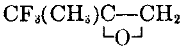
TABLE I

New Compounds

Compound	M.P., °C.[a]	% C[b]		% H[b]		% N[b]		% F[c]	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
 $CF_3(CH_3)\underbrace{C—CH_2}_{O}$	[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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Columbus, Ohio

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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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(1) J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

involving both ionic addition and formation of a polarized complex in the transition state have been proposed.[1,2] Although salts containing the mercury-oxygen bond react with olefins, no similar addition of a salt containing the more stable, covalent mercury-chlorine bond has been found.[3] Fluorine, however, is more electronegative than oxygen and forms reactive ionic compounds with mercury. Thus such a substance as mercuric fluoride might add to fluoroethylenes to form fluoroethyl derivatives of mercury.

Such has now been found to be the case. Reactions of mercuric fluoride with three fluoroethylenes proceeded readily at 50–100° under autogenous pressures to give the corresponding bis(fluoroethyl)mercury compounds in conversions of 56–66%. Tetrafluoroethylene, trifluoroethylene, and 1,1-difluoroethylene formed bis(pentafluoroethyl)-mercury (I), bis(1,2,2,2-tetrafluoroethyl)mercury (II), and bis (2,2,2-trifluoroethyl)mercury (III), respectively, under these conditions.

$$\mathrm{HgF_2 + CF_2 = CF_2 \longrightarrow \underset{I}{Hg(CF_2CF_3)_2}}$$

$$\mathrm{HgF_2 + CHF = CF_2 \longrightarrow \underset{II}{Hg(CHFCF_3)_2}}$$

$$\mathrm{HgF_2 + CH_2 = CF_2 \longrightarrow \underset{III}{Hg(CH_2CF_3)_2}}$$

Compounds II and III, prepared for the first time, correspond to the products expected from an ionic addition of mercuric fluoride to double bonds polarized so as to make the difluoromethylene group the more positive end. This result agrees with earlier work on the addition of ionic reagents to fluoroolefins.[4] Bis(1-chloro-1,2,2,2-tetrafluoroethyl)-mercury was prepared by a similar addition of mercuric fluoride to chlorotrifluoroethylene, but sublimation techniques did not effect removal of all the impurities.

Compound I has been prepared previously by reaction of pentafluoroiodoethane with cadmium amalgam.[5] Reduction of I with aqueous sodium stannite to give two equivalents of pentafluoroethane shows that two pentafluoroethyl groups are attached to each mercury atom. The structures of II and III were determined by examination of the nuclear magnetic resonance spectra for H^1 and F^{19}.

The nuclear magnetic resonance spectra of I, II and III exhibit the splittings of F^{19} and H^1 resonances expected for these structures. Fig. 1 summarizes the centers of group resonances and the coupling constants involved in splitting these resonances. The observation of satellites due to coupling with Hg^{199}, an isotope present in naturally occurring mercury in 17% abundance, is direct evidence for the bonding of the fluoroethyl groups to mercury. To illustrate this coupling with mercury, the spectra for III are presented graphically in Fig. 2.

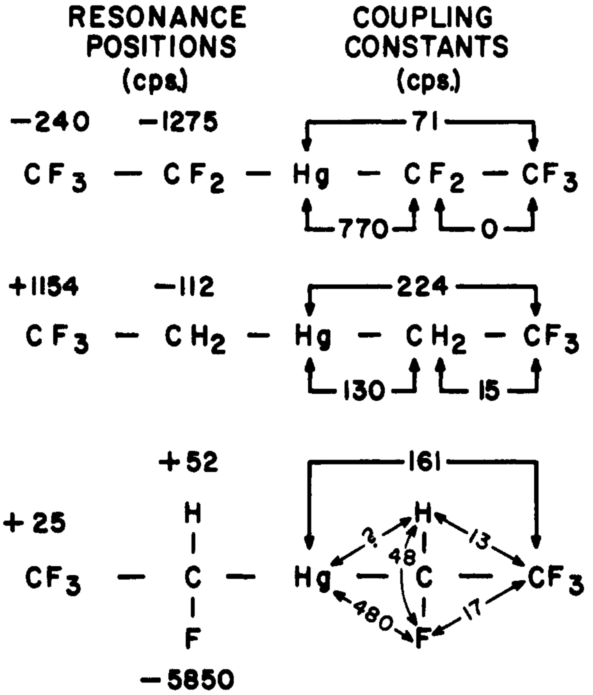

Fig. 1. Summary of coupling constants and centers of group resonances in a 40-megacycle field

Spectra were obtained from a varian high resolution nuclear magnetic resonance spectrometer. Fluorine resonances are relative to trifluoroacetic acid at 0, and proton resonances are relative to water at 0. Resonances at lower magnetic field than the zero points are considered positive

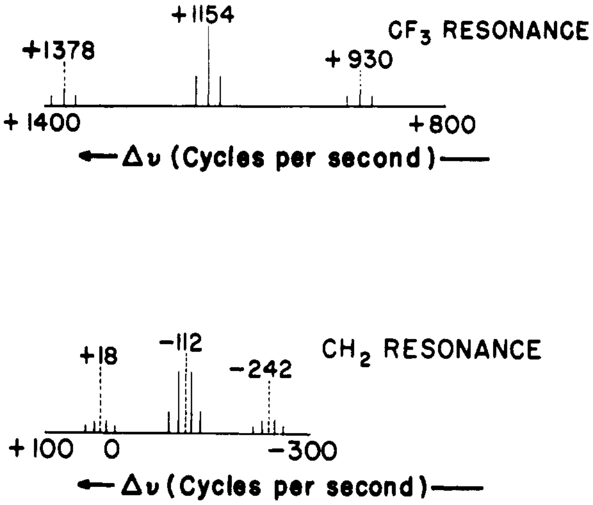

Fig. 2. Graphic representation of F^{19} and H^1 spectra of $Hg(CH_2CF_3)_2$ in carbon tetrachloride at 40 megacycles

Resonances at lower magnetic field than the zero points (CF_3CO_2H for F^{19}, H_2O for H^1) are considered positive

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(2) A. G. Brook and G. F. Wright, *Can. J. Research*, **28B**, 623 (1950).

(3) Mercuric chloride does add readily to acetylenic linkages. Such reactions are described by A. N. Nesmeyanov, N. K. Kochetkov, and V. M. Dashunin, *Isvest. Akad. Nauk. S. S. S. R., Otdel Khim. Nauk*, **77** (1950); *Chem. Abstr.*, **44**, 7225 (1950).

(4) R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 61 (1956).

(5) J. Banus, H. J. Emeleus, and R. N. Haszeldine, *J. Chem. Soc.*, 3041 (1950).

Dry mercuric fluoride forms little organomercurial when heated with trifluoroethylene, and can react explosively with tetrafluoroethylene. However, controllable reactions of fluorinated ethylenes occur readily at 100° or lower when an appropriate solvent for the mercuric fluoride is employed. Arsenic trifluoride is a useful reaction medium,[6] and one experiment suggests that in some cases hydrogen fluoride may be satisfactory with either mercuric fluoride or mercuric oxide.

EXPERIMENTAL

Bis(pentafluoroethyl)mercury. A mixture of 95.6 g. (0.40 mol.) of mercuric fluoride and 60 ml. of arsenic trifluoride was heated at 100° for 1 hr. in a 400-ml. shaker tube lined with stainless steel. Ninety grams (0.90 mol.) of tetrafluoroethylene was then injected at 100° in portions over a period of 2 hr., and the reaction mixture was heated at 100° for an additional 12 hr. under autogenous pressure. Evaporation of arsenic trifluoride at 25° (50 mm.) gave a solid residue from which bis(pentafluoroethyl)mercury was sublimed at 90° (1 mm.). Resublimation at 85° (1 atm.) gave 98 g. (56% yield based on mercuric fluoride) of the white crystalline mercurial, m.p. (sealed tube) 105–106° (Ref. 1 reports m.p. 106–107°). The structure of the product was confirmed by determination of the nuclear magnetic resonance spectrum for F^{19} in acetone (Figure 1). A solution of 4.7 g. of sodium hydroxide and 3.8 g. of stannous chloride dihydrate in 20 ml. of water was stirred with 1.0 g. (0.0023 mol.) of bis(pentafluoroethyl)mercury until no more gas evolved.[7] The gas was collected over water and identified by its infrared spectrum as pure pentafluoroethane, obtained in 100% of theory.

An addition to a fluoroethylene of Hg-F in preference to Hg-O is shown by the following reaction in aqueous hydrofluoric acid. Hydrated mercuric fluoride, prepared from 21.7 g. (0.10 mol.) of mercuric oxide and 15 ml. (0.43 mol.) of 50% aqueous hydrofluoric acid, was reacted with 30 g. (0.30 mol.) of tetrafluoroethylene in an 80-ml. shaker tube lined with stainless steel at 100° for 5 hr. The product was heated at 80° (1 mm.), and the volatile material was condensed in a trap at −78°. The contents of the trap were warmed and filtered, and the solid material was pressed dry on filter paper and sublimed at 85° at atmospheric pressure. The sublimate was 2.4 g. (5% yield based on mercuric oxide) of bis(pentafluoroethyl)mercury, identified by comparison of its nuclear magnetic resonance spectrum with that of an authentic sample. The nonvolatile product was extracted with water and then with concentrated nitric acid to remove free mercury and mercury salts. The insoluble residue was 29 g. of polymer.

Bis(1,2,2,2-tetrafluoroethyl)mercury. Except for tetrafluoroethylene, which polymerizes readily under the reaction conditions, good results were obtained by heating the fluoroethylene and mercuric fluoride up to reaction temperature in the presence of the solvent.[8] Thus an 80-ml. shaker tube charged with 23.9 g. (0.10 mol.) of mercuric fluoride, 25 g. (0.30 mol.) of trifluoroethylene, and 15 ml. of arsenic trifluoride was heated at 50° for 4 hr. under the autogenous pressure of the reactants. Arsenic trifluoride was removed from the product by evaporation under reduced pressure, and the residual crystalline solid was heated at 80–90° under atmospheric pressure. The volatile white mercurial, collected on a cold finger, weighed 26.6 g. (66% yield based on mercuric fluoride) and melted at 78–79°.

Anal. Calcd. for $C_4H_2F_8Hg$: C, 11.93; F, 37.75; Hg, 49.82. Found: C, 12.14; F, 36.91; Hg, 49.20.

The structure of the product was established by its nuclear magnetic resonance spectrum in acetone (Figure 1).

Bis(2,2,2-trifluoroethyl)mercury. A mixture of 23.9 g. (0.10 mol.) of mercuric fluoride, 19 g. (0.30 mol.) of vinylidene fluoride, and 15 ml. of arsenic trifluoride was heated at 100° for 7 hr. under autogenous pressure. The product, after removal of arsenic trifluoride under reduced pressure, was heated at 85° at atmospheric pressure to drive the volatile mercurial up to a cold finger. The solidified condensate was 24.2 g. (66% yield based on mercuric fluoride) of bis(2,2,2-trifluoroethyl)mercury, m.p. 40°.

Anal. Calcd. for $C_4H_4F_6Hg$: C, 13.10; F, 31.09; Hg, 54.71. Found: C, 13.04; F, 29.81; Hg, 54.27.

The structure of this product was established by its nuclear magnetic resonance spectra for H^1 and F^{19} in carbon tetrachloride (Fig. 2).

Bis(1-chloro-1,2,2,2-tetrafluoroethyl)mercury. A mixture of 23.9 g. (0.10 mol.) of mercuric fluoride, 35 g. (0.30 mol.) of chlorotrifluoroethylene, and 15 ml. of arsenic trifluoride was heated with agitation at 100° for 7 hr. under autogenous pressure. Arsenic trifluoride was removed from the product by evaporation under reduced pressure, and the solid residue was heated in a sublimation apparatus at 85° under atmospheric pressure. There was obtained in this way 14.6 g. (31% yield based on mercuric fluoride) of crude mercurial, m.p. 93–95°.

Anal. Calcd. for $C_4Cl_2F_8Hg$: C, 10.2; Cl, 15.0; F, 32.2; Hg, 42.6. Found: C, 9.6; Cl, 13.7; F, 33.3; Hg, 41.3.

Although the major component was established as bis(1-chloro-1,2,2,2-tetrafluoroethyl)mercury by the nuclear magnetic resonance spectrum, fluorinated impurities are evidently present.

Acknowledgment. The author is indebted to Dr. H. Foster for the interpretation and calibration of the nuclear magnetic resonance spectra.

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[6] Dr. E. L. Muetterties of these laboratories has shown that a considerable amount of mercuric fluoride can be dissolved in warm arsenic trifluoride.

[7] Method described by H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2956 (1949).

[8] C. G. Krespan, U. S. Patent 2,844,614, July 22, 1958.