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.

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Preparation and Some Reactions of *n*-Heptafluoropropylmagnesium Iodide

BY O. R. PIERCE AND M. LEVINE

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}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]

(1) A. L. Henne and W. C. Francis, THIS JOURNAL, **73**, 3518 (1951).

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

(3) R. N. Haszeldine, *Nature*, **167**, 139 (1951).

(4) M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).

(5) E. T. McBee, O. R. Pierce and M. C. Chen, private communication.

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}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 $C_5F_{10}O$: 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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The Chemistry of Scandium. IV. The Structure of Scandium Oxinate

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

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

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

(2) The formula of the 8-hydroxyquinoline compound, Sc(C₉H₆-ON)₃·C₉H₇ON, is abbreviated as Sc(On)₃·HOn; 8-hydroxyquinoline or oxine is written as HOn.

following new data lead us to believe that the "extra" molecule is bound merely by weak lattice forces and that the scandium compound is a lattice compound, capable of existence only in the solid state, and similar to Cs_3CoCl_5 and $(NH_4)_3ZrF_7$ discussed by Eméleus and Anderson.[3]

Experimental

The toluene employed as solvent was reagent grade, purified by distillation through a 12 to 15 theoretical plate column. The oxine was purified by double sublimation and contained less than 0.1% total impurities when so prepared. The scandium oxinate was prepared as described previously.[1]

Results and Discussion

Solutions of pure oxine in toluene from $1.41_4 \times 10^{-3}$ to 4.39×10^{-5} mole per liter of toluene at 25° were studied in a Beckman DU spectrophotometer equipped with a thermostated cell compartment. Appreciable absorption was found only in the region 280–400 mμ, with a band maximum at 317 mμ and molar extinction coefficient of 2490 at the band maximum.[4] In this concentration range, Beer's law is obeyed.

Similar studies of the absorption of pure Sc-(On)$_3$·HOn in toluene[5] indicated absorption maxima at 375 and 317 mμ. In solutions ranging from 2.36 to 0.589×10^{-4} molar in Sc(On)$_3$·HOn, Beer's law is not obeyed; the apparent molar extinction coefficient varied regularly from 5200 to 3820 at 375 mμ and from 7775 to 8340 at 317 mμ.

Additional studies were then made of the absorption of systems containing both HOn and Sc-(On)$_3$·HOn. In one series of studies, seven solutions with constant ScOn$_3$·HOn concentration and varying concentrations of added free HOn were examined. A second series of studies consisted of six systems with a fixed concentration of total oxine and oxinate; and varying scandium concentrations. Analysis of the resulting data[6] clearly indicated that there was no dissociation equilibrium in the system of the type: Sc(On)$_3$·HOn $\rightleftharpoons$ ScOn$_3$ + HOn. On the basis of the spectrophotometric data, Sc(On)$_3$·HOn is either completely undissociated, or else completely dissociated in toluene; however, it is not possible to determine from this evidence which is the case.

The apparent molecular weight of the Sc(On)$_3$·HOn in benzene was then determined, by freezing point depression, to be 330 ± 60. Since the calculated molecular weight of the compound is 622 the solutions must contain two particles per molecule and it is apparent that the substance must be completely dissociated into Sc(On)$_3$ and free HOn in benzene and toluene.

It seems reasonable that the energy of solvation

(3) H. J. Eméleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1944, pp. 80–81.

(4) The absorption of the solvent becomes too large below 280 mμ to permit measurements at shorter wave lengths.

(5) It should be noted that these solutions, like solutions of gallium and thallium(III) oxinates recently reported by Moeller and Cohen, Anal. Chem., 22, 686 (1950), are subject to slow photochemical decomposition. In diffuse light this phenomenon does not interfere seriously with the validity of the measurements if they are carried out within a few hours after preparation of the solutions.

(6) L. Pokras, "The Chemistry of Scandium," Ph.D. dissertation, Illinois Institute of Technology, 1952, pp. 68–80.

of the scandium oxinate in toluene and benzene is quite small, probably less than 1 kcal. per mole. The binding cannot be either covalent or ionic because the compound is completely dissociated in these solvents and because such bond energies would have to be of the order of 30 to 50 kcal. per mole. It is difficult to see how solvation could account for the large energies required to dissociate either an ionic or covalent bond, or any bond of intermediate character. It follows that the binding can only be by weak lattice forces in the molecular crystal.

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Diffusion of Hydrocarbon Vapors into Polyisobutylene. II[1]

BY S. PRAGER, E. BAGLEY AND F. A. LONG

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Previous studies[2] of the rates of diffusion of the vapors of several hydrocarbons into polyisobutylene have been extended to higher and lower temperatures in order to determine the temperature coefficients for the diffusion and especially to determine variations in the energy of activation with size and shape of the diffusing molecule. The studies at 35° showed that the diffusion obeyed Fick's law (with the usual assumption of equilibrium concentration of vapor at the polymer surface) but with a concentration dependent diffusion coefficient. Furthermore, the magnitude of the diffusion coefficient at a given concentration depended on the size and particularly on the shape of the diffusing species.

Similar studies have now been made at 25 and 46.5° with the five hydrocarbons: n-butane, n-pentane, isobutane, isopentane and neopentane. The experimental procedures and materials were the same as used previously,[2] as was the method of evaluation of the diffusion coefficients from sorption and desorption data at various pressures. As at 35°, the diffusion coefficients at the other temperatures increased exponentially with concentration, following the equation

$$\bar{D} = \bar{D}_0 e^{AC} \qquad (1)$$

where $\bar{D}$ is the integral diffusion coefficient, C is concentration expressed as grams of hydrocarbon per gram of dry polymer and $\bar{D}_0$ and A are constants characteristic of a given hydrocarbon. All of these studies were made in the concentration range of from $C = 0$ to $C = 0.1$ g. of hydrocarbon per gram of polymer.

Table I gives values of the parameters $\bar{D}_0$ and A for the five hydrocarbons at the three temperatures, 25, 35 and 46.5°. Also included are values of V_m, the molar volume of the hydrocarbons at 25°.[3]

It is seen that at each temperature the values of $\bar{D}_0$, the diffusion coefficient at zero concentration,

(1) Research supported by Army Ordnance.

(2) S. Prager and F. A. Long, THIS JOURNAL, 73, 4072 (1951).

(3) U. S. Nat. Bureau of Standards, API Res. Project 44, Properties of Hydrocarbons.