Prior to 1946, attempts to prepare organomagnesium derivatives of completely halogenated hydrocarbons were unsuccessful [1]. In 1946, Brice [2] described the interaction of C,F,Br with magnesium; in his opinion, the reaction proceeded with the formation of C,F,MgBr. The only proof of the formation of an organomagnesium derivative was the formation of a small amount of C,F,H when the reaction mixture was decomposed with acid, although the reaction conditions did not exclude the formation of this product by the interaction of C,F,Br with the solvent.

The systematic investigation of methods of preparation and of the properties of perfluoroalkylmagnesium halides was begun in 1952 by Haszeldine and co-workers [3]. As a result of more than 300 experiments, they were able to show that the major conditions determining the successful formation of C,F,MgBr are the use of spectroscopically pure magnesium, activation of the magnesium with iodine and alkyl bromides, the use of electron-donor solvents as the reaction medium, and low temperatures (~50 to 0°). The yield of C,F,MgI was as high as 80% when the indicated conditions were observed. Haszeldine also showed that CF,Br can react with magnesium with the formation of CF,MgI, but the reaction rate is approximately 1000 times less in this case. Both C,F,MgI and CF,MgI were reacted with carbon dioxide, aldehydes, ketones, esters, and acid chlorides, and these reactions led to products analogous to those which are formed in the ordinary Grignard synthesis. In 1956, Park showed that perfluorovinyl iodide in ether solution can react with magnesium (activated with iodide) at 0° with the formation of CF,=CFMgI in 50% yield. The only proof of the formation of this compound was similar to the proof offered by Brice, conversion of trifluoroethylene by treatment of the reaction mixture with acid.

We have now shown that by activating the magnesium with ethyl bromide and carrying out the reaction in ether at ~30 to ~20°, it is possible to obtain practically quantitative consumption of the magnesium. By treating the reaction mixture with dilute acid, we were able to obtain a 70% yield of trifluoroethylene.

It was also shown that perfluorovinyl bromide and perfluorovinyl chloride do not react with magnesium under these conditions, and are recovered from the reaction mixture unchanged. It was possible to react perfluorovinyl bromide with magnesium to form the organomagnesium compound if the reaction was carried out in tetrahydrofuran; the yield of CF,=CFMgBr was 45%. Furthermore, it was not even necessary to activate the magnesium with ethyl bromide. Apparently, the assertion [5] that an increase in the basicity of the solvent promotes the formation of

\[ R_2\text{MgI} \]_

at the expense of stabilization of the compound in the form of a complex of the type \[ R_2\text{MgI} \]

In order to prove that a new type of organomagnesium compound was formed, we carried out a reaction between CF,=CFMgI and carbon dioxide.

Treatment of CF,=CFMgI in ether solution at ~40° with solid carbon dioxide and subsequent decomposition of the reaction mixture with 2 N sulfuric acid resulted in a 40% yield of perfluoroacrylic acid, which had previously been synthesized only by an extremely complex multistage route by Henne [6]. This method for the preparation
of perfluoroacrylic acid is recommended as a preparative procedure. Treatment of an ether solution of perfluoroacrylic acid with the calculated amount of diazomethane yields the methyl ester of perfluoroacrylic acid.

**EXPERIMENTAL**

**Preparation of perfluorovinylmagnesium bromide.** The experiment was carried out in a four-neck flask fitted with a stirrer, a thermometer, a diffuser for the introduction of the CF$_2$=CFBr, and an outlet tube connected to a Tischchenko bottle containing H$_2$SO$_4$. 13 g of CF$_2$=CFBr was fed (from a pressure bomb through the diffuser) to the flask which contained 4 g of iodine-activated magnesium and 100 ml of tetrahydrofuran at -20 to -25°. The mixture was then stirred for an hour, after which it was transferred to another flask which had been purged with nitrogen and cooled to -25°. The residual magnesium was washed with two portions of tetrahydrofuran of 10 ml each. The solution of CF$_2$=CFMgBr was cooled to -20°, and 50 ml of 2 N H$_2$SO$_4$ was added with vigorous stirring. The gas evolved was collected in traps at -110°; 1.9 ml of trifluoroethylene was collected, all of which distilled at -56°. Literature data [7]: b.p., -56°; found mol. wt., 82.92 and 80.48; calculated mol. wt., 82.0. This CF$_2$=CFH was converted to the dibromide, CF$_2$Br$_2$, with a b.p. of 76-76.5°; n$^\text{D}_{15}$ 1.4125. Literature data [8]: b.p. 76-76.5°; n$^\text{D}_{15}$ 1.4144; the yield of CH$_2$=CHBr and, consequently, of CH$_2$=CHMgBr was 43.8%.

**Preparation of perfluorovinylmagnesium iodide.** In a four-neck flask fitted with a stirrer, a dropping funnel, a thermometer, and an outlet tube connected to a Tischchenko bottle containing H$_2$SO$_4$ were placed 5 g of magnesium (shavings) and several crystals of iodine which had been sublimed over P$_2$O$_5$. The system was purged with dry nitrogen, and the flask was cooled to -25° by means of external cooling. Stiring was continued for another hour after the addition of the CF$_2$=CFI was complete; the ether solution was decanted from the remaining magnesium (2.58 g of Mg reacted) into another, similar reaction flask, the magnesium was carefully washed with ether, and this ether solution was added to the main solution. The resulting ether solution of CF$_2$=CFMgI was stirred vigorously, and 2 N H$_2$SO$_4$ was added to decompose the perfluorovinylmagnesium iodide. The gas evolved was collected in traps at -110°. A total of 6.5 g of gas was collected. When distilled in a Podbielniak column, all of the gas came over from -50° to -55°. According to the literature, the boiling point of trifluoroethylene is -56° [8]. The yield of CF$_2$=CFH and, consequently, of CF$_2$=CFMgI was 69%.

**Preparation of perfluoroacrylic acid.** Solid carbon dioxide was added over a period of 8 hours to an ether solution of CF$_2$=CFMgI (prepared from 21 g of CF$_2$=CFI and 2.8 g of Mg); the addition was carried out at a temperature of -70 to -40°. The reaction mixture was allowed to stand overnight at a temperature of -80°; on the following day, carbon dioxide was added for another 5 hours. The reaction mixture was heated to 20° and treated with 150 ml of 2 N H$_2$SO$_4$. The ether layer was separated, and the aqueous layer was extracted 15 times with 10-15 ml portions of ether. The combined ether solutions were dried over MgSO$_4$, and were then agitated with mercury. The ether was distilled, and the residue was sublimed under vacuum. 4.8 g of perfluoroacrylic acid, m.p. 36°, was obtained; the yield was 37.7%; mol. wt. found, 127.3 and 126.5; mol. wt. calculated for C$_3$H$_5$O$_2$F$_3$, 126.

Found %: F 44.5; 44.2. C$_3$H$_5$O$_2$F$_3$. Calculated %: F 45.2.

**Preparation of the methyl ester of perfluoroacrylic acid.** 4.77 g of perfluoroacrylic acid in 15 ml of ether was treated, with stirring, with an ether solution of diazomethane (1.7 g of CH$_2$N$_2$ in 50 ml of ether) at -12°. After the evolution of nitrogen (0.6 liter) had ceased and the reaction mixture had acquired a slightly yellow color, the addition of diazomethane was stopped, and the mixture was allowed to stand overnight. The ether solution was dried over MgSO$_4$, and the ether was distilled; distillation of the residue gave 2.7 g of a substance with a b.p. of 84-86° (0.5 g of kettle residue). A second distillation gave a fraction with a b.p. of 84-85°; this fraction, which had a sharp, irritating odor, was the methyl ester of perfluoroacrylic acid; the yield was 58%; n$^\text{D}_{15}$ 1.3590; d$^\text{D}_{15}$ 1.3259; found MR, 23.22; MR calculated, 22.16; mol. wt. found, 135.0 and 138.0; mol. wt. calculated for C$_4$H$_5$O$_2$F$_3$, 140.0.

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