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.

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND 6, OHIO

---

(5) Bourne, Henry, Tatlow, and Tatlow, *J. Chem. Soc.*, 4014 (1952).

(6) Haszeldine and Leedham, *J. Chem. Soc.*, 1548 (1953).

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

GEORGE A. OLÁH AND STEVEN J. KUHN

Received June 25, 1956

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

$$\text{FCOOR} \longrightarrow \text{FR} + \text{CO}_2$$

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

---

* Part XXIV, *J. Chem. Soc.*, in press.

(1) S. Nakanishi, T. C. Myers, and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 3099, 5033 (1955).

(2) P. C. Ray, *Nature*, **132**, 173 (1933).

(3) H. C. Goswami and P. B. Sarkar, *J. Indian Chem. Soc.*, **10**, 537 (1933).

fluoro exchange reaction in connection with our ultraviolet irradiation halogen exchange reaction.[4] By this method we were able to prepare ethyl fluoroformate from ethyl chloroformate in 51% yield (using potassium fluoride and ultraviolet irradiation).[4]

The separation of the fluoro products from the starting chloro or bromo materials in the halogen exchange reactions can be effected generally only with difficulty; a complete separation is possible only when relatively greater quantities are used. It seemed desirable, therefore, to find other ways for the preparation of alkyl fluoroformates. Emeléus and Wood[5] have described, in connection with the preparation of carbonyl fluorides and carbonyl chlorofluoride, the formation of ethyl fluoroformate by the interaction of ethanol with the halogen carbonyls. In the case of carbonyl chlorofluoride, only ethyl fluoroformate was formed; ethyl chloroformate was not present in the reaction product.

In the course of our investigations on the preparation of pure alkyl fluoroformates, we have found that the most suitable method of preparation is the interaction of carbonyl bromofluoride with the corresponding alcohols:

$$COFBr + ROH \longrightarrow FCOOR + HBr$$

In the above reaction no bromoformates are formed.

The reaction can also be effected by the use of carbonyl chlorofluoride analogous to the formation of ethyl fluoroformate as described by Emeléus and Wood.[5] Although chloroformates are not formed in this instance, the yields are lower, and dialkyl carbonates are formed in the reaction as by-products.

Since alkyl fluoroformates can be prepared in this way in one step, without contamination by other halogens, the method of Nakanishi, Myers, and Jensen[1]—with the above modification as proposed by us—would seem to be a general method for the replacement of an hydroxyl group by a fluorine atom. Data on the preparation of alkyl and cycloalkyl fluoroformates from the corresponding alcohols by reaction with carbonyl bromofluoride are given in Table I.

TABLE I

PREPARATION OF ALKYL AND CYCLOALKYL FLUOROFORMATES FROM ALCOHOLS

R in FCOOR	B.P., °C.	Yield, %	Fluorine Calc'd	Fluorine Found
CH_3	40	72	24.4	23.9
C_2H_5	57	84	20.7	20.3
C_3H_7[a]	90–92	81	17.9	17.5
iso-C_3H_7	81–82	75	17.9	17.4
C_4H_9	97–99	85	15.8	15.4
sec-C_4H_9	92–93	75	15.8	15.2
C_6H_{11}[a]	142–144	79	13.0	12.8

[a] These are new compounds, not described previously in the literature.

EXPERIMENTAL

PREPARATION OF CARBONYL HALIDES

Carbonyl bromofluoride was prepared by the reaction $BrF_3 + 2CO \rightarrow COBrF + COF_2$ according to a modification of the suggestion of Kwasnik.[6] Bromine trifluoride (BrF_3, 68.5 g., 0.5 mole) was placed in a three-necked round bottom quartz flask equipped with a nickel-jacketed thermometer, a gas inlet tube for the introduction of CO, and an efficient quartz reflux condenser. The carbonyl fluorides produced were led away from the top of the condenser into two traps the first of which was cooled with an acetone-Dry Ice mixture and the second with liquid oxygen. A carbon monoxide stream was passed through the BrF_3 at a temperature between 10–30°. The carbon monoxide used was generated from formic acid and was washed and dried by successive passage through a pyrogallol solution, conc'd H_2SO_4, and P_2O_5. The gas stream was regulated so that the reaction temperature did not exceed 30°. At lower temperatures the BrF_3 solidifies, while at higher ones there is danger of an explosion. In the first trap carbonyl bromofluoride which possesses a slight brown color is the main condensation product; in the second, liquid oxygen-cooled trap, there is condensed COF_2 contaminated with some COFBr. The carbonyl bromofluoride thus collected was passed through antimony powder to remove bromine and then was fractionated. Below $-60°$ there was obtained the first fraction containing some COF_2, and between -15 and $-30°$ the COFBr was collected. A second fractional distillation of the product gave pure COFBr. Yield, 53.5 g., 85%. The product trapped at liquid oxygen temperatures gave on fractionation 20 g. of COF_2 (60.6%, b.p. -84 and $-83°$) as well as some COFBr.

Carbonyl chlorofluoride was prepared by the reaction of phosgene and antimony^{III} fluoride under pressure according to Emeléus and Wood.[5]

The reaction of carbonyl bromofluoride with alcohols. Carbonyl bromofluoride (0.25 mole) was cooled to $-60°$, and 0.22 mole of the similarly cooled alcohol was dropped into it with stirring and continued effective cooling to control the vigorous reaction.

After addition of the alcohol was complete the reaction mixture was allowed to warm slowly to room temperature and then was held several minutes between 30–40° to complete the reaction. The mixture then was neutralized with anhydrous potassium carbonate, treated with anhydrous $CaCl_2$ to remove any unchanged alcohol present, filtered, and finally was fractionated. The yields, physical constants, and analyses for the prepared fluoroformates are given in Table I.

The reaction of carbonyl chlorofluoride with alcohols. The reaction was carried out with 0.25 mole of carbonyl chlorofluoride, cooled to $-50°$, and 0.22 mole of the corresponding alcohol as in the case of carbonyl bromofluoride. The yields of the fluoroformates are generally 20% less than in the reactions with carbonyl bromofluoride, and dialkyl carbonates are formed as by-products.

CHEMICAL CENTRAL RESEARCH INSTITUTE
OF THE HUNGARIAN ACADEMY OF SCIENCES,
BUDAPEST, XIV. HUNGARIA-KRT. 114.

---

(4) G. Oláh and A. Pavláth, *Acta Chim. Acad. Sci. Hung.*, **3**, 191 (1953).

(5) H. J. Emeléus and J. F. Wood, *J. Chem. Soc.*, 2183 (1948).

(6) W. Kwasnik in *Handbuch der preparativen organischen Chemie*, edited by George Brauer, Ferdinand Enke Verlag, Stuttgart, 1954, p. 169.