

Studies of the Perfluoropropyl Grignard Reagent

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It has been shown (1) that phenylmagnesium bromide reacts with heptafluoro-1-iodopropane to give n-heptafluoropropylmagnesium bromide according to the equation: $\text{C}_6\text{H}_5\text{MgBr} + \text{C}_3\text{F}_7\text{I} \rightarrow \text{C}_3\text{F}_7\text{MgBr} + \text{C}_6\text{H}_5\text{I}$. The preparation of the perfluoropropyl Grignard reagent by this method has the advantages over the direct method (2) of rapidity of preparation and high yield. This reaction was shown to be fast and complete at Dry Ice temperature by the inability to detect in the resulting mixture heptafluoro-1-iodopropane and the isolation of a 95% yield of iodobenzene only five minutes after mixing.

The reaction of n-heptafluoropropylmagnesium bromide with acetone was studied and 85% yields of the tertiary alcohol, 4,4,4,3,3,2,2-heptafluoro-2-methyl-2-pentanol, were obtained. The *aldol* by-products, diacetone alcohol and mesityl oxide, along with other condensation products, are also obtained (3). By preparing the perfluoropropyl Grignard reagent at Dry Ice temperatures, adding the acetone in ether at a fairly rapid rate, and then removing the cooling bath, allowing the reaction mixture to warm to room temperature rather quickly, the side reactions of aldolization and perfluoropropyl Grignard decomposition are minimized and excellent yields of the tertiary alcohol can be obtained. This reaction was used to determine the amount of n-heptafluoropropylmagnesium bromide present at a given time in a series of thermal stability studies.

In these experiments, the perfluoropropyl Grignard reagent was prepared initially at Dry Ice temperature and then held at the desired temperature by means of cyrostats. The reaction mixture was then treated with acetone according to the procedure outlined above. The results are summarized in the following table.

Temp. (°C)	Time (hr)	Yield (%)	% Decomposition
—70	0	85	0
—73	24	76	10.
—73	48	70	17.
—20	6	52	39
—20	12	43	49.
—20	24	33	61
+2	3	18	79
+2	6	6.5	92
+2	12	3	97

The marked influence of temperature on stability can be seen. The perfluoropropyl Grignard reagent is decomposed rapidly at 2°, 92% in 6 hours. It is more stable at —20°C., being 49% decomposed after 12 hours,

but at Dry Ice temperature it is quite stable, being only 10% decomposed after 24 hours.

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Experimental

The Reaction of Heptafluoro-1-iodopropane with Phenylmagnesium Bromide.

A 100 ml round-bottom flask, having a capillary tube and stopcock by means of which the contents could be drained, was equipped with a mercury-sealed Hershberg stirrer, a thermometer well and a closed-circuit addition funnel having a jacket by means of which the contents of the funnel could be cooled. After drying the apparatus carefully, the flask was cooled in a Dry Ice bath through which the capillary tube extended, and 50 ml of anhydrous ether and 7.67 g (0.0259 mole) of heptafluoro-1-iodopropane was placed in the flask. When the temperature of the flask was constant (-62°), 30 ml (0.032 mole) of 1.07 molar phenylmagnesium bromide, cooled to Dry Ice temperature, was added dropwise to the flask during 5 minutes, causing the temperature to rise to -50° . The reaction mixture was then immediately added to a stirred 10% solution of hydrochloric acid at 0° . The ether layer was separated, dried, and fractionally distilled. Ultraviolet spectra analysis of the material boiling below 40° indicated that no heptafluoro-1-iodopropane was present. To check the validity of this type of analysis a mixture of 10 g of iodobenzene, 100 ml of ether and 2-3 ml of a solution of heptafluoro-1-iodopropane in ether (2.5 g/100 ml) was fractionally distilled until no more low-boiling material was obtained. Ultraviolet analysis of this low-boiling mixture showed the characteristic maximum of heptafluoro-1-iodopropane at 257μ . Thus it can be concluded that less than 1% of heptafluoro-1-iodopropane remained after a reaction time of only 5 minutes.

The Reaction of n-Heptafluoropropylmagnesium Bromide with Acetone.

A 500 ml round-bottom three-necked flask was equipped with a Trubore Hershberg stirrer, a closed circuit addition funnel, and a thermometer well. The apparatus was flamed out in a stream of dry nitrogen and subsequently cooled in a Dry Ice bath. Absolute ether (150 ml) and heptafluoro-1-iodopropane (29.6 g., 0.1 mole) were placed in the flask and phenylmagnesium bromide (100 ml, 1.07 molar) was added dropwise to the flask during 30 minutes. The temperature of the contents of the flask remain below -50°C. during the addition. Immediately after the addition of phenylmagnesium bromide, 10 ml (7.9 g., 0.14 mole) of purified acetone in an equal volume of ether was added dropwise to the flask during 15 min. The Dry Ice bath was removed immediately after the addition of acetone, and the contents of the flask were allowed to come to room temperature. After stirring at room temperature for 4 hours, the mixture was cooled to 0° and hydrolyzed with 200 ml of 10% hydrochloric acid. The contents of the flask were allowed to stir for 1 hour; the ether layer was separated, the acid layer washed three times with ether, and the combined ether solutions were dried over Drierite. The acid layer gave a negative test for

fluoride ion with cerous nitrate and zirconium-alizarine test solutions. The ether was partially distilled off through a 1 ft. glass helices-packed column, and the residue fractionally distilled through a Todd column. The material boiling between 71-120° weighed 21.1 g and was shown by infra-red spectra analysis to be 90% 4,4,4,3,3,2,2-heptafluoro-2-methyl-2-pentanol, representing an 85% yield.

Literature Cited

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- (3) A. L. HENNE and W. C. FRANCIS. J. Am. Chem. Soc., **75**: 992 (1953).