tracted with ether, alkalinized with ammonia and extracted again with ether until a negative Mayer's reaction was obtained. This last ether extract was well dried and a few drops of cyclohexane were added to the oily residue, whereupon it was caused to crystallize by scratching. The filtered crystals, recrystallized from cyclohexane, gave prisms, m.p. 130–131°, undepressed by pseudocodamine, m.p. 130–131°.[7] The picrate melted at 156–157°, and was identical with pseudocodamine picrate.

Pseudocorydine hydrochloride. One hundred milligrams of the former benzyl-pseudocorydine hydriodide was suspended in water, the solution covered with a layer of ethyl ether, made alkaline with saturated sodium hydrogen carbonate solution, and extracted with ether until a negative Mayer reaction was obtained. The ether extracts were dried and on evaporation gave 70 mg. of a brown oily residue. Fifteen ml. of 20% hydrochloric acid was added, and the solution was boiled for 1 hr. and evaporated to dryness, *in vacuo*. A crystalline brown residue was obtained, which was recrystallized by dissolving in ethanol and adding ether to turbidity. Thirty mg. (Vacuum) of white needles, m.p. 268–269° (sintering from 262°), was collected. λ_{max} 272 mμ (4.09); 302 mμ (3.70).

Anal. Calcd. for $C_{20}H_{23}NO_4\cdot ClH$: C, 63.56; H, 6.40; N, 3.70; Cl, 9.38. Found: C, 63.43; H, 6.37; N, 3.77; Cl, 9.37.

Pseudocorydine (IV). The hydrochloride (50 mg.) was dissolved in water, covered with a layer of ethyl ether, made alkaline with diluted ammonia and extracted with ether until a negative Mayer reaction was obtained. The dried extracts on evaporation left a white grayish crystalline solid, very soluble in all organic solvents, excepting cyclohexane and petroleum ether. After several recrystallizations from cyclohexane, white long prisms were obtained, melting 184–185° in vacuum. λ_{max} 272 mμ (log ϵ 4.04), 302 mμ (log ϵ 3.66).

Anal. Calcd. for $C_{20}H_{23}NO_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.51; H, 6.98; N, 4.07.

Pseudocorydine gives the same color reactions as isocorydine except with Fröhde's reagent which gives a dark purple color with pseudocorydine and a violet one with isocorydine.

Picrate. Prisms from ethanol m.p. 210–211°.

Anal. Calcd. for $C_{20}H_{23}NO_4\cdot C_6H_3N_3O_7$: N, 9.82. Found: N, 9.52.

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Effects of Perfluoroalkyl Groups on Adjacent Functions

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The adjacency of a perfluoroalkyl group can affect the stability of intermediate reaction products in such an adverse way as to render impractical some conventional reactions. Aldehydes and ketones so fluorinated react with diazomethane to give the expected oxides, but these are cleaved by hydrogen to give secondary and tertiary alcohols, instead of primary and secondary alcohols. Pyrolysis of *N,N'*-di(trifluoroacetyl)hydrazine and *N*-benzenesulfonyl-*N'*-trifluoroacetylhydrazine did not give trifluoroacetaldehyde, but its pyrolysis products, carbon monoxide and fluoroform. Hydrogenolysis of the benzyl ester of *N*-heptafluoropropylcarbamic acid gave toluene with hydrogen fluoride and pentafluoropropionamide instead of heptafluoropropylamine.

The adjacency of a perfluoroalkyl group, besides modifying the polarity of a function, can affect the stability of a conventional reaction product in such a favorable way as to render practical certain reactions otherwise not useful, *e.g.*, the preparation of ketones in good yields from perfluorinated acids and Grignard reagents due to the stability of the intermediate.[2–4] This modifying action is not always an aid and may make impractical some convential reactions.

Most aldehydes and ketones react conventionally with diazomethane to give the next higher homologs, or mixtures of them, and substituted ethylene oxides.[5–7] When electron withdrawing groups are present in the alpha position, the oxide is the major or sole product.[8–10] When trifluoroacetaldehyde and trifluoroacetone were used, the reaction proceeded as expected to give the corresponding oxides, 1,2-epoxy-3,3,3-trifluoropropane (I) and 1,2-epoxy-2-methyl-3,3,3-trifluoropropane (II), respectively. On hydrogenation, unfluorinated oxides give primary and secondary alcohols.[11–13] In contrast, hydrogenation with Raney nickel of the fluorinated oxides gave 2-trifluoromethyl-2-propanol, and 1,1,1-

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trifluoro-2-propanol. Reduction of II with lithium aluminum hydride gave the same tertiary alcohol. The central carbon atom of these oxides should by induction be more positive than the other carbon linked to the oxygen and hence preferentially reduced. Since in the final product it is the end carbon which appears reduced, it seems desirable to assume that a rearrangement takes place during the course of the reaction.

The McFadyen-Stevens aldehyde synthesis has been reported as useful and convenient in the case of aromatic aldehydes;[14-18] applications to aliphatic aldehydes have been unsuccessful except in the case of cyclopropylaldehyde[19] and it has been assumed that the difference was due to the presence of alpha hydrogen in the aliphatic compounds tested. In the present investigation, fluorinated compounds without alpha hydrogens were tested. *N*-benzenesulfonyl-*N'*-trifluoroacetylhydrazine and *N,N'*-di-(trifluoroacetyl)hydrazine were prepared by reaction of trifluoroacethydrazide hydrate with benzenesulfonyl chloride and trifluoroacetyl chloride, respectively. Pyrolysis, in the presence of carborundum or powdered glass, with or without sodium carbonate, in various high boiling media gave only fluoroform and carbon monoxide in both cases. Mass spectroscopic examination of the effluent gases indicated that the molar ratio of fluoroform to carbon monoxide was 1:1. These results seem to indicate that the aldehyde was formed as an intermediate, held tenaciously by the solvent and then decomposed by heating to its components fluoroform and carbon monoxide.

Syntheses of primary amines carrying fluorine on the same carbon atom as the amino group such as heptafluoropropylamine by the Hofmann hypohalite degradation of heptafluorobutyramide or the Schmidt-Curtius degradation of heptafluorobutyric acid azide have been reported as unsuccessful.[20,21] Husted[22] has found that the intermediate heptafluoropropylisocyanate is formed, and that its hydrolysis gives pentafluoropropionamide. It is also known that addition of ammonia to tetrafluoroethylene gives a triazine, 2,4,6-tridifluoromethyl-1,3,5-triazine, instead of 1,1,2,2-tetrafluoroethylamine.[23] On the basis of this, Stewart believed the $-CF_2NH_2$ group was not inherently unstable, but rather, sensitive to spontaneous loss of hydrogen fluoride and to extremely easy hydrolysis. The new method of approach tested here is the use of a benzyl urethane, a derivative known to give a primary amine, carbon dioxide, and toluene on hydrogenolysis.[24] This was to be tested in an anhydrous medium.

In the present investigation, the urethane prepared from benzyl alcohol and heptafluoropropylisocyanate was formed conventionally. On hydrogenolysis with Raney nickel or with palladized charcoal, it gave toluene and carbon dioxide as expected, but with hydrogen fluoride and pentafluoropropionamide instead of heptafluoropropylamine despite all efforts rigidly to exclude moisture. This practical failure is seen as a decomposition of the amino derivative by hydrogen fluoride loss, followed by passage to the lower amide in the presence of water.

EXPERIMENTAL

Reaction of trifluoroacetaldehyde with diazomethane. Polymeric trifluoroacetaldehyde (18 g., 0.184 mol.) was heated with a gas burner and the vapor of the monomer was passed into a solution of diazomethane (about 0.125 mol. prepared from 50 g. of *N*-methyl-*N*-nitrosourea) in 400 ml. of cyclohexane at 0°. The solution in a 1-l., 3-necked round bottom flask was stirred continuously and held under the refluxing of a Dry Ice condenser whose outlet led to a Dry Ice trap and eudiometer to follow the progress of the reaction. The diazomethane was decolorized by the excess of aldehyde after the reaction was allowed to reach room temperature. Fractionation of the solution gave the oxide (9.5 g., 0.097 mole, 53%) boiling at 38–46°. Fluoral hydrate (3 g., 0.026 mole, 14%) was also recovered. The identity of the oxide was established by infrared spectra showing no carbonyl and by comparison of its constants (b.p. 39–40°, n_D^{20} 1.3000) with known values (b.p. 39.1–39.3°, n_D^{20} 1.2997).[25]

Reaction of trifluoroacetone with diazomethane. Using a similar procedure, trifluoroacetone (25.5 g., 0.228 mol.) was distilled from an ampoule into a cyclohexane solution of diazomethane (about 0.125 mol. in 500 ml.) at 0°. Fractionation gave: trifluoroacetone (6.9 g., 0.061 mol., 26.8%) boiling 20–25°, a midcut (4.8 g., about 0.040 mol., about 17.5%), the oxide (10.7 g., 0.084 mol., 36.8%) boiling at 47–58°, and a tail cut boiling up to 80°. Refractionation of the oxide cut gave mostly material boiling at 50–52°, which gave a (−)2,4-DNPH test and an infrared spectra which was carbonyl-free and similar to that of other oxides.

Hydrogenation of I *with Raney nickel.* The oxide (6.5 g., 0.066 mol.) was dissolved in 50 ml. of dry ether and placed in a steel autoclave with 4 g. of Raney nickel and enough hydrogen to obtain a pressure of 5.3 atm. The autoclave, heated to 170°, was rocked mechanically for 15 hr. during which time the pressure fell asymptotically. Fractionation of the contents gave the alcohol (4.1 g., 0.043 mol., 65%) boiling at 65–70°. Infrared spectral comparison showed it to be 1,1,1-trifluoro-2-propanol. The 3,5-dinitrobenzoate derivative melted at 87°, mixed m.p. 87°.

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Hydrogenation of II *with Raney nickel and lithium aluminum hydride.* The oxide (9.2 g., 0.073 mol.) in 50 ml. of dry ether with 5 g. of Raney nickel was hydrogenated in the same way as in the previous case. Fractionation gave the tertiary alcohol as the main product (2.5 g., 0.02 mol., 27%) boiling at 70–82° in addition to a forecut (5 g.) consisting of alcohol and ether. The identity of the alcohol was ascertained by infrared spectra and physical constants of a purified sample of the 70–82° material (b.p. 82°, $n_{\rm D}^{20}$ 1.3370) compared to known values for the tertiary alcohol (b.p. 82°, $n_{\rm D}^{20}$ 1.3350[26]) and for the primary alcohol, 2-trifluoromethyl-1-propanol (b.p. 109°, $n_{\rm D}^{20}$ 1.3399[27]).

The oxide (6.7 g., 0.053 mol.) was added in 20 min. to a slurry of lithium aluminum hydride (2.3 g., 0.06 mol.) in 75 ml. of dry ether at 0°. The mixture, continuously stirred, was protected from moisture by a reflux condenser whose outlet led to a Dry Ice trap. After addition, the mixture was stirred for 1 hr. at 0°, warmed to room temperature for 15 min., and then cooled to 0° for decomposition with wet ether followed by 25 ml. of concentrated hydrochloric acid in 10 ml. of water. The ether layer and extracts of the aqueous layer were dried using Molecular Sieve 4A. Fractionation gave a forecut (2 g.) boiling in the range 40–78°, the main cut (3 g., 0.023 mol., 44%, $n_{\rm D}^{20}$ 1.3352) boiling 78–81° and a tail cut (1.4 g.). The tertiary alcohol was confirmed as before.

Preparation of trifluoroacethydrazide hydrate. Ethyl trifluoroacetate (106.5 g., 0.75 mol.) was refluxed for 3 hr. with 85% hydrazine hydrate (48.9 g., 0.825 mol.) in 150 ml. of 95% ethanol. After removal of the ethanol with a take-off condenser, a viscous liquid (96 g., 0.66 mol., 88%) remained which solidified on standing. Recrystallization from butanol gave crystals, m.p. 138–140°, identified as trifluoroacethydrazide hydrate by comparison of its infrared spectra with that of the unfluorinated analog.

Preparation of N-benzenesulfonyl-N′-trifluoroacetylhydrazine. Benzenesulfonyl chloride (48.6 g., 0.275 mol.) was added through an addition funnel to a solution of trifluoroacethydrazide hydrate (36.5 g., 0.25 mol.) in pyridine (198 g., 2.5 mol.) at 0°. During addition, the solution was continuously stirred and the 500-ml. 3-necked round bottom flask was equipped with a reflux condenser. After reaching room temperature, the stirring action was continued for an additional hour. The reaction mixture was then poured over 500 g. of ice and 30 ml. of concentrated hydrochloric acid. The yellow precipitate resulting was washed with 200 ml. of water and recrystallized from water-acid mixture to give a white product (58.3 g., 0.217 mol., 87%) melting at 212–213° which on sodium fusion gave positive tests for sulfide with lead acetate solution and for fluoride with cerous nitrate solution.

Preparation of N,N′-di(trifluoroacetyl)hydrazine. Trifluoroacetyl chloride (53 g., 0.40 mol.) was vaporized and led into a slurry of sodium phosphate, tribasic (49.5 g., 0.3 mol.) in 245 ml. of dry dioxane containing trifluoroacethydrazide hydrate (36.5 g., 0.25 mol.). This slurry was continuously stirred and protected from moisture by a Dry Ice reflux condenser whose outlet led to a Dry Ice trap. After addition at 0° was completed, the mixture was allowed to reach room temperature and then the stirring was maintained for an additional several hours. The white solid was filtered and extracted for 24 hr. with ethanol in a Soxhlet-type extractor. Removal of solvent from the filtrate and extracts gave an alcoholic residue (74 g.) which on sublimation gave a crystalline product (46.2 g., 0.206 mol., 82.6%) melting at 180–180.5°, and identified by infrared spectral comparison with the unfluorinated analog to be *N,N′*-di(trifluoroacetyl)hydrazine.

An attempted preparation by the method employed in the case of *N*-benzenesulfonyltrifluoroacetylhydrazine using pyridine gave a product (about 80–85%) which on sublimation gave crystals melting at 85° but which had a slight pyridine odor, enhanced by crushing the crystals. Infrared spectra showed it to be identical to *N,N′*-di(trifluoroacetyl)-hydrazine except for additional bands attributable to pyridine. Analysis indicated 2 mol. of pyridine per mole of compound.

Preparation using anhydrous hydrazine, trifluoroacetyl chloride, and sodium carbonate in ether was effected with a 70% yield of product.

Decomposition of N-benzenesulfonyltrifluoroacetylhydrazine. In a typical decomposition, *N*-benzenesulfonyltrifluoroacetylhydrazine (5.3 to 8 g., 0.02 to 0.03 mol.) and an equivalent amount of sodium carbonate in 50 to 100 ml. of solvent were placed in a 200-ml. 2-necked round bottom flask or 425-ml. steel autoclave with a few grams of carborundum or ground glass as surface catalyst. The mixture, continuously stirred in the flask or mechanically rocked in the autoclave, was heated to the boiling point of the mixture or to 200–220° in the autoclave. The effluent gases were led through a train which consisted of a water cooled condenser, a Dry Ice trap, a calcium chloride drying tube, an Ascarite tube, a Dry Ice trap, and an eudiometer. The effluent gases were passed through the train as formed in flask reactions; in autoclave reactions, gases were built up and then released slowly after the reaction was completed. The solvent was either decalin or ethylene glycol. No liquid products were isolated and no solids except small amounts of phenyl disulfide (m.p. and mixed m.p. 61°) in a run using ethylene glycol as the solvent, and starting material. Infrared spectra of the effluent gases from the last run in decalin showed the presence of carbon monoxide and fluoroform.

Decomposition of N,N′-di(trifluoroacetyl)hydrazine. These decompositions were carried out in the same manner as described above for autoclave reactions at 225°. For convenience an infrared gas cell, protected from moisture by Dry Ice traps, was inserted into the train. The effluent gas was found by infrared spectra to be rich in carbon monoxide and fluoroform. Mass spectra data indicated a 1:1 mole ratio of the two gases.

Similar results were obtained with or without base. Decalin, carbitol, and *o*-dichlorobenzene were used as solvents. In the case of carbitol, much ammonia was isolated (12 meq. found on titration in a run using 0.045 mol. of compound after some standing).

Preparation of benzyl ester of N-heptafluoropropylcarbamic acid. Heptafluoropropylisocyanate (32 g., 0.151 mol., prepared by reaction of heptafluorobutyrl chloride and sodium azide followed by heating) was vaporized by use of warm water into a solution of benzyl alcohol (16 g., 0.148 mol.) in 50 ml. of dry ether. The solution, continuously stirred in a 200-ml. 3-necked round bottom flask, was protected from moisture by a Dry Ice condenser whose outlet led to a Dry Ice trap. After addition in 1 hr., the solution was permitted to stand several days at room temperature. The solvent was then removed by aspiration and a low melting solid (46 g., 0.144 mol., 97%) was obtained. Recrystallization from 30–60° petroleum ether gave crystals melting at 34.5–35.5°, which were identified by infrared spectra as the urethane.

Vacuum distillation of the product of an earlier run gave a cloudy liquid distilling at 120°/10 mm. which contained some hydrogen fluoride. Considerable solid also formed which clogged the column. The liquid was identified by infrared spectra as the urethane. The solid melted at 97° and was identified as pentafluoropropionamide by infrared spectra; mixed m.p. with authentic sample, 97°. In addition, a polymeric glassy material, soluble in chloroform, remained as a residue. The amounts of amide, urethane, and polymer were roughly equal, *viz.* 7 g., 7 g., and 6 g. from a run made using 0.083 mol. each of isocyanate and alcohol in 40 ml. of carbon tetrachloride.

Stability of benzyl ester of N-heptafluoropropylcarbamic acid. (*a*) *Standing in solution.* Crude urethane on standing in

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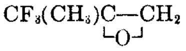
TABLE I

NEW COMPOUNDS

Compound	M.P., °C.[a]	% C[b] Calcd.	% C[b] Found	% H[b] Calcd.	% H[b] Found	% N[b] Calcd.	% N[b] Found	% F[c] Calcd.	% F[c] Found
 $CF_3(CH_3)C—CH_2$ (—O—)	[d]	—	—	—	—	—	—	45.3	44.1
$CF_3CONHNH_2 \cdot H_2O$	138–140	—	—	—	—	—	—	39.7	39.4
$CF_3CONHNHSO_2C_6H_5$	212–213	35.83	36.10	3.61	2.85	10.45	10.34	—	—
$CF_3CONHNHCOCF_3$	180–180.5	21.40	21.50	0.89	1.28	12.50	12.64	—	—
$CF_3CONHNHCOCF_3 \cdot 2C_5H_5N$	85	42.93	42.74	3.15	3.24	—	—	—	—
$C_3F_7NHCO_2CH_2C_6H_5$	34.5–35.5	41.37	41.45	2.51	2.65	4.43	4.39	—	—
$C_2H_5CONHCO_2CH_2C_6H_5$	95	—	—	—	—	—	—	32.87	32.63

[a] Temperatures uncorrected. [b] Analyses by Galbraith Laboratories. [c] Analyses by M. Renoll. [d] B.p. 50–52°, n_D^{20} 1.3146, d_4^{20} 1.203, M.R. 20.55, A.R. for F 1.24.

TABLE II

HYDROGENOLYSIS OF $C_3H_7NHCO_2CH_2C_6H_5$

Run	Urethane, g.	Pressure H_2, atm.	Catalyst	Temp., °C.	Time	Spectra Change
1	2.5	3.3	Pd/C[a]	25	48 hr.	Partial loss of 6.48-band
2	3.0	3.3	Pd/C[a]	25	6 days	Complete loss of 6.48-band
3	3.0	3.3	3 g. Ra-Ni	25	45 hr.	No change
4	3.0	9.3	Pd/C[a]	100	24 hr.	Complete loss of 6.48-band
5	3.0	11.0	3 g. Ra-Ni	125	24 hr.	Complete loss of 6.48-band

[a] The Pd/C consisted of 30 mg. $PdCl_2$ and 120 mg. C.

petroleum ether for several days without protection from moisture gave a crystalline material (5 to 15%) melting at 95°. The solvent gave a positive test for fluoride with cerous nitrate solution. The infrared spectra and analysis indicated the material to be the benzyl ester of *N*-pentafluoropropionylcarbamic acid. No change occurred in this material under hydrogenolysis conditions used later with unchanged urethane.

(*b*) *On standing exposed to air and moisture.* On prolonged standing (several months) in open air, a crystalline solid melting at 87° was obtained. Before recrystallization, a strongly acidic odor was detected. Infrared spectra showed this material to be benzyl carbamate, mixed m.p. with authentic sample, 87°.

(*c*) Under similar conditions as outlined in (*a*) and (*b*) as well as to heat, the methyl ester of *N*-heptafluoropropylcarbamic acid was found to be stable.

Hydrogenolysis of benzyl ester of N-heptafluoropropylcarbamic acid. In a typical run, the urethane (2 to 3 g., 0.006 to 0.009 mol.) in 30 to 40 ml. of dry ether was placed in either a 220-ml. glass bottle in the Parr hydrogenation apparatus or in a 425-ml. steel autoclave. A variety of catalysts, time, temperature, and hydrogen pressure were used. In all cases when reaction occurred, the infrared spectra showed a loss of the 6.48-band characteristic of the starting material (see Table II). Removal of the solvent in run 2 gave pentafluoropropionamide (1.4 g., 0.0085 mol.) identified as before. The solvent contained toluene, identified by odor and infrared spectra, and also gave a positive test for fluoride with cerous nitrate solution.

Under similar conditions, as outlined in Table II, the methyl ester of *N*-heptafluorobutylcarbamic acid was stable.

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Addition of Mercuric Fluoride to Fluoroethylenes

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A convenient new synthesis of polyfluoroethylmercurials has been found in the addition of mercuric fluoride to fluoroethylenes in the presence of a solvent. Volatile bis(polyfluoroethyl)mercury compounds are formed directly and in good conversion. Bis(1,2,2,2-tetrafluoroethyl)mercury and bis(2,2,2-trifluoroethyl)mercury have been characterized.

A basic mercury salt or the mercuric salt of a carboxylic acid will generally add to an olefin to form a monoalkylmercury salt containing a hydroxy, alkoxy, or acyloxy substituent in the alkyl group.[1] The structures of the products formed suggest polar intermediates, and mechanisms

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