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

BY O. R. PIERCE, A. F. MEINERS AND E. T. MCBEE

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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-pentanol[1-3] 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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The Fluoroplatinates. I. Lanthanum, Cerium, Praseodymium and Neodymium Fluoroplatinates

BY THEODORE P. PERROS[1] AND CHARLES R. NAESER

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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 Tapley[2] 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

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[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).

were easily separated from the residual, unreacted, insoluble rare earth fluorides.

Solubility.—The solubilities of the rare earth fluoroplatinates were determined approximately by measuring the least amount of water necessary to dissolve a weighed sample of the salt at a temperature of 30°.

Density.—The densities were determined at 30° with a 1-ml. pycnometer using toluene as the displacement liquid.

Absorption Spectra.—For each compound the absorption spectrum was measured with a model DU Beckman spectrophotometer using matched 1-cm. cells.

Analyses.—The compounds were analyzed according to the accepted analytical procedures. Each of the rare earth elements was determined by precipitation as the oxalate. After filtration of the precipitate, it was titrated with standard permanganate solution. Platinum was determined by reduction of the fluoroplatinate ion with hydrazine. Fluorine was determined gravimetrically as lead fluochloride. The results are summarized in Table I.

TABLE I

ANALYTICAL DATA

Compound	Rare earth, % Calcd.	Rare earth, % Found	Platinum, % Calcd.	Platinum, % Found	Fluoride, % Calcd.	Fluoride, % Found
$La_2(PtF_6)_3$	23.05	22.93	48.58	48.47	28.37	28.22
$Pr_2(PtF_6)_3$	23.30	23.16	48.43	48.12	28.27	28.01
$Nd_2(PtF_6)_3$	23.72	23.45	48.16	48.00	28.12	27.90

Discussion

The fluoroplatinate of cerium was the only one which could not be isolated. This was to be expected, since tetravalent cerium was produced by the action of fluorine. The addition of water to the cerium product resulted in the immediate but gradually complete hydrolysis of the salt. The addition of oxalic acid to a fresh solution of the cerium fluoroplatinate precipitated all of the cerium at once, leaving the fluoroplatinate ion in solution.

The presence of this ion was established by (a) its precipitation as potassium fluoroplatinate through the addition of potassium fluoride and (b) the subsequent analysis of this precipitate. The alkali fluoroplatinates will be the subject of a future paper.

The aqueous solution of lanthanum fluoroplatinate has a pale yellow color. Since lanthanum ions are colorless, this color may be attributed to the fluoroplatinate ion. The absorption spectrum of this compound revealed two characteristic peaks of the fluoroplatinate ion at 273 and 308 mμ. These appeared in all subsequent absorption spectra measurements of other fluoroplatinate compounds.

The color of praseodymium fluoroplatinate is yellow-green, whereas that of neodymium is lavender. In the absorption spectra of these two compounds, the bands characteristic of praseodymium and neodymium as well as those of the fluoroplatinate ions are evident.

The solubilities and densities of the rare earth fluoroplatinates are given in Table II.

TABLE II

Fluoroplatinates	Density	Solubility/100 g. of H_2O
Lanthanum	2.63	7.5
Praseodymium	2.64	7.1
Neodymium	2.66	6.6

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Kinetics of Chlorine Replacement by Ethylate Ion in Ethanol Solutions of Symmetrical Trichlorobenzene[1]

BY THOR R. RUBIN AND A. A. BROOKS[2]

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Previous work on the replacement of aromatic halogen by basic ions indicates the reactions are of second order.[3–5]

Some of the above studies[6–12] involve aromatic compounds which are subject to reduction in anhydrous alcohol solution, particularly at temperatures greater than 70°.

In a preliminary study Holleman[13] showed that symmetrical 1,3,5-trichlorobenzene reacts reasonably rapidly with base in methanol solution without forming large amounts of phenols.

The present results are concerned with the replacement of halogen in 1,3,5-trichlorobenzene by ethylate ion in anhydrous ethanol.

The replacement process of halogen by ethylate on the benzene ring forms under certain conditions several reaction products two of which were identified. One was 3,5-dichlorophenetole (compound A of Table I) the other was 3,5-diethoxychlorobenzene (compound B of Table I).

These compounds were recovered from a relatively large amount of a reaction mixture consisting initially of excess sodium ethylate, 1,3,5-trichlorobenzene and anhydrous ethanol which was kept at 170° in a glass lined bomb for 50 hours under nitrogen. The amount of 3,5-diethoxychlorobenzene recovered was about 15% of the amount of

TABLE I

PROPERTIES OF THE REACTION PRODUCTS AND THEIR DERIVATIVES

		Compound A	3,5-Dichlorophenetole[a]	Compound B	3,5-Diethoxychlorobenzene[b]
B.p., °C. (mm.)		92 (4)	...	111 (4)	....
		106 (8)	...	116 (8)	....
$n^{20}D$		1.5405	...	1.5225	....
Analysis, %	C	50.20	50.28	60.49	59.85
		50.15		60.56	
	H	4.88	4.22	6.71	6.53
		4.52		6.82	
Phenol dev., m.p., °C.		64.4–65.5	68	114.0–116.5	117
Benzoate dev., m.p., °C.		56.8–57.4	55	....	....
Hydrate dev.		....	...	Formed in moist benzene	Insoluble in benzene

[a] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 217. [b] *Ibid.*, pp. 340.

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(1) Taken from the dissertation submitted by A. A. Brooks, in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The Ohio State University.

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