$(OH)C_3H_7$ there is a strong, sharply defined band in this region with a transmittance of only 9%, while for the hydrogen-poorer $C_3F_7CH_2OH$ there is a much weaker absorption (42% transmittance) and the peaks of the band are less sharp; for $C_3F_7CH(OH)C_3F_7$ the carbon–hydrogen absorption is very weak, with 74% transmittance.

For $C_3F_7CH_2OH$ the strong, broad band for associated –OH is at 3 μ with 6% transmittance; it differs very little from that of 1-butanol. The unassociated –OH band appears only as a break in the curve at 2.8 μ with 69% transmittance.

For $C_3F_7CH(OH)C_3H_7$, the associated –OH band is very similar to that of $C_3F_7CH_2OH$, but with a slight shift toward shorter wave lengths at 2.97 μ with 10% transmittance. The reason for such a shift is not apparent, but might perhaps be attributed to steric factors. The non-associated –OH is still overlapped, and appears only as a break at 2.8 μ with 70% transmittance.

For $C_3F_7CH(OH)C_3F_7$ there is a strong difference. The non-associated –OH is now quite prominent at 2.8 μ with 39% transmittance; the associated –OH band is much less intense than in the previous cases, with 36% transmittance, and there is a shift to a shorter wave length at 2.9 μ. All this denotes a weaker hydrogen bonding, attributable to the reduced basicity of the hydroxylic oxygen atom.

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Reactions of Perfluorinated Propylmagnesium Iodide

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Pilot information on perfluorinated Grignard reagents, $C_nF_{2n+1}MgX$ has appeared recently,[1,2,3] and in a preliminary communication[1] we have shown that n-C_3F_7MgI could be formed and combined at low temperature with carbon dioxide or acetone in workable syntheses. The present paper reports further details and observed limitations in the formation and reactions of perfluorinated n-propylmagnesium iodide, C_3F_7MgI. The yields reported are not the best possible, but are either minimal yields or else clear indications that the reactions do not occur to any appreciable extent.

At room temperature, n-C_3F_7I reacts readily with magnesium in ethyl ether or tetrahydrofuran, but the main products are $CF_3CF{=}CF_2$ and fluorinated tars. Hydrolysis to C_3F_7H and titration with aqueous acids agree to show the presence of about 5% of C_3F_7MgI, and this order of magnitude can be confirmed by carbonation or condensation with acetone. The instability of n-C_3F_7MgI at this temperature is such that it is completely decomposed in a few hours.

At lowered temperatures, down to −80°, the stability of n-C_3F_7MgI improves progressively, but its rate of formation is much slower. As these two factors oppose each other, the problem of devising practical applications is not solved by a mere lowering of the temperature. As previously reported,[1] the best results were obtained by forming the Grignard reagent at low temperature in the presence of the compound with which it should condense. This procedure has now been applied to several derivatives with a carbonyl or carboxyl group.

The following results were noted when C_3F_7MgI was prepared at temperatures lower than −40° and in the presence of the condensing agent which should consume it as made, except where otherwise stated: (1) Acetone gave a 10% yield of $C_3F_7C(OH)(CH_3)_2$, which was identified and measured as its dehydration product, $C_3F_7C(CH_3){=}CH_2$. Mesityl oxide appeared as side-product, in quantities which varied with experimental conditions. (2) Butyraldehyde gave a 16% yield of the expected secondary alcohol, $C_3H_7CH(OH)C_3F_7$ and by-products attributed to aldol-type condensation of the aldehyde. (3) Perfluorinated butyraldehyde failed to give more than traces of the expected secondary alcohol, $C_3F_7CH(OH)C_3F_7$, and was recovered as aldehyde hydrate (38%), aldehyde polymer (48%) and perfluorobutyric acid (6%). (4) Ethyl formate gave a 24% yield of perfluorobutyraldehyde isolated as its hydrate, $C_3F_7CH(OH)_2$, but no secondary alcohol even when a large excess of the Grignard reagent was supplied. (5) Ethyl perfluorobutyrate gave 20% of perfluorinated ketone, $C_3F_7COC_3F_7$, but no tertiary alcohol. (6) Perfluorinated butyryl chloride, C_3F_7COCl, stopped the formation of the Grignard derivative. The condensation was therefore carried out in a separate step, which gave a 4% yield of ketone, $C_3F_7COC_3F_7$.

The reaction with a perfluorinated aldehyde, C_3F_7CHO, which could not suffer from competing aldolization but gave, nevertheless, practically no condensation with the Grignard reagent is consistent with the poor yields reported for its condensations with ordinary Grignard reagents.[4,5] With ethyl formate, the formation of C_3F_7CHO only agrees with the observed indifference of this aldehyde to C_3F_7MgI. With derivatives of the perfluorinated acids, the preferential formation of ketones is consistent with the action of ordinary Grignard reagents on these derivatives.[6]

The most practical result is the preparation of perfluorinated ketones from perfluorinated acids which are now commercially available.[7]

To illustrate, $C_3F_7COC_3F_7$ was synthesized from two moles of $C_3F_7CO_2H$, one mole of which was transformed into C_3F_7MgI by the sequence $C_3F_7CO_2H$ to $C_3F_7CO_2Ag$ to C_3F_7I to C_3F_7MgI, and

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

[2] R. N. Haszeldine, *Nature*, **167**, 139 (1951); **168**, 1028 (1951).

[3] R. N. Haszeldine, 120th and 122nd A.C.S. Meetings, September, 1951 and 1952.

[4] E. T. McBee, J. F. Higgins and O. R. Pierce, THIS JOURNAL, **74**, 1387 (1952).

[5] E. T. McBee, O. R. Pierce and J. F. Higgins, *ibid.*, **74**, 1737 (1952).

[6] K. N. Campbell, J. O. Knobloch and B. C. Campbell, *ibid.*, **72**, 4380 (1950).

[7] Minnesota Mining and Manufacturing Co., St. Paul, Minnesota.

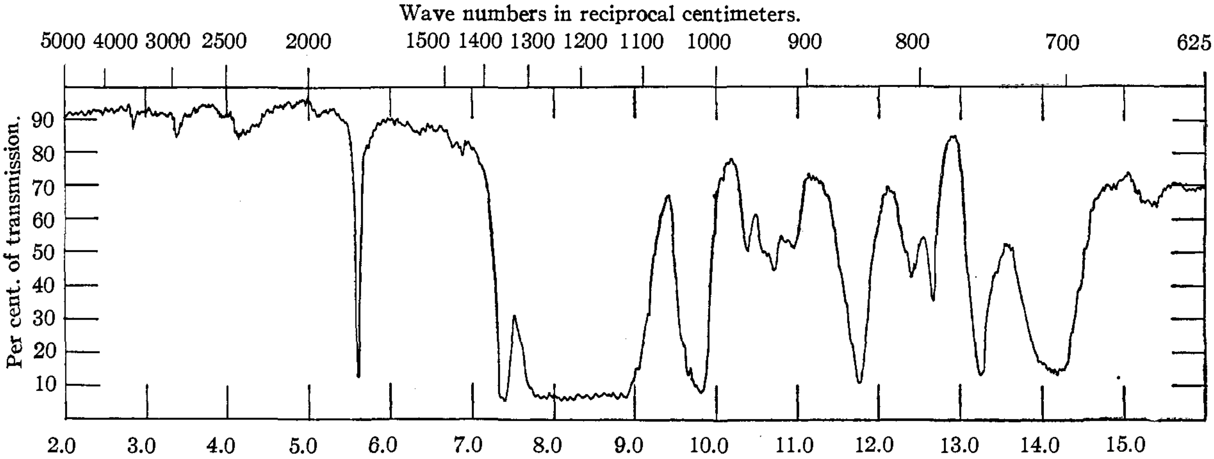

Fig. 1.—$C_3F_7COC_3F_7$.

condensed with an ester of the second mole. Unsymmetrical ketones are similarly obtainable from two different acids.

The perfluorinated ketones are so sensitive to nucleophilic attack that they are split by a reagent as weakly basic as the bicarbonate ion. The perfluorinated secondary alcohol made by reduction of such a ketone has acidity and infrared absorption characteristics which are described in an accompanying paper.[8]

On the basis of all our observations in the forming and utilization of *n*-C_3F_7MgI, the following general recommendations are made: (1) Where its boiling point (65°) does not interfere with the isolation and purification of the final product, tetrahydrofuran appears to be a more satisfactory solvent than ethyl ether in rate of reaction, amount of magnesium consumed and yield of condensation product. (2) A solvent ratio of about 1300 ml. of ether per mole of iodide appears best; with tetrahydrofuran, a slightly greater dilution is expedient. (3) Condensation reagents not subject to aldolization give better yields when the Grignard reagent is formed in their presence. Acyl halides, which practically prevent Grignard formation, are exceptions. (4) After initiation of the reaction at room temperature, if needed, a reaction temperature of about −80° should be maintained for at least 24 hours before completing the consumption of the magnesium at temperatures raised progressively from −60 to −30°. Acyl halides, or aliphatic aldehydes and ketones, are best added after the initial low temperature period, but before the temperature rises above −50°.

Experimental

Preparation of C_3F_7I.—This was prepared in 87% yield from silver perfluorobutyrate by the previously described procedure,[9,10] and with no more than 3% of perfluoropropylene as by-product. The observed physical constants agreed with the literature.

Reaction with Magnesium.—At room temperature, C_3F_7I reacts very readily with magnesium in ether or tetrahydrofuran, but not in perfluorinated butyl ether (b.p. 101°) or perfluorinated triethylamine (b.p. 70°). A basic solvent is thus needed. Addition of ethyl ether to one of the perfluorinated solvents causes the reaction to start. Darkening and tar precipitation occurs promptly and hampers conventional[11] titration of the Grignard. When a delay of one day is allowed before titration, the Grignard reagent is completely absent.

During the attack of the magnesium, 15 to 20% of low-boiling material (−30 to −20°) is formed, the infrared spectrum of which shows it to be a mixture of perfluoropropylene and heptafluoropropane, with the olefin predominant. Addition of bromine gives the known $CF_3CFBrCF_2Br$, b.p. 71°, $n^{28}D$ 1.3579, and the unbrominated material is shown by its infrared spectrum to be C_3F_7H free of C_3F_6.

Subsequent carbonation by the usual procedures gives no better than traces of $C_3F_7CO_2H$, but when the reaction of C_3F_7I on magnesium is performed in an atmosphere of carbon dioxide, the acid is obtained in 4 to 10% yields. For conveniency in handling, this acid was collected as its crystalline amide, m.p. 105°, after esterification and treatment with dry ammonia. This procedure was first tested on known solutions of similar dilution and composition; it was found to supply 60% of the theoretical amount of amide, and such a correcting factor was then applied to the above measurements.

Attack of the magnesium in the presence of a slight excess of acetone gives 8% of crude carbinol $C_3F_7C(OH)(CH_3)_2$, characterized as its product of dehydration over P_2O_5, $C_3F_7C(CH_3){=}CH_2$, b.p. 54–55°, $n^{25}D$ 1.2997, in fair agreement with the literature constants.[12]

In the presence of ethyl perfluorobutyrate, about 8% of crude $C_3F_7COC_3F_7$ (see below) was formed, but no perfluorinated tertiary carbinol could be traced.

Low Temperature Reactions. (a) **Grignard Formation.**—C_3F_7I can attack magnesium at −80°, and the Grignard reagent has sufficient stability at this low temperature to permit the use of fairly high concentrations, and to allow delay before subsequent condensations. But when the magnesium attack was carried out at −40° over a period of 48 hours, and was followed by carbonation the only product isolated was C_3F_6, obtained in 13% yield, and no $C_3F_7CO_2H$.

(b) **Carbonation.**—After initiation at room temperature, a solution of C_3F_7I (38 g. or 0.128 mole) in 60 ml. of dry ether (equivalent to 470 ml. of solvent per mole of iodide), was stirred for 24 hours with magnesium (17 g. or 0.7 g. atom) at −80°, in the presence of powdered Dry Ice in constant excess. Filtration of the remaining metal indicated a 63% consumption of the theoretical amount of magnesium, and working up of the filtrate gave a 41% yield of $C_3F_7CO_2H$ isolated as such, on the basis of the consumed magnesium. The use of a more dilute solution (660 ml. per mole) slowed down the reaction to 48% of magnesium consumption in 67 hours, but did not appreciably affect the yield of $C_3F_7CO_2H$, 38%. With much greater dilutions (5,000 ml. per

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(8) A. L. Henne and W. C. Francis, THIS JOURNAL, **75**, 991 (1953).

(9) A. L. Henne and W. G. Finnegan, *ibid.*, **72**, 3806 (1950).

(10) M. Hauptschein and A. V. Grosse. *ibid.*, **73**, 2461 (1951).

(11) H. Gilman, *et al.*, *ibid.*, **45**, 150 (1923).

(12) Minnesota Mining and Manufacturing Co. technical literature: Heptafluorobutyric Acid, 1949.

mole), the attack of the magnesium could not be maintained below −30°. The use of tetrahydrofuran instead of ether (470 ml. per mole) gave a 54% consumption of magnesium in 48 hours, and a yield of $C_3F_7CO_2H$ of 51%.

(c) **Condensation with Acetone.**—An equimolecular solution of 1/3 mole of C_3F_7I and 1/3 mole of acetone in 125 ml. of ether (370 ml. per mole) was stirred at −80° with an excess of magnesium for 58 hours, after initiation at room temperature. When allowed to warm up, the reaction mixture suddenly boiled over into the traps, from which it was returned. Working up gave a 10% yield of impure tertiary carbinol $C_3F_7C(OH)(CH_3)_2$, b.p. 100–110°, n^{20}_{D} 1.3355, better characterized by dehydration to $C_3F_7C(CH_3){=}CH_2$; see above. This reaction was then repeated at a progressively raised temperature: 18 hours at −40°, 19 hours at −25° and 5 hours at −15°. Even then, only 48% of the theoretical magnesium had been consumed. The working up of this reaction did not give any fluorinated tertiary carbinol, but only mesityl oxide in 31% yield, and high-boiling condensation products. Remembering the results obtained at room temperature, it was concluded that the carbonyl group of acetone interferes with Grignard formation, and that at intermediate temperatures the Grignard reagent causes ketolization instead of condensing with the keto group.

(d) **Condensation with Butyraldehyde.**—After initiating the attack of the magnesium at room temperature with a small amount of iodide, *n*-butyraldehyde (0.5 mole) was added at −40° to a stirred solution of C_3F_7I (0.4 mole) in 370 ml. of ethyl ether (923 ml. per mole of iodide) containing an equivalent quantity of magnesium. The mixture was stirred for 39 hours in the −50 to −40° range, then for 72 hours at about −30° and 17 hours at −20°. Much magnesium remained unconsumed, but was finally taken up during a 36-hour period of stirring at room temperature. In this time, 25.5 g. of low-boiling material was collected. After hydrolysis, working up gave first a mixture of recovered iodide and aldehyde, then a 16% yield of secondary alcohol, $C_3F_7CH(OH)C_3H_7$, b.p. 63.5° (45 mm.), n^{20}_{D} 1.3391. Calcd.: C, 34.71; H, 3.72. Found: C, 34.18; N, 3.75. Dinitrobenzoate, m.p. 63.5–63.8°; Found: N, 6.91. Calcd.: N, 6.42. Analyses by Elek microanalytical laboratories, Los Angeles. The acidity and infrared characteristics of this alcohol are discussed in an accompanying paper.[8] The above conditions were an effort to avoid excessive interference with Grignard formation, and yet avoid aldolization at the expense of condensation.

(e) **Condensation with C_3F_7CHO.**—So little condensation occurred that only traces of the desired $C_3F_7CH(OH)C_3F_7$ were observed; this alcohol, prepared by reduction of $C_3F_7COC_3F_7$ is described in another paper.[8] Simultaneous Grignard formation and condensation was tried on 1/4 mole amounts of reagents in 313 ml. of ether (1250 ml. per mole) in the −50 to −40° temperature range. Even at that low temperature, C_3H_7CHO polymerized partly and, by coating, interfered with but did not prevent the progressive consumption of the magnesium in a 22-hour period. Working up recovered 86% of the aldehyde (48% as polymer and 38% as hydrate) and 6% of $C_3H_7CO_2H$, which accounted for 92% of the reagent. The failure to obtain much secondary alcohol can thus be attributed to the sluggishness of the perfluorinated aldehyde.

(f) **Condensation with Ethyl Formate.**—The experiment was started by initiating the magnesium attack with 5 ml. of C_3F_7I in 25 ml. of tetrahydrofuran at room temperature, quickly cooling to −80° by immersion in a Dry Ice-bath, then rapidly adding the remainder of the iodide (0.17 mole total) in 200 ml. of solvent. Immediately following, a solution of 0.41 mole of formate in 275 ml. of tetrahydrofuran was dripped in over a 90-minute period. The concentration was thus 2850 ml. of solvent per mole of iodide. The mixture was stirred under nitrogen for 23 hours at −80°, then 20 hours at −30°, when it appeared chocolate brown and practically free of magnesium. After hydrolysis and treatment with ferrous sulfate to destroy peroxides, distillation up to 65° removed unreacted reagents and the solvent. The remaining aqueous solution was continuously extracted with ether. After removal of the ether by distillation, the aldehyde hydrate $C_3F_7CH(OH)_2$ distilled at 92–98° (9.2 g.), then the azeotrope of formic acid and water came over at 102–104° (7.0 g.); the residue distilled at 125–130° (20 mm.) (7 g. of wet material) and after drying proved to be 1,4-diiodobutane, b.p. 130° (20 mm.), n^{15}_{D} 1.6201, % iodine 79.02, obtained at the expense of the solvent. The aldehyde hydrate was thus obtained in 24% yield; its 2,4-dinitrophenylhydrazone, m.p. 102–104°, was made in 6 *N* sulfuric acid, and its free aldehyde, b.p. 28°, in agreement with the literature,[12] was obtained by distillation from P_2O_5.

(g) **Condensation with $C_3F_7CO_2Et$.**—Pure ethyl perfluorobutyrate was prepared in 91% yield[13] by mixing one mole of acid and 2 moles of absolute alcohol in a flask equipped with a reflux condenser, pouring 1.5 moles of concentrated sulfuric acid in small portions through the condenser as fast as the exothermic reaction would permit, cooling, decanting the top layer of nearly pure ester and rectifying from a small amount of P_2O_5; observed b.p. 95°, n^{20}_{D} 1.3011, literature values[12] b.p. 95°, n^{20}_{D} 1.3032.

After initiation of the magnesium attack, a mixture of 0.3 mole of iodide and 0.3 mole of ester in 390 ml. of ether (1300 ml. of ether per mole of iodide) was stirred with magnesium for 18 hours at −50°, 24 hours at −40° and 12 hours at −30°, and practically all the magnesium was consumed. After hydrolysis, the mixture was continuously extracted with ether. The ether solution was dried, its ether removed by distillation, and most of the residue rapidly brought over at 27–40° (100 mm.) to a Dry Ice cooled receiver. Redistillation at one atmosphere gave a fraction of crude ketone contaminated with alcohol at 63–85°, then recovered ester at 93–95°, after which a residue was left in the flask. Rectification of the first fraction from P_2O_5 to destroy the alcohol gave the ketone at 74–78° and a small amount of ester at 94°. Rectification of the residue, diagnosed as mostly hemi-ketal was also done from P_2O_5 and gave a small additional amount of ketone. When an attempt was made to simplify the separation by distilling all of the first ether extract from P_2O_5, a considerable amount of ethyl iodide distilling as an azeotrope with the ketone at 54° complicated the procedure; this was due to the solubility of magnesium iodide in ether.

Final distillation from P_2O_5 gave, in 20% yield, pure $C_3F_7COC_3F_7$, b.p. 75° (740 mm.), d^{20}_{4} 1.6250, with a refractive index too low to be read on an Abbe refractometer. *Anal.* Calcd.: C, 22.9; F, 72.7. Found: C, 22.6; F (cor.), 72.5. The carbon microanalysis was obtained from Dr. Robert N. Haszeldine, of Cambridge University. This ketone is very hygroscopic, and is easily split by 5% aqueous alkali into $C_3F_7CO_2H$ characterized by its odor and its amide m.p. 105° (mixed m.p.), and C_3F_7H characterized by its infrared spectrum. Figure 1 shows the spectrum of the ketone $C_3F_7COC_3F_7$ with a strong absorption band (12% transmittance) at 5.8 μ characteristic of the carbonyl function, and with strong absorption for C–F stretching in the 7.1 to 10 μ region. Repeated attempts to prepare a 2,4-dinitrophenylhydrazone, a semicarbazone or an oxime were all unsuccessful. The ketone is insoluble in water or in concentrated sulfuric acid, which shows the non-basic character of its carbonyl oxygen atom.

(h) **Condensation with C_3F_7COCl.**—This is not recommended, as it has no advantage over a condensation with the ester in preparing a ketone. The condensation cannot be performed on nascent C_3H_7MgI, because the acyl chloride stops the reaction of the iodide on magnesium. In trying the condensation at −30° after completing the Grignard formation at low temperature, a 4% yield of ketone was obtained.

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[13] T. S. Reid, Minnesota Mining and Manufacturing Co., private communication.

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Silico-alkylation of Sodio Esters with Trimethylchlorosilane to Form Silyl Esters[1]

BY CHARLES R. HANCE AND CHARLES R. HAUSER

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It has previously been shown in this Laboratory that ethyl isobutyrate and certain other esters may

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[1] Supported by the Office of Naval Research.