Reactions of hexafluorocyclobutene with thiols were complicated by the elimination of hydrogen fluoride to produce unsaturated sulfides which were capable of further reaction. 1-Butylthio-2,3,3,4,4-pentafluorocyclobutene, 1,2-bis-(butylthio)-1,3,3,4,4-pentafluorocyclobutane and 1,2-bis-(butylthio)-3,3,4,4-tetrafluorocyclobutene were obtained from the reaction of hexafluorocyclobutene and 1-butanethiol.

OAK RIDGE, TENN. RECEIVED NOVEMBER 9, 1949

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS CORPORATION]

Reactions of Polyfluoro Olefins. II.[1] Reactions with Primary and Secondary Amines[2]

BY ROY L. PRUETT, JOHN T. BARR, KARL E. RAPP, CARL T. BAHNER, J. DONALD GIBSON AND ROBERT H. LAFFERTY, JR.

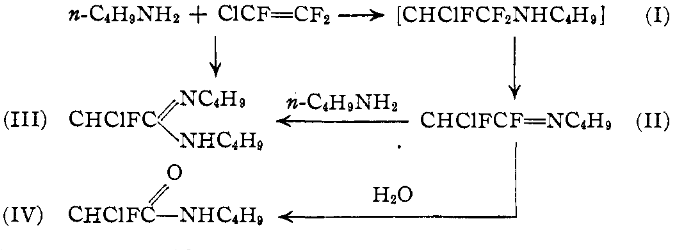
Diethylamine has been treated with aluminum chloride and tetrafluoroethylene at 90° to obtain an unidentified liquid boiling at 176–177° and 761 mm.[3] Rigby and Schroeder[4] have treated polyfluoroölefins, such as tetrafluoroethylene and chlorotrifluoroethylene, with primary and secondary amines in the presence of borax and at temperatures of 50–150°. By that method they obtained N-substituted difluoro- and chlorofluoroacetamides. Hurwitz and Miller[5] have reported that secondary amines react "readily under mild conditions" with polyfluoro ethylenes "to yield saturated products having exclusively α,α-difluoro structures."

An investigation of the reactions of primary and secondary amines, both aliphatic and aromatic, with chlorotrifluoroethylene and hexafluorocyclobutene has been conducted. The results of this investigation show that a catalyst is unnecessary for the addition of either primary or secondary amines to take place under mild conditions and that, using a different concentration of the secondary amine, a compound other than the saturated α,α-difluoro addition product is obtained as the principal reaction product.

The reaction between primary aliphatic amines and chlorotrifluoroethylene, as illustrated by n-butylamine, produced a mixture of N-n-butyl-α-chloro-α-fluoroacetimidyl fluoride (II) and N,N′-di-n-butyl-α-chloro-α-fluoroacetamidine (III).

The imidyl fluoride structure for (II) was indicated by its hydrolysis to the N-n-butyl-α-chloro-α-fluoroacetamide (IV) and by reaction with additional amine to produce a compound identical in composition and refractive index with (III).

By analogy with previously reported reactions of chlorotrifluoroethylene with anionic reagents[1,5,6] it is believed that the imidyl fluoride (II) was formed by loss of hydrogen fluoride from the unstable primary addition product (I).



Aromatic amines reacted in a manner similar to aliphatic amines, although the reaction was much slower. When aniline reacted with chlorotrifluoroethylene, the only product isolated was N,N′-diphenyl-α-chloro-α-fluoroacetamidine. The failure to produce any of the imidyl fluoride intermediate may have been due to difference in reaction conditions. The structure of the amidine was proved by hydrolyzing it to the corresponding amide. The amidine appeared to form a crystalline association compound with dioxane, with a ratio of 1.5 moles of dioxane per mole of amidine.

When secondary amines were treated with chlorotrifluoroethylene, the first reaction was one of addition to form a tertiary amine containing an α,α-difluoro structure. However, when an excess of amine was used, and the reaction conditions modified somewhat, further reaction occurred. It is believed that this reaction proceeded in several definite steps. In the first step, which occurred rapidly and with evolution of heat, the secondary amine added to the olefin. The following steps were much slower and, according to this hypothesis, were alternate losses of HX and addition of dialkyl amine to the resulting olefins. This process continued until all the halogen was removed and

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[1] The previous paper in this series is: Rapp, Pruett, Barr, Bahner, Gibson and Lafferty, THIS JOURNAL, **72**, 3642 (1950).

[2] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Corporation at Oak Ridge, Tennessee.

[3] E. I. du Pont de Nemours and Company, British Patent 583,874; *C. A.*, **41**, 5141 (1947).

[4] Rigby and Schroeder, U. S. Patent 2,409,315 (1946).

[5] Hurwitz and Miller, "Reactions of Chlorofluoro Olefins with Anionic Reagents," Abstracts of Papers, 114th Meeting, American Chemical Society, Washington, D. C., August, 1948, p. 4L.

[6] Hanford and Rigby, U. S. Patent 2,409,274 (1946); Miller, Fager and Griswold, THIS JOURNAL, **70**, 431 (1948); Park, Vail, Lea and Lacher, *ibid.*, **70**, 1550 (1948).

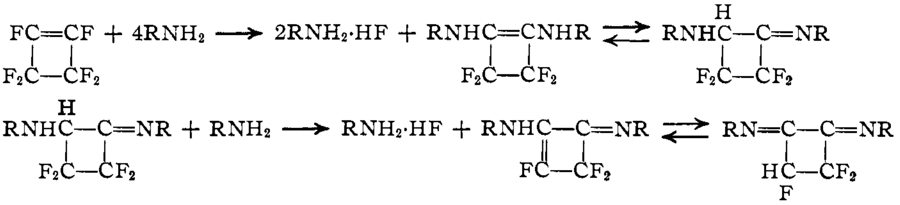
the final product, tetrakis-(dialkylamino)-ethylene, was formed.

This type of compound added halogen easily to form a solid having salt-like characteristics, being water soluble and containing halogen which could be precipitated with silver nitrate.

The presence of two aryl groups in an amine appears to make the amine inert toward addition, since diphenylamine failed to add to either of the polyfluoro olefins used, even upon the application of heat.

The imino compounds formed by the reaction of primary aliphatic amines with hexafluorocyclobutene were basic, being soluble in dilute hydrochloric acid. They were unstable and decomposed when heated even slightly. For this reason it was necessary that all operations used in preparing and isolating these compounds be carried out at room temperature or below.

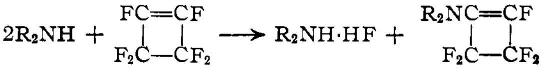
Although the structures of the imino products were not proved, the hypothesis is proposed that the reactions proceeded through the series



It was expected that the reaction of hexafluoro cyclobutene with aniline or 2-naphthylamine would proceed in a manner similar to that of the alkyl amine reactions. In neither case was a product of this type obtained. The aniline reaction gave a tar from which no definite product could be isolated. From 2-naphthylamine the only substance isolated aside from recovered amine was a solid which, according to analytical data and qualitative chemical tests, appeared to be 2-naphthylamine dihydrofluoride. Since the initial alkyl amine products were found to be unstable at or near room temperature, it is probable that the hypothetical primary products of these reactions were unstable at even lower temperatures, which would explain the failure to isolate them.

The tertiary amines prepared by the reaction of dialkyl amines with hexafluorocyclobutene were practically non-basic, being insoluble in dilute hydrochloric acid. They were quite stable, in contrast to the products formed from primary amines and hexafluorocyclobutene.

The reaction which occurred is



Experimental

The hexafluorocyclobutene used was prepared in this Laboratory by the method described by Rapp and associates.[1] Chlorotrifluoroethylene was obtained from the K-25 Fluorothene Plant. *n*-Propyl- and di-*n*-propylamine were obtained from Sharples Chemicals, aniline from General Chemicals Company, *n*-butylamine from Carbide and Carbon Chemicals Corporation, and the other amines from Eastman Kodak Company.

All reactions except one were carried out in either a pressure vessel or a three-neck flask. The pressure vessels used were made of stainless steel and had a capacity of 500 ml. The amine was sealed in the vessel, which was then cooled in a Dry Ice–trichloroethylene-bath and evacuated. The polyfluoro olefin was passed in as a gas, usually while the vessel and contents were immersed in the cooling bath. A "T" tube carrying a pressure gage and valve was then attached. After the reaction vessel and contents had warmed to room temperature, the reaction was allowed to proceed, aided in some cases by mechanical shaking. The progress of the reaction was followed by noting the pressure drop in the reactor. If heating was necessary, it was supplied either by a water-bath or by a thermostatically controlled electrical heater. Removal of excessive heat of reaction was accomplished by immersion in a water-bath. In the cases of diphenylamine with chlorotrifluoroethylene and with hexafluorocyclobutene, and of dimethylamine with chlorotrifluoroethylene, the olefin was introduced under pressure in small portions after the reaction vessel had warmed to room temperature.

The majority of the reactions were carried out at atmospheric pressure and near room temperature. For this type of reaction a three-neck flask was used. In this flask were mounted a gas inlet tube, thermometer, mechanical Hershberg stirrer, and reflux condenser bearing a drying tube. The amine was dissolved in dry diethyl ether in the flask and the olefin was bubbled through at rates of 50 to 150 cc./min. In nearly all cases a heavy precipitate of amine hydrofluoride began to separate immediately. The Hershberg stirrer was used only when necessary to break up the gel caused by the amine salt. Because of the exothermic nature of the reaction, the flask always was immersed in an ice-bath so as to maintain a temperature of 0–25°. The reaction was continued until the desired amount of polyfluoro olefin had been introduced, as shown by the loss in weight of the olefin cylinder. The reaction time varied from one to four hours, depending on the rate of addition of the olefin and the quantity of product desired.

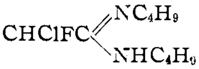
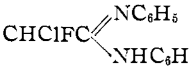
For the reaction of chlorotrifluoroethylene with piperidene, a slightly different apparatus was used. A cylindrical tube, 20 mm. in diameter and 76 cm. long, was used for the reaction vessel. The tube was equipped with a fritted gas-dispersion disk at the bottom, a reflux condenser at the top, and was surrounded with a water jacket. Ice water was circulated through the water jacket and condenser, and a thermometer was suspended in the reaction mixture.

The experimental conditions used in conducting the reactions and the physical properties of the compounds obtained are tabulated in Tables I and II. Analytical data for primary products obtained are tabulated in Table III.

N-*n*-Butyl-α-chloro-α-fluoroacetimidyl Fluoride and N,N′-Di-*n*-butyl-α-chloro-α-fluoroacetamidine.—Chlorotrifluoroethylene was bubbled through a solution of *n*-butylamine in two volumes of ether in the three-neck flask described above. At the end of the reaction time the mixture was filtered to remove the *n*-butylamine hydrofluoride, and the ether was removed under reduced pressure by an aspirator. The remaining oil was distilled through a 50-cm. Vigreux column at a reflux ratio of 10:1 to give N-*n*-butyl-α-chloro-α-fluoroacetimidyl fluoride, a clear mobile liquid which fumed heavily in the air and reacted with alcohols, amines and water. Analytical data gave an empirical formula of $C_4H_{10}ClF_2N$, with one ionizable fluorine.

TABLE I

REACTIONS OF AMINES WITH CHLOROTRIFLUOROETHYLENE

Reactant	Molar[a] ratio	Products	Reaction Temp., °C.	Reaction Time, hr.	Yield, %	Boiling point, °C.	Boiling point, Mm.	$n^{25}D$	d^{25}_4
n-$C_4H_9NH_2$	2.19 0.90	$CHClFCF{=}NC_4H_9$	0–30	3.5	33	51	26	1.4006	1.0936
		 $CHClFC(=NC_4H_9)NHC_4H_9$			12	70[b]	0.01	1.4387	
$C_6H_5NH_2$	0.98 2.00	 $CHClFC(=NC_6H_5)NHC_6H_5$	22–29	720	63	51–52[c]			
$(C_2H_5)_2NH$	0.67 0.71	$(C_2H_5)_2NCF_2CFClH$	23–25	72	87	32–33	5.5–6.0		1.19
$C_5H_{10}NH$	1.36 excess	$C_5H_{10}NCF_2CFClH$	0–10	3	87	46	3.0		1.25
$(CH_3)_2NH$	4.44 0.60	$[(CH_3)_2N]_2C{=}C[N(CH_3)_2]_2$	58–62	8	54	59	0.9	1.4785	0.8612
$(C_6H_5)_2NH$	0.10 0.36	No reaction	25	16					

[a] In this column, the first number refers to moles of amine, the second to moles of chlorotrifluoroethylene. [b] The value given is a minimum value, since no distillation occurred at this temperature and pressure. [c] Melting point, uncorrected.

TABLE II

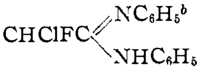
REACTIONS OF AMINES WITH HEXAFLUOROCYCLOBUTENE

Reactant	Molar[a] ratio	Products	Reaction Temp., °C.	Reaction Time, hr.	Yield,[b] %	Boiling point °C.	Mm.	$n^{25}D$	d^{25}_4
n-$C_4H_9NH_2$	0.96 0.14	$(C_4H_9N{=})_2C_4F_3H$	15–25	1	72	65–66[c]			
n-$C_3H_7NH_2$	1.03 0.09	$(C_3H_7N{=})_2C_4F_3H$	15–25	1	56	88–89[c]			
2-$C_{10}H_7NH_2$	0.25 0.13	2-$C_{10}H_7NH_2 \cdot 2HF$[d]	25	18		247–248.5 dec.[c]			
$(C_2H_5)_2NH$	1.00 0.38	$(C_2H_5)_2NC_4F_5$	15–25	4	59	76–77	52–54	1.3914	1.2271
$(n$-$C_3H_7)_2NH$	0.88 0.14	$(C_3H_7)_2NC_4F_5$	15–25	2	35	97–98	23	1.4016	1.160
$(C_6H_5)_2NH$	0.10 0.11	No reaction	60–75	19					

[a] In this column, the first number refers to moles of amine, the second to moles of hexafluorocyclobutene. [b] The yields shown are low, due to incomplete absorption of the olefin. [c] Melting point, uncorrected. [d] This compound was obtained as a by-product of the reaction.

TABLE III

ANALYSIS OF PRIMARY PRODUCTS

Compound	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$CHClFCF{=}NC_4H_9$[a]	42.49	42.62	5.94	5.84	8.31	8.31
 $CHClFC(=NC_6H_5)NHC_6H_5$[b]	64.00	64.14	4.60	4.40	10.66	10.53
$(C_2H_5)_2NCF_2CFClH$[c]	38.00	37.96	5.85	6.08	7.39	7.10
$[(CH_3)_2N]_2C{=}C[N(CH_3)_2]_2$	59.95	60.05	12.08	11.84	27.97	27.31
$C_5H_{10}NCF_2CHClF$[d]	41.70	42.18	5.50	5.97		
$(C_4H_9N{=})_2C_4F_3H$	58.04	58.60	7.71	7.64	11.29	11.25
$(C_3H_7N{=})_2C_4F_3H$	54.53	54.67	6.87	6.87	12.72	13.04
$C_{10}H_7NH_2 \cdot 2HF$	65.56	66.04	6.05	5.34	7.65	7.81
$(C_2H_5)_2NC_4F_5$	44.53	44.73	4.67	4.63	6.50	7.20
$(C_3H_7)_2NC_4F_5$	49.38	49.21	5.80	5.47	5.76	6.20

[a] Calcd.: Cl, 20.91; mol. wt., 169.6. Found: Cl, 20.66; mol. wt., 163.4. [b] Calcd.: Cl, 13.50. Found: Cl, 13.57. [c] Calcd.: ionizable F, 20.04. Found: F, 19.76. [d] Calcd.: ionizable F, 18.85. Found: F, 18.80.

The pot residue from the distillation of the original product was placed in a molecular still and stripped at a pressure of 10 microns at 70°. There remained N,N′-di-n-butyl-α-chloro-α-fluoroacetamidine, a straw-colored viscous oil, soluble in organic solvents and dilute mineral acids. It had a mild pyridine-like odor, and $n^{25}D$ 1.4387. Analytical data indicated the empirical formula $C_{10}H_{20}ClFN_2$.

Structure Proof of N-n-Butyl-α-chloro-α-fluoroacetimidyl Fluoride. 1. Hydrolysis.—The imidyl fluoride was hydrolyzed by shaking with two volumes of water, first with cooling, and finally for five minutes in a hot water-bath. Distillation of the lower layer gave N-n-butyl-α-chloro-α-fluoroacetamide, $n^{25}D$ 1.4436.[7]

2. **Reaction with n-Butylamine.**—Ten milliliters of n-butylamine was added to a solution of 5.5 g. of the imidyl fluoride in 15 ml. of dry diethyl ether and refluxed fifteen minutes. The ether solution was filtered from the precipitate of amine hydrofluoride, washed with 30 ml. of water, dried and the ether removed. The residual oil was dissolved in ethanol, thrown out with water, and again dried over calcium chloride, $n^{25}D$ 1.4392. *Anal.* Calcd. for $C_{10}H_{20}ClFN_2$: Cl, 15.92. Found: Cl, 15.82.

N,N′-Diphenyl-α-chloro-α-fluoroacetamidine.—Aniline and chlorotrifluoroethylene reacted in the pressure vessel described above. The time indicated in Table I is in excess of that required for complete reaction. The reason for this long reaction time was that no pressure drop occurred, so that there was no means of determining when the reaction was complete. The reaction product obtained

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(7) Rigby and Shroeder, ref. 4, found $n^{25}D$ 1.4431.

after standing even longer was considerably darker than that obtained at the end of one month, indicating that shorter lengths of time probably would be better.

After allowing the excess gas to escape, the reaction product was removed from the vessel and quickly treated with excess water, taking care that all lumps were broken up. The product separated as a black, semisolid, lower layer. This was separated from the water and dissolved in an equal volume of dioxane. The mixture was frozen and allowed to warm until the dioxane had melted, after which a light brown solid weighing 59.5 g. was filtered from the cold dioxane. This was purified by several recrystallizations from dioxane, the final product being white and melting at 64.5–65.5°.

A weighed sample of this solid was placed in a cylindrical tube containing a fritted glass disk, and nitrogen was forced through the solid. The tube and contents were weighed from time to time until the loss in weight became negligible. This operation required about six hours. During this time the solid became semi-liquid and then crystallized again, the melting point of this product being 51–52°. The loss in weight was 32% of the total, corresponding to a ratio of 1.5 moles of dioxane to one of amidine.

N-Phenyl-α-chloro-α-fluoroacetamide.—One gram of the above amidine was dissolved in dilute hydrochloric acid and the solution was allowed to stand at room temperature for two days. This procedure produced white crystals, which after recrystallization from methanol–water melted at 80–81°. *Anal.* Calcd. for C_8H_7ONFCl: C, 51.22; H, 3.76; N, 7.46; Cl, 18.90. Found: C, 51.16; H, 3.70; N, 7.76; Cl, 18.83.

N-(2-Chloro-1,1,2-trifluoroethyl)-diethylamine.—For the reaction of chlorotrifluoroethylene and diethylamine, the pressure vessel and contents were allowed to stand at room temperature without shaking. A water-bath was used to absorb the heat evolved.[8] The product was transferred directly from the reactor to the still-pot, taking care that it was exposed to the air no more than necessary. It was distilled through a 50-cm. Vigreux column, using a reflux ratio of about 4:1. Nearly all the product distilled at a constant temperature; only a small amount of tarry residue remained. This distillate reacted readily with water, alcohols and amines.

N,N-Diethyl-α-chloro-α-fluoroacetamide.—A quantity of the reactive amine was hydrolyzed by stirring with excess water. Much heat was evolved during the reaction and it was necessary to cool the mixture in an ice-bath. The lower layer of amide was washed with water and distilled through a 50-cm. Vigreux column. This gave a clear liquid of b. p. 47° at 0.7 mm., $n^{25}{}_D$ 1.4499, $d^{25}{}_4$ 1.1635. *Anal.* Calcd. for $C_6H_{11}ONFCl$: C, 42.99; H, 6.67; N, 8.37; Cl, 21.15; mol. wt., 167.6. Found: C, 43.04; H, 6.67; N, 7.94; Cl, 20.90; mol. wt., 168.5.

The reaction with water was quantitative, producing two moles of hydrogen fluoride and one mole of N,N-diethyl-α-chloro-α-fluoroacetamide for each mole of amine hydrolyzed. This, together with the fact that no chloride ion was produced in the hydrolysis, proved that only the $(C_2H_5)_2NCF_2CClFH$ isomer was present. These facts agree with the findings of Hurwitz and Miller[5] and of Huskins and Tarrant,[9] who showed that dialkyl amines react with chlorotrifluoroethylene to produce only the α,α-difluoro isomers, and that hydrolysis of these amines produces only chlorofluoracetamides.

N-(2-Chloro-1,1,2-trifluoroethyl)-piperidine.—Piperidine reacted with chlorotrifluoroethylene in a manner analogous to the reaction of diethylamine. The reaction was carried out in the absorption tube previously described, taking care to exclude moisture. An effort was made to hold the temperature at 0–10°, but the evolution of heat was so great that the temperature in narrow zones occasionally rose to 40–50° for short periods of time. When completion of the reaction was indicated by the fact that chlorotrifluoroethylene ceased to be absorbed, the product was distilled under anhydrous conditions through a 50-cm. Vigreux column. Eighty-seven per cent. of the material distilled as a single compound, leaving a small amount of tarry black residue in the still-pot. This distilled amine also reacted very rapidly with water, fuming upon exposure to air.

Tetrakis-(dimethylamino)-ethylene.—The reaction of dimethylamine with chlorotrifluoroethylene was carried out in the pressure vessel using a large excess of the amine to ensure that the reaction would proceed as far as possible rather than stop at some intermediate stage. After the reactor was loaded with the amine and evacuated at −78°, it was placed on a mechanical shaker and the whole system was sprayed with water. Chlorotrifluoroethylene gas was introduced in small portions under pressure, keeping the temperature below 32°. After the desired amount of the olefin had been added and no further heat of reaction was evolved, cooling was discontinued and the vessel was heated until no further pressure decrease was noted. The product consisted of a brown water-soluble solid and a black liquid. The distillation of this liquid through a 50-cm. Vigreux column produced a single product, tetrakis-(dimethylamino)-ethylene. This was a clear, slightly yellow, mobile liquid which was strongly luminescent in contact with air. It reacted with oxygen to form a white solid, and reacted vigorously with water, alcohols and solutions of bromine and iodine.

1,2-Dibromo-tetrakis-(dimethylamino)-ethane.—About three grams of the luminescent liquid was dissolved in ether. A solution of bromine in ether was added slowly until a slight coloration persisted, during which time a heavy precipitate of slightly yellow solid formed. This solid was filtered, washed with more ether and purified by recrystallization from acetone at −78°. The final product was slightly yellow and melted at 252–254° (dec.). When dissolved in water, the compound precipitated silver bromide from a solution of silver nitrate. *Anal.* Calcd. for $C_{10}H_{24}N_4Br_2$: C, 33.35; H, 6.72. Found: C, 33.37; H, 6.97.

Attempted Reaction of Diphenylamine with Chlorotrifluoroethylene.—Diphenylamine failed to react with chlorotrifluoroethylene. An ethereal solution of the amine was charged into the reactor and the olefin was introduced under pressure. Upon opening the vessel sixteen hours later and removing the ether by evaporation, 91% of the diphenylamine was recovered.

N,N′-Di-*n*-butyl- and N,N′-Di-*n*-propyl-3,3,4-trifluoro-1,2-cyclobutanediimine.—*n*-Butylamine and *n*-propylamine were treated with hexafluorocyclobutene under identical conditions. The amine was dissolved in two volumes of dry diethyl ether and the reaction conducted in a three-neck flask. The reaction product was filtered to remove the bulk of the amine hydrofluoride and then washed with water. The solution was distilled at room temperature under reduced pressure until all the ether and most of the excess amine were removed. The residue was then mixed with water and the mixture was allowed to separate into two layers. The lower layer was drawn off, mixed with more water and stirred well. After a few minutes the whole mass solidified to form a slightly yellow solid, which was purified by recrystallization from acetone at −78°.

N,N′-Di-*n*-butyl-3,3,4-trifluoro-1,2-cyclobutanediimine Monohydrochloride.—A portion of the above butylimine was dissolved in dry diethyl ether and dry hydrogen chloride gas was passed through the solution. The heavy oily layer which separated solidified when the mixture was thoroughly cooled. Filtering and washing with more ether produced a white water-soluble solid, m. p. 85–87°, which was more stable than the original imine. *Anal.* Calcd. for $C_{12}H_{20}N_2F_3Cl$: Cl, 12.45. Found: Cl, 12.25.

2-Naphthylamine Dihydrofluoride.—An ethereal solution of 2-naphthylamine reacted with hexafluorocyclobutene in a pressure vessel. The product was obtained from

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[8] In one case where no water-bath was used an explosion occurred, probably due to the high pressure caused by the heat of reaction.

[9] Huskins and Tarrant, "Preparations and Reactions of Certain Fluorochloroethylenes," Report to Office of Naval Research under Contract N8onr503, June 15, 1949.

the reactor as a solid–liquid mixture. Evaporation of the ether produced more solid. The combined solid portions were macerated with dilute hydrochloric acid and filtered. The solid obtained by this operation was divided into two fractions by treatment with acetone. The acetone-soluble part was recovered by dilution with excess water and, after purification, was found to be identical in melting point and mixed melting point with 2-naphthylamine. The insoluble portion was concluded to be 2-naphthylamine dihydrofluoride. This substance was insoluble in all common organic solvents and in cold water. It dissolved in boiling water, but cooling the solution produced fluffy crystals of 2-naphthylamine. It dissolved in diethylamine to produce 2-naphthylamine and white water-soluble crystals.

N,N-Diethyl- and N,N-Di-*n*-propylpentafluoro-1-cyclobutenylamine.—Both compounds were prepared in the three-neck flask. The ethyl- or *n*-propylamine was dissolved in ether and the hexafluorocyclobutene was bubbled through the solution. After the desired amount of the butene had been introduced, the ethereal solution was washed with a 20% solution of sodium hydroxide. The solution was then concentrated on a hot water-bath, after which it was treated with dilute hydrochloric acid. A lower layer formed, which was separated, washed with water, dried and distilled through a short Vigreux column.

Attempted Reaction of Diphenylamine with Hexafluorocyclobutene.—As was the case with chlorotrifluoroethylene, no reaction occurred between diphenylamine and hexafluorocyclobutene. The reactants were dissolved in ethereal solution and heated together in a pressure vessel. Upon opening the vessel and evaporating the ether, the starting material was recovered unchanged.

Analyses.—Various methods were used for analyzing the samples.[10] The carbon and hydrogen were determined by combustion. In general, chlorine was determined by Carius tube and nitrogen by combustion train method. In some cases chlorine was determined by peroxide fusion and nitrogen by the Kjeldahl procedure. The analyses listed as ionizable fluorine were done by a special method. A small weighed sample was mixed with a measured excess of 0.005 *N* NaOH for five minutes and the amount of acid liberated determined by back-titration with standard acid.

Conclusions

Tertiary amines containing a chlorotrifluoroethyl or a pentafluoro-1-cyclobutenyl group can be prepared easily and in excellent yields by the reaction of secondary amines with chlorotrifluoroethylene or with hexafluorocyclobutene. Further reaction with excess amine results in complete dehalogenation of the polyfluoroethylene. With primary amines, the products obtained are imino- or imido-type compounds.

The reaction of chlorotrifluoroethylene with secondary amines is one of addition. By analogy, the mechanism of the primary amine reaction appears to be an addition followed by loss of hydrogen fluoride to form a carbon–nitrogen double bond. The hypothesis is proposed that amines and hexafluorocyclobutene also react by addition, with subsequent loss of hydrogen fluoride to give unsaturated amines and imino compounds.

In view of experimental observations, the following generalizations would seem valid: Primary amines react more readily than secondary amines with polyfluoro olefins. Hexafluorocyclobutene reacts more readily with amines than does chlorotrifluoroethylene. The addition products of secondary amines with hexafluorocyclobutene have a greater tendency for spontaneous loss of hydrogen fluoride than do those with chlorotrifluoroethylene. Aliphatic amines react more readily with polyfluoro olefins than do aromatic amines. Amines containing fluorine attached to a carbon adjacent to the nitrogen are extremely susceptible to reactions involving the fluorine. The basicity of tertiary amines and amidines is greatly reduced by the presence of a polyfluoro group close to the nitrogen atom.

Summary

The reactions of chlorotrifluoroethylene and hexafluorocyclobutene with primary and secondary amines have been investigated. With aliphatic amines these reactions occurred readily and gave a variety of products. In the case of primary aliphatic amines, the products were imino- or imido-type compounds, while secondary amines gave substituted tertiary amines. Primary aromatic amines reacted slowly to yield products of the imino-type structure, but diphenylamine was inert toward both polyfluoro olefins.

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[10] Analyses were performed by Clark Microanalytical Laboratories, Urbana, Illinois, Miss Frances Ball and Mr. R. R. Rickard of the Microchemical Group of the Analytical Research Section and Mr. R. E. Millspaugh of the Special Analyses Group of the Works Laboratory.