

60 and 85° as compared with the much smaller increase between 25 and 50°.

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A New Synthesis of *n*-Heptafluoropropyl Grignard Reagent

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The synthesis and reactions of *n*-heptafluoropropylmagnesium iodide have been reported in recent literature,¹⁻³ and in all cases the Grignard reagent was prepared by reaction of 1-iodoheptafluoropropane with magnesium metal. In this Laboratory, a Grignard reagent has been prepared in good yield from this iodide by reaction with phenylmagnesium bromide in diethyl ether at 0-10°. The reagent obtained was found to give a normal addition reaction with acetone in high yield, employing simultaneous addition of the phenyl Grignard reagent and acetone to a solution of the iodide. A study of the scope of this rather unusual Grignard exchange reaction is in progress.

Experimental

In a typical experiment, a 3-necked round bottom flask was equipped with a mercury-sealed Hershberg stirrer and two closed circuit addition funnels. A mercury bubble counter and Dry Ice-cooled vapor traps were attached to one of the addition funnels and dry nitrogen was introduced through the other. The flask was flamed with a Bunsen burner and, on cooling, 59.2 g. (0.2 mole) of 1-iodoheptafluoropropane in 250 ml. of anhydrous ether was added to the flask. The flask and contents were then cooled by means of an ice-water bath. Into one of the addition funnels was placed 110 ml. of 1.88 *M* phenylmagnesium bromide (0.207 mole) in ether, and into the other was placed 17.4 g. (0.3 mole) of acetone (commercial grade, 99%) in an equal volume of anhydrous ether. The Grignard reagent and the acetone were then added simultaneously to the ether solution of 1-iodoheptafluoropropane. A white flocculent precipitate formed as soon as a few drops had been added. The addition was conducted over a period of four hours and the reaction mixture was stirred at ice-bath temperatures for an additional eight hours. The reaction mixture was then light yellow in color and contained a considerable quantity of the white flocculent material. No escaping gas was observed and no material condensed in the vapor trap.

The reaction mixture was then hydrolyzed with 300 ml. of ice-cold 10% sulfuric acid. The solid completely dissolved and the mixture was separated into two sharply divided portions. The ether layer was separated and washed once with water. The water layer was extracted three times with ether and the ether portions were combined and dried with Drierite. The ether was distilled through a short column (14 mm. barrel, stainless steel, "heli-pak" packing) and the residue was rectified through the same column. After a short forerun (2-3 cc.), 29.6 g. of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol¹⁻³ boiling at 107-108° was obtained, representing a 65% yield based on the 1-iodoheptafluoropropane. Also, 33.8 g. of iodobenzene was formed, which raises to 83% the accounting of the 1-iodoheptafluoropropane.

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(1) O. R. Pierce and M. Levine, *THIS JOURNAL*, **73**, 1254 (1951).

(2) A. L. Henne and W. Francis, private communication.

(3) R. N. Haschick, *J. Chem. Soc.*, 3423 (1952).

The Fluoroplatinates. I. Lanthanum, Cerium, Praseodymium and Neodymium Fluoroplatinates

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During the investigation of the effect of fluorine on certain rare earth fluorides, the reaction between fluorine, platinum and a rare earth fluoride was noted. The product was determined to be the fluorine analog of the chloroplatinates, namely, a fluoroplatinate. This is the first of a series of papers dealing with the preparation and properties of compounds containing the fluoroplatinate ion.

Of the platinum complexes having the general formula $(PtX_6)^{-2}$ in which X is a halogen, a number of compounds have been prepared which contain either chlorine, bromine or iodine as X. With regard to fluorine, there is only one original reference citing the preparation and properties of a compound containing the complex $(PtF_6)^{-2}$. This is the work of Schlesinger and Tapley² who prepared K_2PtF_6 . This compound was formed by heating finely divided platinum with $3KF \cdot HF \cdot PbF_4$ in a platinum boat. Their efforts to prepare other fluoroplatinic salts were unsuccessful.

In this investigation the fluoroplatinates of lanthanum, cerium, praseodymium and neodymium were prepared and some of their physical properties determined. The rare earth fluoroplatinates were prepared by treating an intimate mixture of platinum and the respective fluoride with elemental fluorine at 525°.

Experimental Methods and Materials

Rare Earth Fluorides.—The rare earth oxides from which the rare earth fluorides were prepared, were a part of the Welsbach collection. Only trace amounts of the neighboring rare earth elements were found in each respective rare earth oxide. The rare earth trifluorides were prepared by precipitation from rare earth chloride solutions with hydrofluoric acid. Absolute alcohol was used to wash the precipitates.

Platinum.—The platinum foil from which the platinum boats were fashioned was 0.0015 inch thick. The boat had the dimensions 4.8 cm. × 1.0 cm. × 0.7 cm.

Fluorine.—Fluorine was prepared by the electrolysis of molten potassium bifluoride. The fluorine generator was constructed according to the description given by Von Wartenburg.³ The anode was made of carbon.

Reaction Tube.—Fluorination was carried out in a nickel tube, 14" in length, 7/8" inside diameter and 1/8" in thickness. During the runs, the tube was heated in a calibrated electric combustion furnace. The connections between the nickel tube and the fluorine inlet consisted of plaster of Paris stoppers.

The Rare Earth Fluoroplatinates.—All samples were prepared by identical procedures. A rare earth fluoride was spread evenly in a thin layer on the bottom of a platinum boat. Several strips of platinum foil were placed lengthwise on top of the layer of salts, and then covered with another thin layer of the rare earth fluoride. This process was repeated until the capacity of the boat had been reached. The sample was then placed in the reaction tube. While the tube was being heated to 525°, the system was flushed with dry air. The sample was fluorinated for five hours. In each instance, after the completion of a run, the platinum foil had disappeared in the formation of the fluoroplatinate. The rare earth fluoroplatinates are soluble in water and thus

(1) Abstracted from a portion of the thesis submitted by Theodore P. Perros in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) H. Schlesinger and M. Tapley, *THIS JOURNAL*, **46**, 276 (1924).

(3) H. Von Wartenburg, *Z. anorg. allgem. Chem.*, **244**, 377 (1940).