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SHORT COMMUNICATION

SYNTHESIS OF SOME PERFLUOROALKYLEETHER COMPOUNDS

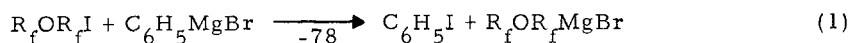
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The synthesis of perfluoroalkylether iodides and polyfluoroalkylether iodides have been described [1,2]. From one of these iodides, perfluoroisopropyl, 2-iodotetrafluoroethyl ether,  $(CF_3)_2CFOCF_2CF_2I$ , the organometallic compound  $(CF_3)_2CFOCF_2CF_2MgBr$  [2] was synthesized through the metal-halogen exchange reaction [3,4]. This Grignard as well as a series of Grignards of the general formula  $(CF_3)_2CFO(CF_2CF_2)_nMgBr$  ( $n=1, 2, 3, 4$ ) were recently prepared and derivatized with  $(CH_3)_3SiCl$  and  $(CH_3)_2SiHCl$  to give satisfactory yields of silylated products [6].

The perfluoroalkylether iodides ( $R_fOR_fI$ ) via their organometallic intermediates offer the possibility of synthesizing numerous  $R_fOR_f$  substituted compounds. Perfluoroalkyl Grignard and lithium compounds exhibit thermal sensitivity and as such must be used at low temperatures. At these temperatures the rates of reactions are generally slow and unless a very reactive substrate is present, the yield of product is generally low. At higher temperatures the rate of organometallic decomposition may be faster than the rate of reaction with the substrate. Even though perfluoroorganometallic magnesium and lithium compounds have these limitations they can be used with certain precautions to give reasonable yields of products.

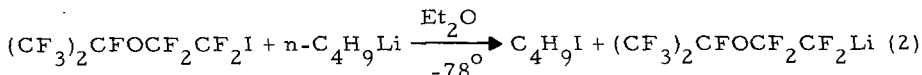
We have found, utilizing the halogen-metal exchange reaction, that in diethyl ether as the solvent, the reaction is quantitative.



Ethylmagnesium bromide reacts equally as well under stoichiometric conditions. In tetrahydrofuran as the reaction medium, the exchange reaction with either  $C_6H_5MgBr$  or  $C_2H_5MgBr$  does not proceed to completion. By using an excess (~10%) of the Grignard the  $R_fOR_fI$  may be completely converted to the  $R_fOR_fMgBr$ . In certain reactions the excess Grignard may create a problem since it will be competing for the substrate and provides additional unwanted derivatives. We [5], as well as others [6], have found that in diethyl ether the perfluoroalkyl Grignard reagents are poor nucleophiles and consequently low yields of products may be realized. In tetrahydrofuran the nucleophilic character of these Grignard reagents is increased sufficiently such that reasonable yields of products may be obtained. It is thus convenient to prepare the Grignard reagent in diethyl ether and perform the subsequent reactions with a substrate in tetrahydrofuran.

As indicated previously the perfluoroaliphatic Grignard and lithium compounds are thermally unstable. The Grignard  $(CF_3)_2CFOCF_2CF_2MgBr$  exhibits stability at  $-78^\circ$  for at least 16h. If the Grignard is allowed to reach ambient temperature and then hydrolyzed, a complex mixture of products results. These compounds have not been fully characterized, however, a partial identification by gas chromatogram-mass spectral analysis indicated the following products to be present;  $(CF_3)_2CFOCF_2CF_2H$ ,  $(CF_3)_2CFOCF=CF_2$ ,  $(CF_3)_2CFOCFHCF_2Br$ ,  $(CF_3)_2CFOCF=CFBr$ ,  $CF_2=CFBr$  and possibly a dimer of  $(CF_3)_2CFOCF=CF_2$ . The ratio of products varies with warm-up time of the Grignard prior to hydrolysis as would be expected. A more detailed analysis of all the products must still be made in order to determine the mode of thermal decomposition.

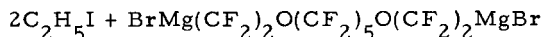
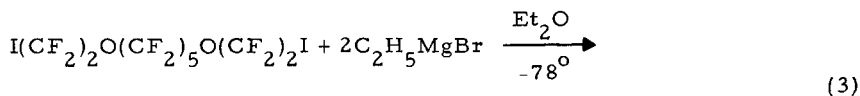
Utilizing the metal-halogen exchange reaction we have now prepared the organolithium reagent.



The exchange reaction is rapid and quantitative at  $-78^\circ$  in diethyl ether. After 20h at  $-78^\circ$  no significant decomposition of the organolithium com-

compound was noticed as determined by gas chromatographic analysis. When the temperature of the organolithium compound was raised to  $-30^{\circ}$  and kept at this temperature for approximately 2h, the principal decomposition product was  $(CF_3)_2CFOCF=CF_2$ . When  $C_6F_5Li$  was used in place of  $n-C_4H_9Li$ , the resulting organolithium compound was unstable even at  $-78^{\circ}$  and provided  $(CF_3)_2CFOCF=CF_2$  (62%) as the principal product. Thermal decomposition of the organolithium compound yields fewer products as compared to the Grignard reagent. The utility of these organometallic compounds as synthesis intermediates may be shown by their reaction with water to yield the  $(CF_3)_2CFOCF_2CF_2H$  (100%) with carbon dioxide followed by esterification to yield the ester  $(CF_3)_2CFOCF_2CF_2CO_2C_2H_5$  (86%) and with hexafluoroacetone to yield the tertiary alcohol  $(CF_3)_2CFOCF_2CF_2C(CF_3)_2COH$  (49%) and with chlorosilanes to yield the silylated derivatives [6].

The di-Grignard reagent  $BrMg(CF_2)_2O(CF_2)_5O(CF_2)_2MgBr$  can similarly be prepared through the metal-halogen exchange reaction.



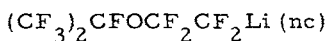
Hydrolysis of the di-Grignard reagent at  $-78^{\circ}$  gave the  $H(CF_2)_2O(CF_2)_5O(CF_2)_2H$  product indicating di-Grignard formation. Gas chromatographic analysis showed complete conversion of the diiodide. Carbonation of the di-Grignard yielded after esterification  $C_2H_5O_2C(CF_2)_2O(CF_2)_5O(CF_2)_2CO_2C_2H_5$ .

## EXPERIMENTAL

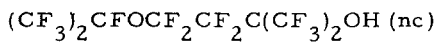


Phenylmagnesium bromide (3.3 ml, 2.92 molar) was slowly added to a diethyl ether solution (30 ml) of  $(CF_3)_2CFOCF_2CF_2I$  (4.0g, 0.0097 mole) cooled to  $-78^{\circ}$  containing n-decane (1.0g) as an internal standard. After

stirring for 1h, the reaction was hydrolyzed with 6N HCl, phase separated, the diethyl ether layer washed with water and dried ( $\text{MgSO}_4$ ). Gas chromatographic analysis (12' 10% Apiezon L on Chromosorb W) indicated that 97.5% of the starting iodide reacted. A new peak appeared which was isolated and identified as the hydrolysis product of the Grignard,  $(\text{CF}_3)_2\text{CFOCF}_2\text{CF}_2\text{H}(\text{nc})$  b.p.  $46^\circ$ . Analysis: Found: C, 21.22; H, 0.59%.  $\text{C}_5\text{F}_{11}\text{HO}$  requires C, 20.99; H, 0.35%. Mass spectral analysis gave no parent ion peak, however, a typical  $(\text{M}-\text{HF})^+$  peak at 266 was found. The  $^{19}\text{F}$  NMR was consistent with the structure.

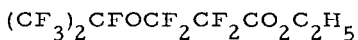


n-Butyllithium (0.022 mole, hexane solution) was slowly added to a diethyl ether solution (25 ml) of  $(\text{CF}_3)_2\text{CFOCF}_2\text{CF}_2\text{I}$  (10.3g; 0.025 mole) cooled to  $-78^\circ$ . After stirring for 1h, gas chromatographic analysis indicated complete reaction of the iodide. After 20h at  $-78^\circ$  analysis indicated no decomposition of the organolithium compound. The reaction mixture was allowed to warm up slowly (1h) to  $-30^\circ$  and kept at this temperature for 2h. Hydrolysis of the reaction mixture with 6NHCl and gas chromatographic analysis indicated a new product peak. Isolation of this product by vacuum transfer yielded  $(\text{CF}_3)_2\text{CFOCF}=\text{CF}_2$  [7] (2.20g; 0.0083 mole, 37% yield) mass spectral analysis gave the parent ion peak  $\text{M}^+266$  and  $(\text{M}-19)^+$  247. Infrared analysis indicated C-F at  $1110-1300\text{ cm}^{-1}$  and C=C at  $1880\text{ cm}^{-1}$ . When the above reaction was repeated using  $\text{C}_6\text{F}_5\text{Li}$  in place of  $n\text{-C}_4\text{H}_9\text{Li}$  at  $-78^\circ$  the yield of the  $(\text{CF}_3)_2\text{CFOCF}=\text{CF}_2$  increased to 62%.

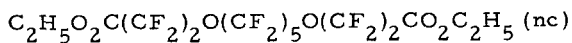


The Grignard  $(\text{CF}_3)_2\text{CFOCF}_2\text{CF}_2\text{MgBr}$  (0.075 mole in 300 ml of diethyl ether) was prepared as described above. Anhydrous THF (100 ml) was added to the Grignard followed by slow addition of hexafluoroacetone below the surface of the solution. Although it probably is not required, an excess of hexafluoroacetone (37g; 0.22 mole) was added. The reaction was

stirred at  $-78^{\circ}$  for 16h, and was slowly allowed to warm to room temperature over 4.5h. The solvent and excess hexafluoroacetone were evaporated in an aspirator. 6N HCl was added to the residue, the bottom organic layer was phase separated, washed with water and dried ( $\text{MgSO}_4$ ). Distillation from a small amount of conc.  $\text{H}_2\text{SO}_4$  yielded the alcohol b.p.  $123-124^{\circ}$ , (16.7g; 49.3% yield). Analysis: Found: C, 21.24; H, 0.28%  $\text{C}_8\text{F}_{17}\text{HO}_2$  requires C, 21.25; H, 0.22%. Mass spectral analysis gave no parent ion peak; however, a typical  $(\text{M}-20)^+$  peak at 432 was found.  $^{19}\text{F}$  NMR was consistent with the structure.



To a diethyl ether solution of  $(\text{CF}_3)_2\text{CFOCF}_2\text{CF}_2\text{MgBr}$  prepared as described above from  $(\text{CF}_3)_2\text{CFOCF}_2\text{CF}_2\text{I}$  (19.9g; 0.048 mole) and  $\text{C}_2\text{H}_5\text{MgBr}$  (0.048 mole) at  $-78^{\circ}$  was added tetrahydrofuran (30 ml). Carbon dioxide was slowly bubbled through the reaction mixture for 16h. The reaction was allowed to warm to ambient temperature with continued carbonation. The solvent was removed by aspiration, the residue was treated with 6N HCl (~100 ml) and the mixture extracted with diethyl ether. After drying ( $\text{MgSO}_4$ ), the solvent was aspirated leaving 17.0g. This crude acid product was esterified with anhydrous  $\text{C}_2\text{H}_5\text{OH}$  (150 ml) containing conc.  $\text{H}_2\text{SO}_4$  (10 ml). This mixture was added to cold water whereby a lower insoluble layer was formed, separated, dried and analyzed by gas chromatography (12' polyphenylether on Chromosorb P) indicating an 86% yield of the ester. Distillation gave the product, b.p.  $103^{\circ}$ . Analysis: Found: C, 26.91; H, 1.41%.  $\text{C}_8\text{F}_{11}\text{H}_5\text{O}_3$  requires C, 26.83; H, 1.41%. Mass spectral analysis gave  $\text{M}^+$  at 358 and a  $(\text{M}-\text{C}_2\text{H}_5)^+$  at 329. Infrared and  $^{19}\text{F}$  NMR were consistent with the structure.



A solution of  $\text{C}_2\text{H}_5\text{MgBr}$  (0.280 mole in diethyl ether) was slowly added to  $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{I}$  (100g, 0.136 mole) dissolved in diethyl ether (1000 ml) at a rate to keep the temperature between  $-78^{\circ}$  to  $-70^{\circ}$ .

After stirring the reaction for 30 min., an aliquot sample was removed and analyzed by gas chromatography. Analysis indicated absence of the diiodide and the appearance of a new peak which was isolated by preparative column chromatography. Analysis: Found: C, 22.55; H, 0.10%. The hydrolysis product of the di-Grignard  $\text{H}(\text{CF}_2)_2\text{O}(\text{CF}_2)_5\text{O}(\text{CF}_2)_2\text{H}$  requires C, 22.31; H, 0.41%. Mass spectral analysis gave no parent ion peak at 484; however, a typical  $(\text{M}-\text{HF})^+$  peak at 464 was found. The  $^{19}\text{F}$  NMR and  $^1\text{H}$  NMR were also consistent with the structure.

Carbonation of the remaining reaction mixture was carried out for 20h at  $-78^\circ$  after which the reaction mixture was allowed to slowly warm to ambient temperature with continued carbonation. The resulting mixture was hydrolyzed with 6N HCl, phase separated, dried ( $\text{MgSO}_4$ ) and concentrated, yielding a viscous liquid (80g). This material was esterified with anhydrous  $\text{C}_2\text{H}_5\text{OH}$  containing conc.  $\text{H}_2\text{SO}_4$  (~5 ml) for approximately 20h. Distillation gave the desired diester b.p.  $88^\circ/0.33$  mm (26% yield). Analysis: Found: C, 28.5%; H, 1.40%.  $\text{C}_{15}\text{F}_{18}\text{H}_{10}\text{O}_6$  requires C, 28.7; H, 1.60%. Mass spectral analysis gave a parent ion peak  $\text{M}^+$  628. Infrared,  $^{19}\text{F}$  NMR and  $^1\text{H}$  NMR were consistent with the structure.

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