binol. A sample of methylisopropylcarbinol treated with nitric acid under the same conditions as in the hydration of the trimethylethylene was not converted to the *t*-amyl alcohol to an extent measurable by the infrared spectrum.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

Preparation and Some Reactions of *n*-Heptafluoropropylmagnesium Iodide

BY O. R. PIERCE AND M. LEVINE

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An investigation of the reaction of heptafluoro-1-iodopropane with magnesium metal has been reported by Henne[1,2] and Haszeldine.[3] A study of the perfluoropropyl Grignard reagent was initiated in this Laboratory to develop techniques applicable to the preparation of a fluorine-containing silane. The investigation reported here outlines the experimental conditions which were studied in an attempt to obtain maximum yields of the Grignard reagent as indicated by addition products, using acetone, ethyl trifluoroacetate, heptafluorobutyraldehyde and 1,1,1-trifluoro-2-propanone. It should be pointed out that the Grignard reagent acts as a catalyst in aldol-type condensation reactions thereby reducing the yield of addition products in those instances in which the carbonyl compound contained α-hydrogen atoms.

Experimental

Preparation of Heptafluoro-1-iodopropane.—This material was prepared as described previously.[4]

Preparation of 3,3,4,4,5,5,5-Heptafluoro-2-methyl-2-pentanol.—Magnesium turnings, 6 g. (0.25 mole), were placed in a three-necked, round-bottom flask fitted with an efficient stirrer, separatory funnel, and reflux condenser to which was attached a Dry Ice cooled trap. The entire apparatus was dried and 100 ml. of dry tetrahydrofuran was added. A small amount of heptafluoro-1-iodopropane was introduced into the reaction flask at room temperature and the mixture was stirred vigorously until reaction had started as indicated by evolution of heat and the formation of a brown precipitate. The reaction flask was cooled immediately to −30 to −40°, and maintained at this temperature during the addition of 74 g. (0.25 mole) of heptafluoro-1-iodopropane. The extent of reaction was followed by the formation of a precipitate as the magnesium metal disappeared. The reaction became exothermic in those experiments when cooling of the reaction flask was not accomplished immediately following initiation of Grignard formation. When all the halide had been added, stirring of the mixture was continued for two hours.

Acetone, 25 g. (0.5 mole) was added dropwise at −30° and the reaction temperature was allowed to rise gradually to 25°. The reaction mixture was then hydrolyzed with water resulting in the formation of magnesium salts. The contents of the flask were then poured onto a 10% sulfuric acid–ice mixture. Upon rectification, there was obtained 20 g. of unreacted heptafluoro-1-iodopropane and 12 g. of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol, b.p. 107–108°, $n^{20}\text{D}$ 1.3250, which represents a conversion of 21% and a 48% yield. Assignment of the structure was based on agreement with the reported properties of the tertiary alcohol.[5]

Preparation of 1,1,1-Trifluoro-3,3,4,4,5,5,5-heptafluoro-2-pentanone.—The Grignard reagent was prepared as previously described. Ethyl trifluoroacetate, 18 g. (0.12 mole), was added dropwise at −30° to the reaction flask and the temperature of the mixture was allowed to warm to 25°. Heat was evolved and a gummy precipitate formed. The mixture was stirred at 50° for several hours. The reaction products were then heated to reflux and, upon cooling, were hydrolyzed with a 10% sulfuric acid-ice mixture. Upon rectification, there was obtained 18 g. (24%) of unreacted heptafluoro-1-iodopropane and 22.1 g. of material, b.p. 104–105°, $n^{20}\text{D}$ 1.3449, $d^{20}{}_4$ 1.388. Since the infrared spectrum indicated the presence of a solvated ketone, this material was heated with phosphorus pentoxide, and there was obtained 15 g. (0.06 mole) of the ketone, $CF_3–CO–C_3F_7$, b.p. 30–31°, which represents a yield of 50% of the theoretical.

Anal. Calcd. for $C_6F_{10}O$: C, 22.57; H, 0.0; F, 71.4. Found: C, 22.28; H, 0.016; F, 70.0.

Preparation of 1,1,1,2,2,3,3,5,5,6,6,7,7,7-Tetradecafluoro - 4 - heptanol.—Heptafluorobutyraldehyde, 60 g. (0.3 mole), was added dropwise to the Grignard reagent (100 g. of heptafluoro-1-iodopropane and 8 g. of magnesium turnings), at −50°. The reaction mixture was allowed to come to room temperature at which point it became so viscous that additional solvent was added in order to continue stirring. Following hydrolysis and rectification, there was obtained 40 g. of material, b.p. 94–95°. Both the infrared spectrum and analytical data indicated that the alcohol was contaminated with a small amount of tetrahydrofuran, and it was found necessary to isolate the alcohol as the 3,5-dinitrobenzoate ester, m.p. 106–107°. The ester was found to react with ethanol and was recrystallized from petroleum ether and benzene. The conversion obtained in this manner represents 33% of the theoretical.

Anal. Calcd. for $C_{14}H_4O_6N_2F_{14}$: C, 29.9; H, 0.8. Found: C, 30.3; H, 0.98.

Reaction of the Grignard Reagent with 1,1,1-Trifluoro-2-propanone.—1,1,1-Trifluoro-2-propanone, 25 g. (0.25 mole), was added slowly to the Grignard reagent and the products were treated as previously described (the techniques of the reaction are such that it is inconvenient to add the Grignard reagent to 1,1,1-trifluoro-2-propanone). Distillation of the reaction mixture resulted in sublimation of a solid which, recrystallized from a mixture of benzene and petroleum ether, melted sharply at 93–94°. There are indications that this material is a polymer of 1,1,1-trifluoro-2-propanone.

Anal. Calcd. for $C_3H_3F_3O$: C, 32.1; H, 2.67. Found: C, 30.5; H, 2.63.

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DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

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The Chemistry of Scandium. IV. The Structure of Scandium Oxinate

BY L. POKRAS, M. KILPATRICK AND P. M. BERNAYS

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In a recent paper[1] on the 8-hydroxyquinoline compound of scandium[2] it was noted that, as in the cases of the analogous thorium, uranium and plutonium derivatives, the compound includes an "extra" molecule of oxine. For such compounds it is difficult to understand the nature of the chemical binding between the expected normal oxinate and the "extra" oxine molecule. The

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[1] L. Pokras and P. M. Bernays, THIS JOURNAL, **73**, 7 (1951).

[2] The formula of the 8-hydroxyquinoline compound, $Sc(C_9H_6ON)_3 \cdot C_9H_7ON$, is abbreviated as $Sc(On)_3 \cdot HOn$; 8-hydroxyquinoline or oxine is written as HOn.