ture, the alkoxide solution generally solidified. Then 10 g. (0.060 mole) of fluorene was added to the cooled solution and the tube was sealed. After heating the tube for from 15 to 24 hours at 220–230°, the tube was cooled, opened, and extracted with benzene, water, and finally benzene. Neutralization of the mixture with 10% hydrochloric acid was followed by separating the aqueous layer and extracting it with benzene. The organic layers were combined, distilled to remove benzene and residual alcohol, and then distilled at reduced pressure (about 0.5 mm.). The product solidified in the receiver and was recrystallized from methanol.

Method II. To a 500 ml., 3-necked flask equipped with a Dean-Stark trap filled with xylene, a thermometer reaching almost to the bottom of the flask, and a gas-inlet tube, and holding a mixture of 25 ml. of cyclohexanol and 25 ml. of xylene was added in pieces 1.56 g. (0.040 atom) of potassium. The addition was carried out under nitrogen and at such a rate as to maintain the temperature below 50°. The nitrogen-inlet tube then was replaced by a stopper and a mixture of 1 g. of U. O. P. nickel with 20.75 g. (0.125 mole) of fluorene was added in one portion, along with 250 ml. of xylene, and the mixture was refluxed for 24 hours. At this point 1.6 ml. (71%) of water had been collected. After cooling, filtering, and washing until neutral with water, the xylene and excess alcohol were distilled and finally the residue was collected at 142–148° (0.1 mm.). Recrystallization from methanol gave 21.4 g. (0.086 mole, 69%) of colorless product, m.p. 112–116°.

Method III. In this procedure the U. O. P. nickel was replaced by Davison sponge nickel catalyst. The latter was prepared for use by washing it six times with anhydrous methanol and then with the alcohol to be used.

Method IV. The Dean-Stark trap was replaced by a Soxhlet extraction apparatus in which the thimble was filled with calcium hydride.

Attempted preparation of molecular addition compounds. Tetranitrofluorenone, chloranil, trinitrofluorene, picrolonic acid, picric acid, 1,3,5-trinitrobenzene, styphnic acid, and picric acid in a variety of solvents failed to give molecular addition compounds. The first two gave evidence of some reaction as evidenced by the appearance of a blood-red color in acetonitrile, but all attempts to isolate a pure material were fruitless.

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The Reduction of Perfluoroalkyl Isocyanates with Lithium Aluminum Hydride

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The reduction of alkyl isocyanates to methylalkylamines by means of lithium aluminum hydride has been reported by Finholt, Anderson, and Agre.[2] The present work was undertaken to determine whether a similar reduction of perfluoroalkyl isocyanates would be of value as a novel synthesis of methylfluoroalkylamines.

Treatment of perfluoropropyl and perfluoroheptyl isocyanate with excess lithium aluminum hydride has now been found to produce the corresponding methyl-1,1-dihydroperfluoroalkylamines in yields of 74% and 61%, respectively. The reactivity of fluorine atoms *alpha* to the nitrogen atom in amines has been noted before.[3] In the present work this reactivity has resulted in a reduction at these positions in addition to the desired reaction with the isocyanate group.

To avoid the reduction of the *alpha* fluorine atoms, an obvious modification is the use of limited quantities of the lithium aluminum hydride. This proved unsuccessful since the reaction of perfluoropropyl isocyanate with a one-half mole-ratio of the hydride gave a small yield (2.4%) of N-1,1-dihydroperfluoropropyl formamide together with high molecular weight materials. Therefore, the replacement of the *alpha* fluorine atoms of the isocyanate by hydrogen precedes the complete reduction of the isocyanate group.

Since the fluorine atoms *alpha* to a nitrogen atom are so susceptible to reducing agents, the treatment of either N-perfluoroalkyl urethans or perfluoroalkyl isocyanates with lithium aluminum hydride does not offer much promise as a possible synthesis of perfluoroalkylamines.

EXPERIMENTAL

Reagents. Perfluoropropyl and perfluoroheptyl isocyanates were prepared from the corresponding acid chlorides by the Curtius reaction.[4] Since the boiling point of the perfluoropropyl isocyanate (27–28°) is very close to that of the acid chloride (38–39°), in order to obtain a pure sample it was necessary to distil through a helices-packed column. Great care must be observed in this distillation. In one experiment, while dismantling the equipment after removal of the product, a violent explosion of the column hold-up completely destroyed the apparatus. This explosion was due to a higher-boiling fraction composed of either the acid azide or hydrazoic acid.

Ethereal solutions of lithium aluminum hydride were prepared by extracting commercial hydride with dry ether in a Soxhlet apparatus to eliminate insoluble material. The ethereal solution was standardized by measuring the volume of hydrogen liberated when 1 ml. of the solution was added to butanol.

Perfluoropropyl isocyanate reduction with excess lithium aluminum hydride. To a solution of 0.2 mole of lithium aluminum hydride in 150 ml. of ether, kept below 5°, was added dropwise 22 g. (0.10 mole) of perfluoropropyl isocyanate dissolved in 30 ml. of anhydrous ether. Upon completion of the addition, stirring was continued at room temperature for two hours. After a small quantity of water

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(1) From the thesis to be submitted by Robert G. Taborsky to the Graduate School of Western Reserve University in partial fulfillment of the requirements for the doctor's degree. Presented at the Atlantic City meeting of the American Chemical Society, September, 1956.

(2) Finholt, Anderson, and Agre, *J. Org. Chem.*, **18**, 1338 (1953).

(3) Pruett, Barr, Rapp, Bahner, Gibson, and Lafferty, *J. Am. Chem. Soc.*, **72**, 3646 (1950).

(4) Albrecht and Husted, U. S. Patent 2,617,817 (1952).

had been introduced to destroy excess hydride, a solution of 10 g. of sodium hydroxide in 100 ml. of water was added. The ether layer was separated and the aqueous layer was extracted with three 70-ml. portions of ether. The combined ether solutions were dried over Drierite and distilled through a helices-packed column to give 12.0 g. (73.5% yield) of methyl-1,1-dihydroperfluoropropylamine, b.p. 61–62°, n_D^{20} 1.3084, d_4^{20} 1.2557.

Anal. Calc'd for $C_4H_6F_5N$: C, 29.40; H, 3.70. Found: C, 30.07; H, 3.97.

Conventional treatment of the amine with *p*-nitrobenzoyl chloride gave the *p-nitrobenzamide,* m.p. 57–58°.

Anal. Calc'd for $C_{11}H_9F_5N_2O_3$: C, 42.00; H, 2.88. Found: C, 42.58; H, 2.88.

The melting point of the *p*-nitrobenzamide was not depressed by the addition of an authentic sample prepared, as described below, from the reduction product of N-methyl perfluoropropionamide.

Treatment of an ether solution of the amine with anhydrous hydrogen chloride precipitated the *hydrochloride salt,* m.p. 209° with decomposition.

Anal. Calc'd for $C_4H_7ClF_5N$: F, 47.9. Found: F, 48.3.

In preliminary experiments the perfluoropropyl isocyanate was not carefully purified and 1,1-dihydroperfluorobutyl alcohol (the reduction product of perfluorobutyryl chloride) was isolated from the reaction with lithium aluminum hydride in addition to the expected amine.

The structure of the methyl-1,1-dihydroperfluoropropylamine was proved by synthesis through an alternate route. Addition of 27 g. of perfluoropropionyl chloride to an excess (50 ml.) of 40% aqueous methylamine, cooled to 5°, gave 19.2 g. (79% yield) of N-methyl perfluoropropionamide, b.p. 156.5°, m.p. 32.5–33.5°.

Anal. Calc'd for $C_4H_4F_5NO$: C, 27.1; H, 2.26. Found: C, 26.65; H, 2.40.

Conventional reduction[5] of 11.4 g. of this amide with lithium aluminum hydride in ether gave 3.9 g. (37% yield) of the corresponding amine, b.p. 60–62°. The *p-nitrobenzamide* of this amine melted at 57–57.5°.

Reaction of lithium aluminum hydride with an excess of perfluoropropyl isocyanate. A solution of 0.24 mole of lithium aluminum hydride in 150 ml. of ether was added dropwise over a period of three hours to a solution of 100 g. (0.47 mole) of perfluoropropyl isocyanate in 400 ml. of ether. The reaction was so vigorous that for safe performance it was necessary to cool with a Dry-Ice bath and to blanket with nitrogen. The mixture was allowed to come to room temperature and 200 ml. of ether together with unreacted isocyanate (b.p. 27–28°) was removed by distillation through a fractionating column. A solution of 140 g. of potassium sodium tartrate in 200 ml. of water was added to the distilland, the mixture was stirred for one-half hour, and the water phase was separated and extracted with three 100-ml. portions of ether. The combined ether layers was dried with Drierite and distilled to give 15.5 g. of a semisolid distillate and a brown non-volatile residue. By chilling a chloroform solution of the distillate, 6 g. of perfluoropropionamide, m.p. 98–99° from chloroform (lit.[6] m.p. 96°), was obtained. A mixture with an authentic sample did not depress the m.p. This amide was formed by hydrolysis of unreacted isocyanate. Distillation of the chloroform mother liquors gave 2.0 g. of N-1,1-dihydroperfluoropropyl formamide, b.p. 81–83° (8 mm.), n_D^{25} 1.3439.

Anal. Calc'd for $C_4H_4F_5NO$: C, 27.10; H, 2.26; F, 53.5; N, 7.91. Found: C, 27.24; H, 2.11; F, 51.83; N, 7.50.

The b.p. and index of refraction also correspond to those of an authentic sample of N-1,1-dihydroperfluoropropyl formamide. Hydrolysis of an aliquot of the fraction with aqueous hydrochloric acid, evaporation of the solution to give the amine hydrochloride, and treatment of this salt with benzoyl chloride and sodium hydroxide gave N-1,1-dihydroperfluoropropyl benzamide, m.p. 97.5–98°. The m.p. of the benzamide was not depressed by mixing with an authentic sample.

The reference sample of N-1,1-dihydroperfluoropropyl formamide, b.p. 83° (8 mm.), n_D^{25} 1.3438, d_4^{25} 1.4680, was prepared in 1.8 g. (56%) yield by refluxing 2.6 g. of 1,1-dihydroperfluoropropylamine[6] with 1.34 g. of ethyl formate.

A reference sample of N-1,1-dihydroperfluoropropyl benzamide (m.p. 97.5–98°) was prepared from the amine by a Schotten-Bauman reaction.

Anal. Calc'd for $C_{10}H_8F_5NO$: C, 47.5; H, 3.16. Found: C, 47.69; H, 3.34.

Reduction of perfluoroheptyl isocyanate with excess lithium aluminum hydride. By a procedure identical with that just described, treatment of 9.0 g. (0.022 mole) of perfluoroheptyl isocyanate with 0.05 mole of lithium aluminum hydride led to the formation of 1.3 g. of nonvolatile material and 4.9 g. (61.5% yield) of methyl-1,1-dihydroperfluoroheptylamine, b.p. 55° at 26 mm., n_D^{20} 1.3119, d_4^{25} 1.5855.

Anal. Calc'd for $C_8H_6F_{13}N$: C, 26.41; H, 1.65; F, 68.10. Found: C, 26.47; H, 1.75; F, 68.83.

Treatment of the amine with benzoyl chloride and aqueous sodium hydroxide gave the *benzamide,* m.p. 63° after recrystallization from alcohol.

Anal. Calc'd for $C_{15}H_{10}F_{13}NO$: C, 38.60; H, 2.14. Found C, 38.64; H, 2.01.

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Synthesis and Investigation of Organic Fluorine Compounds. XXV.* The Preparation of Alkyl Fluoroformates and Remarks Relative to a New Published Preparation of Alkyl Fluorides

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Nakanishi, Myers, and Jensen[1] have published a new preparation of alkyl fluorides by the pyridine or boron trifluoride-catalyzed decarboxylation of fluoroformates:

$$FCOOR \longrightarrow FR + CO_2$$

The above authors prepared the starting fluoroformates by the thallous fluoride-halogen exchange method of Ray[2] which has also been used by Goswami and Sarkar[3] for the preparation of fluoroformates. A simple method for the preparation of alkyl fluoroformates is a prerequisite to the new alkyl fluoride method. Since thallous fluoride is not readily accessible in all organic laboratories, it seemed suitable in the course of our earlier experiments to investigate the use of potassium fluoride for the

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