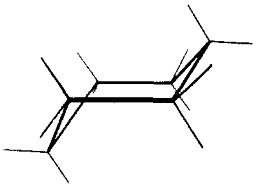
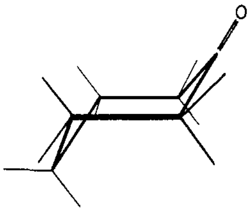
a somewhat less strained, non-planar structure,[7] there is little reason to doubt that the ring ketone will continue to be stabilized relative to the hydrocarbon by the reduction in the number of unfavorable conformations.[55]

The parent cyclohexane structure is nicely staggered with no bond oppositions (XXXVIII). Introduction of a trigonal atom alters this nice symmetrical arrangement and introduces some measure of unfavorable conformations (XXXIX).[56]



XXXVIII



XXXIX

According to this physical interpretation, the introduction of the carbonyl group stabilizes the cyclopentane ring and destabilizes the cyclohexane ring largely by altering the number and degree of unfavorable conformations involving the two alpha methylene groups. We have observed, however, that the effect is not restricted to carbon rings with alpha methylene groups. The lactones with but one alpha methylene group show the effect. Ethylene and trimethylene carbonates (XV, XVI), *with no alpha methylene groups*, exhibit the same effect of ring size on stability as that of the corresponding carbocyclic derivatives.

This observation suggests that the two alpha methylene hydrogen atoms are not essential for the production of these strained conformational effects. In the carbonates the two lone pairs of each oxygen atom must produce a conformational effect similar to that produced by the two carbon-hydrogen bonds in the parent structure.

A comparison of the potential barrier to rotation in dimethyl ether with that in propane should offer a suitable test of this proposal. The potential barrier in the oxygen derivative is reported to be 2700 cal.,[57] not significantly smaller than the value of 3400 cal. reported for propane.[58,59]

Conclusion.—In conclusion it may be stated that a large number of different experimental observations, with remarkably few exceptions, are satisfactorily correlated with the aid of the proposed generalization. The generalization is in accord with the available thermochemical data. Moreover, it appears to have a sound theoretical basis. A systematic search for apparent exceptions and experimental study of the many predictions should provide a rigorous test of its adequacy and utility.

Acknowledgment.—We wish to acknowledge the invaluable assistance of E. J. Prosen of the National Bureau of Standards in assembling and interpreting the thermochemical data.

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COLUMBUS, OHIO

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(55) In this treatment it is assumed that in the staggered arrangement the interaction of the doubly-bonded carbonyl group with the two alpha methylene groups will be quite small and not significantly greater than the interactions which occur with a singly-bonded group in the same position. Justification for this view is offered by a comparison of the potential barrier in acetone, 1400 cal./mole with that in propane, 3300 cal./mole. Thus replacement of the two hydrogen atoms in the methylene groups by a doubly-bonded oxygen atom has decreased the potential barrier by 1900 cal., or 950 cal. per carbon-hydrogen bond. This is practically identical with the estimated barrier per carbon-hydrogen bond in ethane. [For a summary of the available data on potential barriers see J. A. McCoubrey and A. R. Ubbelohde, *Quart. Rev.*, **5**, 364 (1951)].

(56) For a recent discussion of the conformations of substituted cyclohexanones, see E. J. Corey, THIS JOURNAL, **75**, 2301 (1953).

(57) F. A. French and R. S. Rasmussen, *J. Chem. Phys.*, **14**, 389 (1946).

(58) K. S. Pitzer, *ibid.*, **12**, 310 (1944).

(59) A similar comparison of the potential barrier in methanol with that in ethane appears to involve difficulties arising from the highly ionic character of the hydrogen-oxygen bond and its resulting strong tendency to form hydrogen bonds. See W. Weltner, Jr. and K. S. Pitzer [THIS JOURNAL, **73**, 2606 (1951)] for a discussion of the barrier in methanol and pertinent literature references.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Preparation and Reactions of Perfluoroalkyllithiums[1]

BY O. R. PIERCE, E. T. MCBEE AND G. F. JUDD

RECEIVED SEPTEMBER 21, 1953

The conditions of formation of heptafluoropropyllithium and trifluoromethyllithium by interchange with butyl- or methyllithium have been studied and an over-all yield of the perfluoropropyllithium reagent of 77% was obtained as shown by hydrolysis to heptafluoropropane. Reaction of this reagent with carbonyl compounds having an active hydrogen led to aldol-type products as well as the expected addition product, the best yield occurring with propionaldehyde (50%) and the lowest, benzophenone (0%). The scope and limitations of the reactions are discussed.

Introduction

Earlier attempts to prepare a lithium reagent directly from lithium and iodotrifluoromethane[2] were unsuccessful. Studies involving the direct formation of perfluoropropyl Grignard reagents,[3-6] however, have demonstrated the existence of a fluorine-containing organometallic compound and such materials as carbon dioxide, acetone, acetaldehyde and formaldehyde have reacted with

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(1) This paper represents part of the thesis submitted by G. F. Judd to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented before the Fluorine Symposium, 124th meeting of the American Chemical Society, Chicago, Illinois, September, 1953.

(2) R. N. Haszeldine, *J. Chem. Soc.*, 2952 (1949).

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

(4) *Ibid.*, **75**, 992 (1953).

(5) R. N. Haszeldine, *J. Chem. Soc.*, 3423 (1952).

(6) O. R. Pierce and M. Levine, THIS JOURNAL, **75**, 1254 (1953).

it in yields as high as 77%. Fainberg and Miller[7] have inferred the existence of heptafluoropropylzinc iodide by isolating heptafluoropropane as an acid hydrolysis product. In this Laboratory it was found that when heptafluoro-1-iodopropane was refluxed with zinc dust in a commercial grade of dioxane, 42% of it was converted to heptafluoropropane.

This paper demonstrates that a convenient and practical synthesis of fluorine-containing organolithium compounds can be achieved by halogen–metal interchange. The conditions for formation and use of perfluoropropyllithium have been studied extensively and are less troublesome to achieve than those for direct formation of perfluoropropylmagnesium iodide.

When butyl-, phenyl- or methyllithium was added slowly to a rapidly stirred solution of heptafluoro-1-iodopropane in ethyl ether, a vigorous reaction ensued, and the corresponding iodides were isolated from the respective interchanges. When the solution from methyllithium interconversion was warmed to reflux temperature a 97% yield of hexafluoropropene was obtained and none of the heptafluoropropane noted by Haszeldine[5] in preparation of the Grignard reagent. Depending on the alkyllithium used, the amount of hexafluoropropene obtained varied widely. Methyllithium was used in practically all of this work, since it can be stored for a considerable period of time without decomposition, and gives a smooth interchange. An optimum yield value for the reagent was obtained by hydrolyzing the reaction mixture with 3 *N* sulfuric acid, and determining the amounts of heptafluoropropane produced and heptafluoro-1-iodopropane recovered. Since heptafluoro-1-iodopropane underwent no change when it was refluxed in ether with 3 *N* sulfuric acid, the heptafluoropropane must necessarily have arisen from perfluoropropyllithium. A study of the experimental conditions affecting the over-all reaction has shown that the synthesis is best conducted by adding methyllithium simultaneously with the other reactant to a solution of heptafluoro-1-iodopropane in ether at −40 to −50°.

At 0°, decomposition of the reagent occurred to the complete exclusion of addition to benzophenone. With ethyl heptafluorobutyrate at 4–6°, the reagent gave 35% hexafluoropropane and 28% of 1,1,1,2,2,3,3,5,5,6,6,7,7,7-tetradecafluoro-4-heptanone. These reactions demonstrate the lesser reactivity of this fluorine-containing organometallic in addition reactions compared to ordinary alkyl- or aryllithiums and its instability with respect to decomposition into hexafluoropropene and lithium fluoride.

Heptafluoropropyllithium reacted with propionaldehyde, acetone and benzaldehyde to give aldol-type products and heptafluoropropane as well as the fluorine-containing alcohols. Methyllithium also converted propionaldehyde to propion-trialdol at −50°, as well as to 2-butanol. No case has been reported where normal alkyllithiums cause such aldolizations, although Nielsen, *et al.*,[8] have utilized methylanilinomagnesium bromide to effect mixed and straight aldol condensations with good success and Henne[3] reported that heptafluoropropylmagnesium iodide converted acetone to mesityl oxide. Other Grignard reagent-catalyzed condensations of ketones and esters have recently[9] been reported and Levine and Hawell[10] have used lithium salts of substituted amines for ester condensations.

A study of the effect of mode of addition, reagent concentration and dilution on the yield of 4,4,5,5,-6,6,6-heptafluoro-3-hexanol and by-products from the reaction of heptafluoropropyllithium with propionaldehyde indicated that any condition which promoted increased base concentration in the reaction mixture decreased the yield of addition product and increased aldolization and heptafluoropropane formation.

The yield of alcohol produced from propionaldehyde and heptafluoropropyllithium was found to be strongly influenced by temperature. Between −40 and −50° an optimum value was obtained which fell sharply as the temperature was raised to 3° or lowered to −74°.

The scope of this reaction was studied with propionaldehyde, acetone, benzaldehyde, acetyl chloride, ethyl benzoate, benzophenone and perfluorobutyraldehyde. Also diethylsilicon dichloride has been converted to a mixture of fluoroorganosilanes. In general, these reactions demonstrate that the perfluoropropyllithium reagent will undergo both displacement and addition reactions which are common to Grignard reagents and alkyllithiums.

The reactions conducted thus far do not confirm the existence of trifluoromethyllithium although trifluoromethyl iodide reacted vigorously with methyllithium at −74°. When this reaction was conducted in the presence of sulfuric acid, propionaldehyde, benzaldehyde, or ethyl heptafluorobutyrate, only tetrafluoroethylene, recovered starting material and condensation products in the case of the aldehydes, were obtained. These differences in properties of molecules containing the trifluoromethyl group and the perfluoropropyl group have been observed in the chemical behavior of certain perfluoro acid derivatives.[11]

Heptafluoropropane was absent from all the previously mentioned reactions if there were no reactants present having enolizable or strongly acidic hydrogen atoms. It is unlikely, therefore, that homolytic fission of the heptafluoropropyllithium occurred in any of these reactions or heptafluoropropane would result from free-radical attack on the solvent.

Experimental

The physical properties and analyses of the compounds prepared from heptafluoropropyllithium and various reactants are summarized in Table I.

Rectifications were performed with a Todd Precise Fractionation Assembly employing an 11 mm. i.d. barrel and packed with 1/8 in. stainless steel helices.

Preparation of Starting Materials.—Iodotrifluoromethane and heptafluoro-1-iodopropane were made as described pre-

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[7] A. H. Fainberg and W. T. Miller, A. C. S. National Meeting, New York City, N. Y., Sept. 1951.

[8] A. T. Nielsen, C. Gibbons and C. A. Zimmerman, THIS JOURNAL, **73**, 4696 (1951).

[9] K. Sisido, H. Nozaki and O. Kurihara, *ibid.*, **74**, 6254 (1952).

[10] R. Levine and M. Hawell, *J. Org. Chem.*, **15**, 167 (1950).

[11] D. R. Husted and A. H. Ahlbrecht, THIS JOURNAL, **75**, 1605 (1953).

TABLE I

COMPOUNDS PREPARED FROM HEPTAFLUOROPROPYLLITHIUM REACTIONS

Formula	B.p.		$n^{20}D$	M.p.,	Analyses,[a] %					
	°C.	Mm.		°C.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Fluorine Calcd.	Fluorine Found
C_3F_6	−30	743	....	..						
C_3F_7H	−15	743	....	..						
$C_3F_7CHOHC_2H_5$	115	743	1.3250	..						
$C_3F_7COH(CH_3)_2$	107	743	1.3260	..						
$C_3F_7CHOHC_6H_5$	89	9.5	1.4141	..	43.50	43.63	2.53	2.65		
$C_3F_7COH(CH_3)CH_2COC_3F_7$	68.5	29	1.3194	..	28.30	28.42	1.43	1.78		
$(C_3H_7)_2CO$	75	743	1.26985	..						
$(C_3F_7)_3COH$	115	743	1.2890	10	22.34	22.99	0.18	0.84	74.40	73.25
$C_9H_{18}O_3$	95	3	1.4368	..	62.10	62.21	10.35	10.35		
$Et_2Si(C_3F_7)_2$	79	12	1.3380	..	28.30	28.34	2.36	2.54	67.90	62.41

[a] Fluorine analyses were by H. Clark, University of Illinois and the other elements by Galbraith Laboratories, Knoxville, Tennessee.

TABLE II

DERIVATIVES

Formula	B.p.		$n^{20}D$	M.p.,	Analyses,[a] %							
	°C.	Mm.		°C.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Bromine Calcd.	Bromine Found	Nitrogen Calcd.	Nitrogen Found
$C_3F_7CHCHCH_3$	62	743	1.3018	...	34.30	34.30	2.30	2.30				
$C_3F_7CHBrCHBrCH_3$	97.2	64	1.4009	...	19.45	19.61	1.35	1.46	43.95	43.68		
$C_6H_4BrF_7$	75	743	1.3689	...	24.90	24.34	1.38	1.64	27.8	28.14		
$C_3F_7CHC_6H_5O_2CNHC_6H_5$	..	....	....	97.5	51.7	51.75	3.04	3.05			3.54	3.77
$C_3F_7CHEtO_2CNHC_6H_5$	..	....	....	106.5	45.00	45.04	3.46	3.58			4.03	4.96
$C_3F_7CMe_2O_2CNHC_6H_5$	..	....	....	128	45.00	44.81	3.46	3.57			4.03	4.81
$(C_3F_7)_3CO_2CC_6H_3(NO_2)_2$[b]		(3.5)	....	80	28.9	30.08	0.94	1.12			3.96	4.51

[a] Fluorine analyses were by H. Clark, University of Illinois and the other elements by Galbraith Laboratories, Knoxville, Tennessee. [b] This compound was carefully purified, but did not analyze precisely. This was attributed by Galbraith in the case *of nitrogen to the "active" carbon atom.*

viously.[12] Iodotrifluoromethane was purified by distilling through Ascarite and then rectifying, b.p. −19°. The heptafluoro-1-iodopropane was purified by washing with 5% base at 0° and then rectifying to give a product b.p. 40.1°, $n^{20}D$ 1.3258.

Methyllithium was prepared by passing gaseous methyl bromide into ether containing lithium wire at 15° until the lithium disappeared. The solution was decanted into storage bottles fitted with transfer tubes and aliquots were titrated periodically. Concentrations of methyllithium as high as 3.12 *N* were prepared and used. The yield based on lithium wire was 99%.

Butyllithium was prepared according to the method of Gilman, *et al.*,[13] and stored at −78° for subsequent use. Phenyllithium was prepared according to Wittig.[14]

Analysis of Methyllithium Solution.—Twenty-five milliliters of methyllithium solution prepared as described previously was added to a well-stirred mixture of 10 ml. of ether and 100 ml. of water contained in a 1-liter, 3-neck flask. The volume of the exit gas was measured by passing it through two traps containing concentrated sulfuric acid followed by one containing glass wool into a wet flow meter. The solution in the 3-neck flask was titrated with standard base. The corrected volume of methane was 1.33 and 1.322 liters of methane, respectively, from two separate runs, and 27.38 and 27.18 ml. of 2.176 *N* sulfuric acid, respectively, were consumed in titrating the hydrolysate from these samples. The molarity of methyllithium as determined by liberated methane or acid titration is the same: 2.367 ± 0.007. This proves the total concentration of bases in the methyllithium solution is due to methyllithium.

Preparation of Heptafluoropropyllithium.—A one-liter 3-necked flask having two 24/40 side and one 34/5 center joints and a built-in thermometer well was swept with nitrogen and then charged with 500 ml. of anhydrous ether. Two 500-ml. addition funnels with pressure-equalizing side arms and standard taper joints were placed in the side joints of the flask and a Tru-Bore water-cooled stirrer was mounted in the central joint. Nitrogen was passed into the one addition funnel and then led through a trap cooled to −78° to a mercury by-pass. The exit tube leading into the mercury was immersed less than one mm. so as to indicate slight pressure increase in the system. Nitrogen was passed through the system as the stirrer was started and the flask contents cooled to −74°. The nitrogen flow was then stopped and the nitrogen inlet closed with a glass stopper. One funnel was charged with 178 ml. (0.5 mole) of 2.8 *N* methyllithium and the second funnel charged with 148 g. (0.5 mole) of heptafluoro-1-iodopropane which was added dropwise to the rapidly-stirred solution. It was necessary to add the methyllithium rapidly enough so that solid did not clog the addition funnel outlet. The time of addition was one-half hour. Too rapid addition was avoided, since the reaction was exothermic and caused decomposition of the perfluoropropyllithium.

(a) **Decomposition.**—The solution as described above was rapidly warmed to room temperature, after which the addition funnel with an exit tube was removed and a water-cooled condenser with a standard taper 24/40 outer joint was put in its place. The joint was attached to an exit tube leading to the cold trap and the solution was refluxed for half an hour, finally replacing the condenser with a 1′ Vigreux column for distillation. The gases were distilled from trap to trap twice and then rectified through an 18-plate low-temperature column. Fifty-eight grams of hexafluoropropene, b.p. −30.5°, mol. wt. (Dumas) 150 was obtained, which is a 77% conversion. When the hexafluoropropene was mixed with bromine in a sealed tube an exothermic reaction occurred at room temperature and 1,2-dibromohexafluoropropane[5] was formed in 85% yield, b.p. 70.2°, $n^{20}D$ 1.3592. Analysis of the ether–heptafluoro-1-iodopropane–methyl iodide azeotrope by infrared spectra indicated 25.4 g. of heptafluoro-1-iodopropane was unreacted. The yield of hexafluoropropene was 93%.

In a second experiment, 98 g. of ethanol was added to the reaction mixture. Here, 64.3 g. (85.8% conversion) of hexafluoropropene and 17.1 g. of heptafluoro-1-iodopropane were obtained, a 97% yield.

(b) **Hydrolysis to Heptafluoropropane.**—The preparation of perfluoropropyllithium was carried out as described previously using 148 g. (0.5 mole) of heptafluoro-1-iodopropane

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(12) A. L. Henne and W. C. Francis, THIS JOURNAL, **73**, 3518 (1953).

(13) H. Gilman, E. A. Zoellner, W. M. Selby and C. Boatner, *Rec. trav. chim.*, **54**, 584 (1935).

(14) G. Wittig, "Preparative Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 576.

and 150 ml. (0.44 mole) of 2.96 *N* methyllithium. Three normal sulfuric acid, 168 ml. (0.5 mole) was added to the reaction mixture after warming to 0° over one hour and then the solution was slowly warmed to reflux temperature over 35 hours. Fifty-four and two-tenths grams of heptafluoropropane,[5] mol. wt. (Dumas) 167, b.p. −14.5°, and 52.9 g. of unreacted heptafluoro-1-iodopropane were obtained (99.4% yield, 63.8% conversion).

(c) **Reaction of 3 *N* Sulfuric Acid with Heptafluoro-1-iodopropane.**—One hundred and forty-eight grams of heptafluoro-1-iodopropane (0.5 mole) was added to 650 ml. of ether cooled by an ice-bath in the reaction flask previously described, but modified by replacing the exit funnel with a water-cooled condenser. A liquid nitrogen-cooled trap was inserted between the −78° trap and mercury by-pass, and then 168 ml. (0.5 mole) of degassed 3 *N* sulfuric acid was added and the solution was vigorously stirred for one hour. No reaction was observed and only 2–3 ml. of liquid collected in the Dry Ice-cooled trap and none in the liquid nitrogen-cooled trap. The solution was then refluxed for two hours, during which time the light yellow color disappeared, but further formation of liquid in the Dry Ice–trichloroethylene-cooled trap was not observed.

The solution was cooled, separated and the aqueous layer extracted with three 50-ml. portions of ether which were combined with the main portion, dried over Drierite and sodium hydroxide. Analysis of the solution by refractive index gave 142 g. (96.1 ± 1.6%) of recovered heptafluoro-1-iodopropane. Only ether was recovered from the Dry Ice–trichloroethylene-cooled trap.

Reactions of Heptafluoropropyllithium with Various Reactants: General Procedure. Reaction with Propionaldehyde.—This reaction was conducted by adding 106 ml. (0.25 mole) of 2.36 *N* methyllithium and 29.2 g. (0.5 mole) of freshly distilled propionaldehyde dissolved in 100 ml. of ether simultaneously to 0.25 mole of heptafluoro-1-iodopropane dissolved in 200 ml. of ether. The heptafluoro-1-iodopropane was kept at −40 to −45° with rapid stirring in the 1-liter flask previously described, by adding Dry Ice periodically to an external Dry Ice–trichloroethylene bath. The usual addition time was one hour. After mixing the reactants the exit addition funnel was replaced by a condenser and the temperature was raised to reflux at a rate of 20° per hour, the solution refluxed for half an hour, and then hydrolyzed with an equivalent amount of 3 *N* sulfuric acid. The layers were separated and the ether extracts of the aqueous layer were combined and dried over Drierite. The ether solution was then distilled through a 1′ Vigreux column. The fraction, b.p. 33–43°, was weighed, and analyzed for recovered heptafluoro-1-iodopropane. Dry benzene was added to the residue, and small amounts of water and 2-butanol were distilled below 89° at 316 mm. pressure. The fluorinated alcohol then distilled at 89–110° at 316 mm.[15] A one-gram aliquot of this material was treated with phenyl isocyanate to give the phenylurethan from which the yield was determined. At the optimum temperature of −42° a 50% conversion and 94% yield was obtained. The phenylurethan was recrystallized from pentane three times, m.p. 106–106.5°, and showed no depression when mixed with an authentic sample of the urethan made from the alcohol that was prepared from a reaction of ethyl and isopropyl Grignard reagents with ethyl heptafluorobutyrate.[16] Dehydration of the fluorinated alcohol with phosphorus pentoxide gave 70.3% of 4,4,5,5,6,6,6-heptafluoro-2-hexene. An exothermic reaction of the olefin with bromine occurred at room temperature and, after heating in the absence of light at 85°, there was obtained 47.3% of 4,5-dibromo-1,1,1,2,2,3,3-heptafluorohexane.[5] There was also obtained a small amount of dehydrobromination product from this reaction, $C_6H_4BrF_7$.

The residue from the previous rectification was reduced to 5 mm. pressure and heated to 100°, and a fraction boiling below 30° was distilled through an 8-inch Vigreux column. Benzene was added to give two layers. The lower layer was separated and rectified to give a liquid, b.p. 186°, n^{20}_D 1.3200. The liquid was insoluble in and denser than alcohol, water and benzene, but soluble in chloroform, did not absorb bromine from carbon tetrachloride, or form a phenylhydrazone. Infrared absorption showed strong absorption at 5.8, 5.9 and 6.0 μ, which is characteristic of a double bond. *Anal.* Calcd. for C_9F_{18}: C, 24.0; F, 76.0. Found: C, 28.29; F, 72.77. This compound was not formed in sufficient yield for an adequate purification and identification. At −50°, 2% hexafluoropropene, 8% heptafluoropropane and 37% heptafluoro-1-iodopropane were recovered. From the residue boiling above 110° at 316 mm. propionaldol and tripropionaldol were isolated.

Reaction with Acetone.—Acetone (Carbide and Carbon Chemicals Corp.) was refluxed with alkaline permanganate for several days and the product rectified through an 18.5 plate column to give a product b.p. 56.4°, n^{20}_D 1.3591. One-half mole was then treated with heptafluoropropyllithium in exactly the same way as with propionaldehyde to give 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol. The crude alcohol was heated for 48 hours at 100° in a sealed tube with a slight excess of phenyl isocyanate and a drop of pyridine to give the phenylurethan from which the yield was determined. The urethan showed no depression with a sample made from the alcohol obtained from methylmagnesium iodide and ethyl heptafluorobutyrate.[17] At −74°, 29% of the secondary alcohol, 3% hexafluoropropene and 7% heptafluoropropane were obtained. From the residue was obtained 33% mesityl oxide, which was identified as the 2,4-dinitrophenylhydrazone, m.p. 202–203°. The m.p. was not depressed when mixed with an authentic sample.

Reaction with Benzaldehyde.—Using the general procedure previously described and keeping the reaction flask at −74°, 0.5 mole of freshly distilled benzaldehyde (b.p. 63.8° at 11 mm., n^{20}_D 1.5458) was converted into 37.4 g. (54.4%) of 4-phenyl-2,2,3,3,4,4,4-heptafluoro-1-butanol. This alcohol gave a phenylurethan, m.p. 97–97.5°, that showed no depression in m.p. when mixed with an authentic sample.[16]

Reaction with Acetyl Chloride.—One-half mole of acetyl chloride was freshly distilled and then added in the usual way with 0.25 mole of methyllithium to 0.25 mole of the iodide at −74°. The reaction mixture was raised to reflux temperature at a rate of 5° per hour and then refluxed 18 hours. The ether was removed at atmospheric pressure. The other products were removed into a trap by heating and gradually adjusting the temperature and pressure to 150° and 1 mm. pressure. Three and three-tenths grams (6.24%) of 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoro-4-methyl-6-one-4-nonanol was obtained. Thirty-five and six-tenths grams (48.1%) of heptafluoro-1-iodopropane was recovered and 4 g. (10%) of a mixture of hexafluoropropene and heptafluoropropane, mol. wt. 159, was obtained.

Reaction with Ethyl Benzoate.—Methyllithium (0.25 mole) and ethyl benzoate (0.46 mole) were added simultaneously to 100 g. (0.34 mole) of heptafluoro-1-iodopropane at −74° over one hour. The solution was stirred one hour at −74°, three hours at 0–12°, nine hours at 12–16°, and 36 hours at 18–36°. After hydrolysis there was obtained 2.6 g. (4.8%) of heptafluoropropyl phenyl ketone, b.p. 64° at 12 mm., 46.3 g. (0.312 mole) of recovered ethyl benzoate and 5.4 g. (0.044 mole) of benzoic acid. Hexafluoropropene, b.p. −29.5°, mol. wt. (Dumas) 151, was obtained in 17.8 g. (47%) conversion and 40 g. (40%) of heptafluoro-1-iodopropane was recovered. The fluorinated ketone was identified by treating it with 30% sodium hydroxide solution to give heptafluoropropane and benzoic acid.

Reaction with Benzophenone.—The heptafluoropropyllithium was prepared by adding 67.7 ml. (0.2 mole) of 3.3 *N* methyllithium to 50.2 g. (0.2 mole) of heptafluoro-1-iodopropane in 240 ml. of ether at −74°. Thirty-six and four-tenths grams (0.2 mole) of benzophenone in 70 ml. of ether solution was then added to the mixture at 0°, the solution was stirred 31 hours at 0°, and then hydrolyzed with 100 ml. of 1 *N* sulfuric acid. Pure benzophenone (33.6 g., 0.185 mole, 92%), 17 g. (56%) of hexafluoropropene, b.p. −30°, mol. wt. (Dumas) 157, and 32 g. (53%) of heptafluoro-1-iodopropane were recovered.

Reaction with Heptafluorobutyraldehyde.—Heptafluoropropyllithium was prepared by adding 178 ml. (0.5 mole) of 2.8 *N* methyllithium to 148 g. (0.5 mole) of heptafluoro-1-iodopropane at −74°. A small amount of heptafluorobutyraldehyde was then added with resultant polymer formation. The temperature was raised to 0°, the balance of the aldehyde added, the temperature raised to 18°, and

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[15] E. T. McBee, O. R. Pierce and W. F. Marzluff, THIS JOURNAL, **75**, 1609 (1953).

[16] Dr. J. C. Siegle, private communication.

[17] Dr. M. Levine, private communication.

the solution hydrolyzed. The layers were separated and a solid filtered from the ether layer.

The ether extract gave 45.1 g. of perfluorobutyraldehyde polymer, 24.7 g. of monomer and 21.0 g. of the hydrate, b.p. 95°, m.p. 60°, which accounts for 90% of the butyraldehyde. The polymer was identified by heating to give the monomer, which was identified as the 2,4-dinitrophenylhydrazone, m.p. 102–103°. This sample did not depress the m.p. of an authentic sample.

Reaction with Ethyl Heptafluorobutyrate.—One mole of methyllithium and 0.5 mole of ethyl heptafluorobutyrate were added simultaneously to one mole of heptafluoro-1-iodopropane in 100 ml. of ether at −45° during one-half hour, the resulting solution stirred for six hours between −15° and −35° and then warmed to room temperature at a rate of 3° per hour. All material boiling below 80° was then removed through a 1′ Vigreux column. Boric acid (30.5 g., 0.5 mole) was dissolved in 200 ml. of diethylene glycol and one mole of water removed by heating to 80° at 11 mm. pressure. This acid mixture was added to the reaction flask, and all material boiling below 120° at 11 mm. was distilled into a Dry Ice–trichloroethylene cooled trap. In one instance, foaming occurred and was reduced by adding 75 ml. of heptadecane. The perfluoroketone was obtained as an azeotrope b.p. 79–84°, and was purified by shaking with concentrated sulfuric acid, removing the lower layer, repeating this washing twice, distilling from sulfuric acid at 1 mm. and 28° and then rectifying. Four grams (2%), of perfluoro-4-heptanone was obtained which had an infrared spectrum identical to that of Henne.[4] One hundred grams (37%) of tris-(perfluoropropyl)-carbinol, b.p. 114–116.2°, was obtained in this rectification and was purified by treating with phosphorus pentoxide and re-rectifying. It formed a phenylurethan and 3,5-dinitrobenzoate. The alcohol dissolved in 5% sodium hydroxide from which it could not be extracted with ether. The sodium salt entered the ether layer when 30 and 50% base were used and by reprecipitation with pentane an odorless powder was obtained which gave an insoluble lower layer and odor of alcohol when added to 3 *N* sulfuric acid. Carbon dioxide precipitated aqueous base extracts of the alcohol. This is confirmation of the observations of Haszeldine[18] on the acid strength of this alcohol.

Reaction with Diethylsilicon Dichloride.—Forty-three grams (0.25 mole) of diethylsilicon dichloride in 150 ml. of ether was added dropwise with 214 ml. (0.5 mole) of methyllithium to 148 g. (0.5 mole) of heptafluoro-1-iodopropane in 200 ml. of ether at −52 to −48° over one-half hour. The solution was stirred one-half hour, warmed up slowly over 12 hours to 20°, and the ether removed. Diphenyl ether, 242 g., was added and all materials boiling below 135° and 22 mm. were distilled into a −78° trap. Rectification gave 10.8 g. (10.2%) of diethyldi-(perfluoropropyl)-silane, which was stable to 3 *N* sulfuric acid at 100° and methanolic sodium hydroxide below 75°. Above 75°, the latter solution caused decomposition to heptafluoropropane and a water-soluble silicon compound. Heptafluoropropyldiethylsilicon chloride (12.9 g., 17.8%) was obtained, b.p. 119° at 743 mm., $n^{20}\mathrm{D}$ 1.3538. *Anal.* Calcd.: C, 28.90; H, 3.45; Cl, 12.20; F, 45.7. Found: C, 31.58; H, 4.96; Cl, 10.06; F, 44.71. An attempt to purify this material by re-rectifying at 80° and 2 mm. was unsuccessful. There were also recovered 18 g. (42%) of diethylsilicon dichloride and 46 g. (61%) of pure hexafluoropropene. In a subsequent experiment using approximately equivalent amounts of reactants (0.6 mole) and where final warming was at a rate of 15° per hour, 40 g. (32%) of diethyldi-(perfluoropropyl)-silane, b.p. 148°, 50 g. (63%) of diethylsilicon dichloride and 22 g. (24%) of hexafluoropropene were obtained, and none of the monosubstituted product.

Interconversion Experiments with Iodotrifluoromethane and Methyllithium. Reaction with Propionaldehyde.—Iodotrifluoromethane (106 g., 0.54 mole) was distilled into 200 ml. of ether cooled to −55°. To this solution maintained between −47 and −52° was added 214 ml. (0.51 mole) of 2.36 *N* methyllithium and 58 g. (1 mole) of propionaldehyde (dissolved in 150 ml. of ether) over a period of one hour. The solution was warmed up at a rate of 10° per hour and refluxed for one-half hour and then hydrolyzed. From the ether layer was obtained 47 g. (81%) of aldol condensation product, 4 g. (14.7%) of tetrafluoroethylene and 10 g. (9.4%) of iodotrifluoromethane.

Reaction with Benzaldehyde.—Methyllithium (214 ml., 2.36 *N*, 0.5 mole) was added simultaneously with 53 g. of benzaldehyde (0.5 mole) over one hour into 104 g. (0.53 mole) of iodotrifluoromethane in 200 ml. of ether and cooled to −60°. The solution was then warmed up to reflux at a rate of 5° per hour, hydrolyzed with 178 ml. of 3 *N* sulfuric acid, and the ether layer washed with 3% sodium hydroxide solution. After removal of the ether and rectification of the residue, no fluorine-containing fractions were obtained, but 34.9 g. of aldehyde condensation products was obtained. Tetrafluoroethylene (3.4 g., 13.6%, mol. wt. 102) was obtained and 18.1 g. (18.5%) of iodotrifluoromethane was recovered.

Reaction with Concentrated Sulfuric Acid.—Iodotrifluoromethane (18.1 g., 0.09 mole) was dissolved in 200 ml. of ether at −45° and 42.3 ml. (0.1 mole) of 2.36 *N* methyllithium added to it. Then 3 ml. of concentrated H_2SO_4 dissolved in 100 ml. of ether was added, resulting in a solid precipitate. Concentrated sulfuric acid (12 ml.) in 100 ml. of ether was then added, giving a pasty slurry which was dissolved by warming to −15°. The solution was refluxed one-half hour, 100 ml. of water was added and the reaction mixture separated to give 6 g. (33.1%) of iodotrifluoromethane and 2 g. (43%) of tetrafluoroethylene. No fluoroform could be detected in the spectra of any of the gases.

Reaction with Ethyl Heptafluorobutyrate.—One hundred and sixty-five grams of iodotrifluoromethane (0.84 mole) was cooled to −50° in a jacketed addition funnel and added simultaneously over two hours with 360 ml. (0.85 mole) of 2.36 *N* methyllithium to 102 g. (0.42 mole) of ethyl heptafluorobutyrate dissolved in 300 ml. of ether and cooled to −74°. Gases were collected in a cold trap followed by a liquid nitrogen-cooled trap. After addition, the solution was stirred 48 hours below −30° and separated as described for heptafluoropropyllithium and ethyl heptafluorobutyrate. Only ethyl heptafluorobutyrate, 25 g. (15%) of iodotrifluoromethane and 10 g. (24%) of tetrafluoroethylene, were obtained.

Reaction of Methyllithium with Propionaldehyde at −50°.—Methyllithium (107 ml., 2.36 *N*, 0.25 mole) was added simultaneously with 29 g. (0.5 mole) of propionaldehyde dissolved in 75 ml. of ether during 45 minutes to ether cooled to −55°. The solution turned blue as the reagents were mixed at −45 to −55°, and was homogeneous. The color faded when the temperature was raised to −30°, and the solid began to precipitate at 30°. The solution was refluxed an half hour, hydrolyzed with 87 ml. of 3 *N* sulfuric acid (0.25 mole). The ether layer and three 50-ml. ether extracts were washed with 25 ml. of water and 20 ml. of 5% sodium bicarbonate followed by 20 ml. of water and then dried and rectified. There were obtained 12.8 g. (69.3%) of 2-butanol, b.p. 100°, $n^{20}\mathrm{D}$ 1.3954, and 11 g. of tripropionaldol. The latter compound was proven by its infrared spectra which was identical to that of tripropionaldol which was isolated from the reaction of heptafluoropropyllithium with propionaldehyde.

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(18) R. N. Haszeldine, private communication to A. L. Henne.[12]