{F}{\underset{C_8F_{17}}{C}}\text{-}\overset{-}{C}F_2 \right] \overset{+}{M}gBr \xrightarrow{-MgBrF} n\text{-}C_6F_{13}\underset{C_8F_{17}}{C}{=}CF_2 \quad (5)$$

Path B



$$n\text{-}C_6F_{13}CF{=}CF_2 + \underset{(I)}{n\text{-}C_8F_{17}MgBr} \longrightarrow \left[n\text{-}C_6F_{13}\overset{F}{\underset{-}{C}}\text{-}\overset{F}{\underset{F}{C}}C_8F_{17} \right] \overset{+}{M}gBr \xrightarrow{-MgBrF} \underset{\text{(2 isomers)}}{C_{16}F_{32}} \quad (6)$$

If the Grignard adds *via* Path A, only one product, a terminal olefin, would result. NMR spectral analysis of the $C_{16}F_{32}$ product did not however indicate a terminal olefin $(R_f)_2C{=}CF_2$. Since a mixture of two $C_{16}F_{32}$ products was obtained, it appears that the reaction proceeds *via* Path B. The intermediate anion could eliminate a fluoride ion by two different routes during the formation of two olefins and a MgBrF salt. Since separation of the mixture of olefins was not possible, a complete structural analysis for the individual components could not be undertaken at this time. Mass spectral and NMR analyses indicate that both products are $C_{16}F_{32}$ internal olefins.

Reactions with various substrates

In spite of the relative instability of the perfluoroalkyl Grignard reagents, by using appropriate conditions of time, temperature and solvent media it is possible to make practical use of the organometallic intermediates. The results of reactions between (I) and various substrates under diverse conditions are listed in Table 2.

$n\text{-}C_3F_7MgI$ has been reported[2, 4, 7] to react with acetone to yield the carbinol $n\text{-}C_3F_7C(OH)(CH_3)_2$ in yields ranging from 10–65%. It can be seen from Table 2 that under appropriate conditions perfluoroalkylcarbinols can be obtained in yields as high as 90%. Higher yields of the carbinol are produced in diethyl ether than in tetrahydrofuran. An indication of the storage stability of $n\text{-}C_8F_{17}MgI$ in diethyl ether after 20 h at −70 °C can be obtained from its subsequent derivatization with acetone to yield the carbinol in 82% yield. Chlorotrimethylsilane, $(CH_3)_3SiCl$, a reagent that has been extensively reported as a derivatizing agent for organometallic compounds, does not react with (I) in diethyl ether. It appears that the rate of reaction between $(CH_3)_3SiCl$ and the Grignard reagent is slower than the rate of decomposition of the Grignard and only decomposition products of (I) were found. In tetrahydrofuran, however, n-$C_8F_{17}Si(CH_3)_3$* can be readily obtained in 77% yield. If the solution of (I) in tetrahydrofuran is stored at −70 °C for 20 h prior to derivatization, the yield of n-$C_8F_{17}Si(CH_3)_3$ decreases to 42%. This smaller yield again indicates the lower stability of Grignard reagent (I) in tetrahydrofuran as compared to diethyl ether.

TABLE 2

REACTIONS OF PERFLUORO-n-OCTYLMAGNESIUM BROMIDE

Solvent	Temperature	Time	Substrate	Derivative	Yield (%)
Et_2O	a	a	$(CH_3)_2C{=}O$	n-$C_8F_{17}C(CH_3)_2OH$	90
Et_2O	b	b	$(CH_3)_2C{=}O$	n-$C_8F_{17}C(CH_3)_2OH$	58
Et_2O	c	c	$(CH_3)_2C{=}O$	n-$C_8F_{17}C(CH_3)_2OH$	82
THF	d	d	$(CH_3)_2C{=}O$	n-$C_8F_{17}C(CH_3)_2OH$	52
THF	e	e	$(CH_3)_3SiCl$	n-$C_8F_{17}Si(CH_3)_3$	77
THF	c	c	$(CH_3)_3SiCl$	n-$C_8F_{17}Si(CH_3)_3$	42
Et_2O	e	e	$(CH_3)_3SiCl$	n-$C_8F_{17}Si(CH_3)_3$	0
THF	e	e	$(CF_3)_2C{=}O$	n-$C_8F_{17}C(CF_3)_2OH$	64
Et_2O	d	d	$(CF_3)_2C{=}O$	n-$C_8F_{17}C(CF_3)_2OH$	49
Et_2O/THF	f	f	CO_2	n-$C_8F_{17}CO_2C_2H_5$	70

[a] 15 min at −70 °C then warmed up to room temperature over 3 h.
[b] Hydrolyzed at −70 °C after 1 h.
[c] Grignard reagent kept at −70 °C for 20 h prior to derivatization for 30 min at −70 °C and then warmed up to room temperature over 3 h.
[d] 1 h at −70 °C and then warmed up to room temperature over 3 h.
[e] 2 h at −70 °C and then warmed up to room temperature over 2 h.
[f] Carbonated for 20 h at −70 °C and then warmed up to room temperature with continued carbonation.

Perfluoroaliphatic tertiary alcohols may be synthesized through the reaction between (I) and hexafluoroacetone, $(CF_3)_2C{=}O$. Surprisingly the yields are higher in tetrahydrofuran than in diethyl ether. Carbonation of the Grignard reagent in diethyl ether produces a mixture of products. The principal product identified was the bromo-olefin (II), indicating that the rate of decomposition of the Grignard reagent is faster than the rate of carbonation. If, however, the carbonation is performed in a diethyl ether: THF mixture (90:10 by volume) and

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* This compound was previously prepared by H. Gilman, D. S. Sethi, B. B. Singh and M. R. Smith, Jr., *Air Force Materials Laboratory Tech. Report 64-383, Pt. VIII*, Dec. 1971 by a similar reaction but under slightly different experimental conditions. Yields as high as 100% were reported by these investigators.

the product subsequently esterified* with ethanol, a 70% yield of the ester $C_8F_{17}CO_2C_2H_5$ is obtained. In this solvent mixture, the rate of carbonation must be faster than in diethyl ether alone since a good yield of the acid derivative was obtained.

EXPERIMENTAL

General comments

Reactions involving organometallic reagents were carried out under dry nitrogen with 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 the Thiokol Chemical Corporation. Tetrahydrofuran was dried by refluxing over metallic sodium followed by distillation 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 using CCl_4 solutions. Chemical shifts are expressed in ppm relative to tetramethylsilane (TMS) as internal standard for ^1H and fluorotrichloromethane ($CFCl_3$) as internal standard for ^{19}F NMR spectra. GLC analyses were performed on an F & M Model 700 instrument using a column 1.8 m in length containing 10% SE-30 on Chromosorb W and a column 3.6 m in length containing 10% Apiezon L on Chromosorb W. Mass spectral analyses were performed on a CEC-21-110B mass spectrometer. When possible, all products were characterized by GLC retention time with calibrated known samples and by mass spectral and NMR analysis. Yields of all products were determined by GLC analysis using appropriate hydrocarbon internal standards. Empirical response factors were determined separately using standard solutions.

Preparation of n-$C_8F_{17}MgBr$ (I)

The n-$C_8F_{17}I$ was introduced into the flask together with the selected solvent (Et_2O or THF) and an internal standard (n-$C_{12}H_{26}$). The mixture was then cooled to −70 °C in a Dry Ice/acetone bath and treated with RMgX (ethyl- or phenyl-magnesium bromide) at a rate sufficient to keep the temperature below −60 °C. The resulting white slurry was stirred for the time specified in Table 1 at −70 °C and then used as such for further reaction.

In the case of hydrolysis, the Grignard reagent was hydrolyzed at −70 °C with dil. HCl (6 mol l^{-1}) and allowed to warm to room temperature. The mixture was then extracted with diethyl ether (3 ×) and the combined ethereal extracts dried

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* Perfluoroaliphatic acids form hydrates readily and are more conveniently isolated and characterized as the ethyl esters.

over anhydrous $MgSO_4$. GLC analysis of the ethereal fraction indicated the degree of exchange from the amount of n-$C_8F_{17}I$ or n-$C_8F_{17}H$ and C_2H_5I or C_6H_5I present in the hydrolyzed reaction mixture.

Stability of (I) in diethyl ether at —70 °C

The Grignard reagent (I) (4 mmol), prepared as described above in diethyl ether from phenylmagnesium bromide, was stirred for 20 h at —70 °C, hydrolyzed (6 mol l^{-1} HCl) and warmed to room temperature. The diethyl ether layer was phase-separated and the acid layer extracted with additional diethyl ether (2 × 25 cm^3). The ethereal extracts were combined and dried (anhyd. $MgSO_4$). Very little decomposition was noted, with 1*H*-perfluoro-octane[1] (97%) and phenyl iodide (100%) being the only products detected by GLC analysis. A repeat of this experiment at —40 °C for 4 h showed 39% decomposition after work-up, as measured indirectly by determining the amount of 1*H*-perfluoro-octane (61%) remaining.

Thermal decomposition of (I) at room temperature in diethyl ether

The Grignard reagent (I) (4 mmol), synthesized from phenylmagnesium bromide in diethyl ether, was allowed to warm from —70 °C to room temperature at a slow rate (2–3 h) and stirred at this temperature for an additional 18 h. The mixture was then hydrolyzed (6 mol l^{-1} HCl) and the diethyl ether layer decanted. The aqueous layer was extracted with diethyl ether (2 × 25 cm^3) and the etheral extracts combined and dried (anhyd. $MgSO_4$). GLC–mass spectral analysis revealed phenyl iodide (100%) and the *trans* isomer of 1-bromoperfluoro-octene (52%) to be the major products, along with traces of 1*H*-perfluoro-octane (4%), perfluoro-octene (< 4%) and two isomers of $C_{16}F_{32}$. The major product, the bromo-olefin, was separated by preparative GLC and further characterized. Mass spectral analysis of 1-bromoperfluoro-octene (nc) indicated peaks at 460 (M) and 191 ($M - C_5F_{11}$). The *trans* isomer was confirmed by ^{19}F NMR spectroscopy which gave the following data: a triplet at 80 (3F, CF_3); a multiplet at 125 (2F, $CF_3\underline{CF_2}$); a multiplet at 122 [6F, $(-CF_2-)_3$]; a multiplet at 116 (2F, $\underline{CF_2}CF{=}$); a doublet of triplets centered at 104 (1F, $\underline{CF}{=}CFBr$); and a doublet centered at 152 (1F, $\overset{a}{CF}{=}\overset{b}{\underline{CF}}Br$) with a coupling constant *J*(a–b) = 140 Hz. Analysis: Found: C, 21.16; Br, 17.03%. $C_8F_{15}Br$ requires C, 20.84; Br, 17.34%.

Stability of (I) in THF at —70 °C

The Grignard reagent (I) (4 mmol), prepared as described above from phenylmagnesium bromide in THF, was stirred for 20 h at —70 °C, hydrolyzed (6 mol l^{-1} HCl) and warmed to room temperature. The mixture was treated with benzene (50 cm^3) which caused a third layer, an oil, to drop out of solution. The small oil layer was separated and the remainder of the mixture extracted with benzene (2 × 25 cm^3). The benzene extracts were combined and dried (anhyd. $MgSO_4$). GLC analysis of the benzene solution revealed some decomposition as measured by the amount of 1*H*-perfluoro-octane (59%) remaining. Phenyl iodide (100%) was the only other material present in the benzene extracts. A repeat of this experiment at −40 °C for 4 h showed considerable decomposition with only 14% of 1*H*-perfluoro-octane remaining after hydrolysis. GLC–mass spectral analysis of the non-benzene oil layer revealed two major components with the empirical formula $C_{16}F_{32}$.

Thermal decomposition of (I) at room temperature in THF

The Grignard reagent (I) (4 mmol), synthesized from phenylmagnesium bromide in THF, was warmed from −70 °C to room temperature at a slow rate (2–3 h) and stirred for 25 h at this temperature. The mixture was then hydrolyzed (6 mol l^{-1} HCl) and treated with benzene (50 cm^3) when three liquid component layers resulted. The bottom oil layer was removed and the remaining two layers (benzene–water) were further extracted with benzene (2 × 25 cm^3). The benzene extracts were combined and dried (anhyd. $MgSO_4$). GLC–mass spectral analysis of the benzene layer revealed the following compounds present: phenyl iodide (100%), perfluoro-octene (4%) and 1*H*-perfluoro-octane (4%). GLC–mass spectral analysis of the bottom oil layer revealed two major components, each with a molecular ion appearing at 781 (M − F) and having the empirical formula $C_{16}F_{32}$. ^{19}F NMR analysis of the mixture did not indicate a terminal $(R_f)_2C{=}CF_2$ olefin but did however reveal a $R_fCF{=}CFR_f'$ type of structure, suggesting an internal olefin. ^1H NMR analysis showed that no protons were present.

Reaction of (I) with acetone in diethyl ether

To the Grignard reagent (I) (4 mmol), prepared from phenylmagnesium bromide (4 mmol) in diethyl ether (−70 °C), was added an excess of anhydrous acetone (8 mmol, 0.59 cm^3). The mixture was stirred for 15 min and then allowed to warm to 25 °C (3 h). The solution was then hydrolyzed with 6 mol l^{-1} HCl. The diethyl ether layer was separated and the acid layer extracted with additional diethyl ether (2 × 25 cm^3). The ethereal extracts were combined and dried (anhyd. $MgSO_4$). GLC–mass spectral analysis of the ether solution showed $n\text{-}C_8F_{17}C(CH_3)_2OH$ (nc) (90%) and phenyl iodide (100%) to be the major products, with a small amount of 1*H*-perfluoro-octane (7.4%). An analytical sample of the alcohol was prepared by concentration of the reaction mixture to a slurry and elution of the latter as a pentane solution on a silica gel chromatographic column. The column was eluted with a pentane–diethyl ether mixture, starting with 100 cm^3 of pentane and increasing in increments of 10 cm^3 to 100 cm^3 of diethyl ether. Concentration of the appropriate fractions yielded a solid, which when sublimed

(48 °C/0.25 mmHg) gave a white solid, m.p. 42–43 °C. Analysis: Found: C, 27.92; H, 1.52%. $C_{11}H_7F_{17}O$ requires: C, 27.62; H, 1.48%. Mass spectral analysis indicated peaks at 477 (M – H), 463 (M – CH_3), 459 (M – F), 439 (M – HF_2), 419 [M – $C(CH_3)_2OH$], 69 (CF_3) and 59 [$C(CH_3)_2OH$]. ^{19}F NMR spectroscopy gave the following data: a triplet at 80 (3F, $\underline{CF_3}$); a multiplet at 126 (2F, $CF_3\underline{CF_2}$); a multiplet at 121 [10F, $(-\underline{CF_2}-)_5$]; and a multiplet at 118 [2F, $\underline{CF_2}C(CH_3)_2OH$]. ^1H NMR spectroscopy indicated a singlet at 1.90 (1H, $O\underline{H}$) and a singlet at 1.50 (6H, $C\underline{H}_3$).

Reaction of (I) with acetone in diethyl ether at –70 °C

The Grignard reagent (I) (4 mmol), prepared as described above from phenylmagnesium bromide (4 mmol) in diethyl ether (–70 °C), was treated with an excess of acetone (8 mmol, 0.59 cm^3). After stirring at this temperature for 1 h, the reaction mixture was hydrolyzed (6 mol l^{-1} HCl) at –70 °C and warmed to room temperature. The diethyl ether layer was separated and the acid layer extracted with diethyl ether (2 × 25 cm^3). The ethereal extracts were combined and dried (anhyd. $MgSO_4$). The major products found present by GLC analysis were phenyl iodide (98%), 1*H*-perfluoro-octane (41%) and n-$C_8F_{17}C(CH_3)_2OH$ (58%).

Stability of (I) in diethyl ether at –70 °C as determined by reaction with acetone

The Grignard reagent (I) (4 mmol), prepared from phenylmagnesium bromide (4 mmol) in diethyl ether (–70 °C), was stirred for 20 h at this temperature and then treated with an excess of anhydrous acetone (8 mmol, 0.59 cm^3). The mixture was stirred for 30 min at –70 °C and then allowed to warm to room temperature over a period of 3 h. The solution was hydrolyzed (6 mol l^{-1} HCl), the diethyl ether layer decanted and the acid layer extracted with additional diethyl ether (2 × 25 cm^3). The ethereal layers were combined and dried (anhyd. $MgSO_4$). GLC–mass spectral analysis revealed the major components to be n-$C_8F_{17}C(CH_3)_2OH$ (82%) and phenyl iodide (98%), with a small amount of 1*H*-perfluoro-octane (9%).

Reaction of (I) with acetone in THF

To the Grignard reagent (I) (4 mmol), prepared as described above from phenylmagnesium bromide in THF (–70 °C), was added an excess of acetone (8 mmol, 0.59 cm^3). The reaction mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature. The solution was then hydrolyzed (6 mol l^{-1} HCl), treated with diethyl ether (50 cm^3) and extracted. The diethyl ether layer was separated and the acid layer again extracted with diethyl ether (2 × 25 cm^3). The ethereal extracts were combined and dried (anhyd. $MgSO_4$). GLC analysis of this solution revealed the major components to be phenyl iodide (91%) and n-$C_8F_{17}C(CH_3)_2OH$ (52%).

Reaction of (I) with trimethylchlorosilane

The Grignard reagent (I) (4 mmol), prepared as described above from phenylmagnesium bromide in anhydrous THF (—70 °C), was treated with an excess of trimethylchlorosilane (12 mmol, 1.54 cm^3) and stirred at this temperature for 2 h. After warming to room temperature (2 h), the mixture was hydrolyzed with a saturated solution of ammonium chloride and treated with pentane (50 cm^3). The pentane layer was extracted and the aqueous layer extracted with additional pentane (2 × 25 cm^3). The pentane extracts were combined and dried (anhyd. $MgSO_4$). GLC–mass spectral analysis revealed the following components: phenyl iodide (100%), 1*H*-perfluoro-octane (8%) and n-$C_8F_{17}Si(CH_3)_3$ (77%). A large-scale preparation yielded the desired silane as a colorless liquid, b.p. 70 °C/ 9.6 mmHg. Analysis: Found: C, 26.90; H, 1.82; F, 65.68%. $C_{11}H_9F_{17}Si$ requires C, 26.83; H, 1.83; F, 65.65%. Mass spectral analysis indicated peaks at 400 [M – $FSi(CH_3)_3$], 381 [M – F,$FSi(CH_3)_3$], 92 [$FSi(CH_3)_3$] and 73 [$Si(CH_3)_3$]. ^{19}F NMR spectroscopy gave the following data: a triplet at 82 (3F, CF_3); a multiplet at 127 (2F, $CF_3\underline{CF_2}$); a multiplet at 122 [8F, $(-\underline{CF_2}-)_4$]; a multiplet at 119 (2F, $\underline{CF_2}CF_2Si-$); and a multiplet at 129 (2F, $\underline{CF_2}Si-$). ^1H NMR spectroscopy indicated a singlet at 0.30 [$Si(CH_3)_3$].

Reaction of (I) with hexafluoroacetone in THF

The Grignard reagent (I) (4 mmol), prepared from phenylmagnesium bromide in THF (—70 °C), was treated with an excess of hexafluoroacetone (24 mmol, 4 g). The reaction mixture was stirred at —70 °C for 2 h and then allowed to warm to room temperature (2 h). The solution was hydrolyzed (6 mol l^{-1} HCl), treated with diethyl ether (50 cm^3), extracted and the ethereal layer separated. The acid layer was extracted with additional diethyl ether (2 × 25 cm^3) and the combined ethereal extracts were dried (anhyd. $MgSO_4$). GLC analysis revealed the following components: phenyl iodide (87%) and n-$C_8F_{17}C(CF_3)_2OH$ (nc) (64%). An analytical sample of the alcohol was separated by GLC. Found: C, 22.60; H, 0.48%. $C_{11}HF_{23}O$ requires C, 22.54; H, 0.17%. Mass spectral analysis indicated peaks at 567 (M – F), 517 (M – CF_3), 400 (C_8F_{16}), 167 [$C(CF_3)_2OH$] and 69 (CF_3). ^{19}F NMR spectroscopy gave the following data: a triplet at 81 (3F, $\underline{CF_3}$); a multiplet at 126 (2F, $CF_3\underline{CF_2}$); a multiplet at 122 [8F, $(-\underline{CF_2}-)_4$]; a multiplet at 120 [2F, $\underline{CF_2}CF_2C(CF_3)_2OH$]; a multiplet at 113 [2F, $\underline{CF_2}C(CF_3)_2OH$]; and a multiplet at 72 [6F, $C(CF_3)_2OH$].

Reaction of (I) with carbon dioxide

Carbon dioxide was bubbled into the Grignard reagent (I) (20 mmol) prepared from ethylmagnesium bromide (20 mmol) in diethyl ether (100 cm^3) at —70 °C. After approximately 15 min, tetrahydrofuran (10 cm^3) was added to the turbid reaction mixture. Carbonation was continued at —70 °C for 20 h. The alcohol/Dry Ice bath was then removed and the reaction mixture allowed to warm slowly as carbonation continued. At room temperature, the turbid reaction mixture was hydrolyzed with 25 % H_2SO_4. The clear two-phase mixture was phase-separated, the aqueous layer extracted with diethyl ether (3 ×) and the combined ethereal extracts dried (anhyd. $MgSO_4$) and concentrated. To the resultant amber liquid was added anhydrous ethanol (10 cm^3) plus 0.5 cm^3 of conc. H_2SO_4. After refluxing for 4 h, the solution was cooled and an internal standard ($C_{12}H_{26}$) added. The reaction mixture was analyzed by GLC which revealed n-$C_8F_{17}CO_2OC_2H_5$ (nc) (70%) as the major product. Two smaller components were also indicated, n-$C_8F_{17}H$ and another component of unknown composition. Distillation of the crude reaction mixture yielded a pure analytical sample of the ester, b.p. 200 °C/760 mmHg. Mass spectral analysis indicated peaks at 491 (M − H), 477 (M − CH_3), 463 (M − C_2H_5), 419 (C_8F_{17}), 169 (C_3F_7), 119 (C_2F_5) and 69 (CF_3). ^{19}F NMR spectroscopy gave the following data: a triplet at 81.8 (3F, $\underline{CF_3}$), a multiplet at 119 (2F, $\underline{CF_2}CO_2C_2H_5$); a multiplet at 122 and 123 [10F, $\underline{(-CF_2-)_5}$]; and a multiplet at 127 (2F, $CF_3\underline{CF_2}$). ^1H NMR spectroscopy indicated the following data: a triplet at 1.40 (3H, $\underline{CH_3}$) and a quartet at 4.43 (2H, $CH_3\underline{CH_2}$).

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