zation from chloroform, 4.2 g. of crude triphenylsilanol which melted at 128–150° (cor.) after recrystallization from ligroin (b.p. 60–90°), and 5.9 g. of crude triphenylsiloxytriphenyltin which melted at 138–142° (cor.) after recrystallization from ligroin (b.p. 60–90°).

Attempted Preparation of Trimethylsilyltriphenyltin.—To a stirred solution of triphenyltinlithium, prepared as described above from 19.2 g (0.05 mole) of triphenyltin chloride, was added a solution of 8.2 g. (0.075 mole) of chlorotrimethylsilane in 50 ml. of tetrahydrofuran over a period of 4 min. The resulting black suspension gave a negative Color Test I and was stirred at room temperature for an additional 2 hr. After hydrolysis with 2 *M* hydrochloric acid and addition of ether the precipitate which formed was filtered. The ether layer was separated and dried over sodium sulfate. The precipitate which had formed at the interface was identified by infrared analysis and mixture melting point as hexaphenylditin. An additional small amount of hexaphenylditin was obtained from the ether layer. The total amount of hexaphenylditin obtained was 12.0 g. (68.7%), m.p. 233–236° (cor.). No attempt was made to isolate any other products resulting from the metal-halogen interchange.

Attempted Preparation of Triphenyltin Carboxylic Acid.—A solution of triphenyltinlithium prepared as described above from 0.05 mole of triphenyltin chloride was poured into a flask containing Dry Ice, forming a black mixture with a negative Color Test I. After the Dry Ice had disappeared, dry carbon dioxide was bubbled into the mixture intermittently for 20 hr. The mixture was hydrolyzed with cold 1 *M* hydrochloric acid and filtered to give 14.8 g. (85%) of hexaphenylditin, identified by a comparison of the infrared spectra and a mixture melting point with an authentic sample of hexaphenylditin. Work-up of the filtrate gave only a small amount of material which did not melt below 300°.

Secondary and Tertiary Perfluoroörganomercury Compounds

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Addition of mercuric fluoride to terminal fluoroölefins has been found to be a general method for the preparation of secondary and tertiary alkyl mercurials. Compounds we have prepared in this manner are bis(perfluoroisopropyl)mercury, bis(3H-1-trifluoromethylpentafluoropropyl)mercury, bis(3-chloro-1-trifluoromethylpentafluoropropyl)mercury, and bis(perfluoro-*t*-butyl)mercury. These organomercury compounds are unaffected by strong acids and bases at moderate temperatures. They are cleaved by halogens to secondary and tertiary perfluoroalkyl halides, which are useful for synthesis of other branched-chain fluorocarbon derivatives.

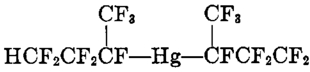
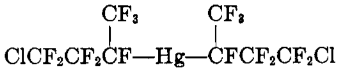
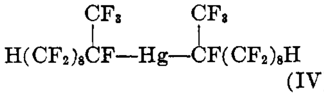
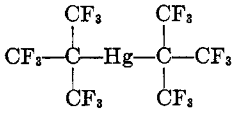
Several methods for preparing primary perfluoroalkyl mercurials have appeared in the literature. In one, fluoroalkyl iodides are heated with silver, copper, cadmium, zinc, or magnesium amalgam,[1] and in another mercuric fluoride is added to fluoroethylenes in arsenic trifluoride solution.[2] Branched fluoroalkyl mercurials are another matter, and until very recently no routes to such compounds were known. Because such branched mercurials should be starting materials for a great many secondary and tertiary fluoroalkyl derivatives, a largely unexplored area of chemistry, we have examined the addition of mercuric fluoride to terminally unsaturated fluoroölefins. This method has already been reported as a route to bis(perfluoroisopropyl)mercury,[3] a precursor of hexafluorothioacetone.

Preparation.—The synthesis described by Krespan, which utilizes arsenic trifluoride as a solvent, is not well suited for addition of mercuric fluoride to fluoroölefins containing more than two carbon atoms. However, the reaction proceeds readily with a large number of fluoroölefins when anhydrous hydrogen fluoride[4] is used as a solvent. Mercuric fluoride is soluble in hydrogen fluoride at 100° and autogenous pressure in an autoclave. Branched-chain mercurials synthesized by this method are given in Table I. The low yields for III and IV undoubtedly can be improved by more detailed examination of reaction conditions. The method can also be used to obtain the fluoroethyl mercurials, bis(pentafluoroethyl)mercury and bis(1-chloro-1,2,2,2-tetrafluoroethyl)mercury, described by Krespan.[2] In addition, we have made a new fluoroethyl derivative, bis(1,1-dichloro-2,2,2-trifluoroethyl)mercury, which was prepared in 69% yield from 1,1-dichloro-2,2-difluoroethylene.

TABLE I

FLUOROMERCURIALS FROM FLUOROÖLEFINS AND MERCURIC FLUORIDE

$$2R_1R_2C{=}CF_2 + HgF_2 \xrightarrow{HF} [R_1R_2CCF_3]_2Hg$$

Olefin	Product	Yield, %
$CF_3CF{=}CF_2$	$(CF_3)_2CF{-}Hg{-}CF(CF_3)_2$ (I)	60
$HCF_2CF_2CF{=}CF_2$	 $HCF_2CF_2\overset{CF_3}{\overset{\vert}{C}}F{-}Hg{-}\overset{CF_3}{\overset{\vert}{C}}FCF_2CF_2H$ (II)	73
$ClCF_2CF_2CF{=}CF_2$	 $ClCF_2CF_2\overset{CF_3}{\overset{\vert}{C}}F{-}Hg{-}\overset{CF_3}{\overset{\vert}{C}}FCF_2CF_2Cl$ (III)	*ca.* 5
$H(CF_2)_3CF{=}CF_2$	 $H(CF_2)_3\overset{CF_3}{\overset{\vert}{C}}F{-}Hg{-}\overset{CF_3}{\overset{\vert}{C}}F(CF_2)_3H$ (IV)	Low
$(CF_3)_2CF{=}CF_2$	 $CF_3{-}\underset{CF_3}{\overset{CF_3}{C}}{-}Hg{-}\underset{CF_3}{\overset{CF_3}{C}}{-}CF_3$ (V)	33

Usual conditions for these preparations are 100–150° and autogenous pressure. For bis(nonafluoro-*t*-butyl)mercury (V), temperatures of 180–200° were necessary. Addition of mercuric fluoride to the internal double bonds in such compounds as octafluoro-2-butene and

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[1] (a) A. A. Banks, H. J. Emeleus, R. N. Haszeldine, and V. Kerrigan, *J. Chem. Soc.*, 2188 (1948); (b) H. J. Emeleus and R. N. Haszeldine, *ibid.*, 2948, 2953 (1949); (c) J. Banus, H. J. Emeleus, and R. N. Haszeldine, *ibid.*, 3041 (1950).

[2] C. G. Krespan, U. S. Patent 2,844,614 (July 29, 1958); *J. Org. Chem.*, **25**, 105 (1960).

[3] (a) E. G. Howard and W. J. Middleton, U. S. Patent 2,970,173 (January 31, 1961); (b) W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 2589 (1961); (c) W. T. Miller, Jr., M. B. Freedman, J. H. Fried, and H. F. Koch, *ibid.*, **83**, 4105 (1961).

[4] Use of hydrogen fluoride as a solvent was first suggested to us by Professor W. T. Miller, Jr.

hexafluorocyclobutene was not successful even at high temperatures. Efforts to prepare R_fHgF led only to bismercurials.

Structure.—The structures of the organomercury compounds were established by nuclear magnetic resonance studies. The α and β fluorine peaks of bis(perfluoroisopropyl)mercury (I) are widely separated, and the ratio of their areas is 1:6 (Fig. 1a). This is unlike the spectrum of diisopropylmercury,[5] in which the protons of the isopropyl group were not resolved because of overlapping of the peaks associated with the α and β protons. The α fluorine appears as a septet with relative intensities of 1:6:15:20:15:6:1 centered at 5109 c.p.s.[6] and a spin–spin coupling constant J of 12 c.p.s. (Fig. 1d). In addition, there are two, weak, symmetrical satellite bands at 4848 and 5370 c.p.s. due to the Hg^{199} isotope[5] (Fig. 1c). The six β fluorines appear as a doublet centered at 124 c.p.s. with a coupling constant of 12 c.p.s. in agreement with that found for the α fluorines (Fig. 1b). The doublet is also flanked symmetrically by two small satellite doublets at 60 and 72 and at 176 and 188 c.p.s. These results are in agreement with those expected for the iso rather than the normal perfluoropropyl group.

Bis(perfluoro-*t*-butyl)mercury (V) in confirmation of its structure shows a single fluorine n.m.r. peak at -447 c.p.s.[6] flanked by a pair of satellites at -372 and -522 c.p.s. The fluorine n.m.r. spectra of both bis(3H-1-trifluoromethylpentafluoropropyl)mercury (II) and bis(3-chloro-1-trifluoromethylpentafluoropropyl)mercury (III) have four resonance peaks with areas in the ratio of 2:2:1:3, which is in accord with a secondary alkyl structure rather than a primary one.

Reaction Mechanism.—Miller[3] has postulated an electrophilic mechanism for the addition of mercuric fluoride to fluoroölefins. The attack of mercuric ion upon terminal fluoroölefins and not upon internal fluoroölefins suggests that the difluorocarbonium ion $-\overset{\oplus}{\mathrm{C}}\mathrm{F}_2$ is more stable than the monofluorocarbonium ion $-\overset{\oplus}{\mathrm{C}}\mathrm{F}-$. The ability of halogens and especially fluorine to increase their covalency is well known.[7]

Properties.—The secondary perfluoroalkylmercury compounds are dense, colorless, distillable liquids. Bis(perfluoroisopropyl)mercury, which boils at 116–117° and melts at 20–21°, has a liquid range close to that of water. Its density is 2.53. Less symmetrical mercurials are slightly lower in density, although none in the series I through IV is below 2.4. The highly symmetrical tertiary alkyl mercurial V is a crystalline solid that sublimes so easily it has no appreciable liquid range at atmospheric pressure.

Secondary and tertiary perfluoroalkyl mercurials are more stable to heat and chemicals than corresponding primary compounds. They differ in this respect from nonfluorinated organomercurials in which case secondary and tertiary alkyl mercurials are less stable than primary ones.[8] Anhydrous bis(perfluoroisopropyl)mercury does not change when heated several hours at 250°. At 350° or upon irradiation with strong ultraviolet light, it is decomposed to mercury and perfluoro-2,3-dimethylbutane.[9] Secondary and tertiary perfluoroalkyl mercurials are unaffected by aqueous alkali or boiling concentrated nitric acid and, when anhydrous, are stable to such metals as copper, iron, and aluminum at temperatures as high as 250°. However, in the presence of a trace of water they react vigorously with aluminum, even at room temperature.

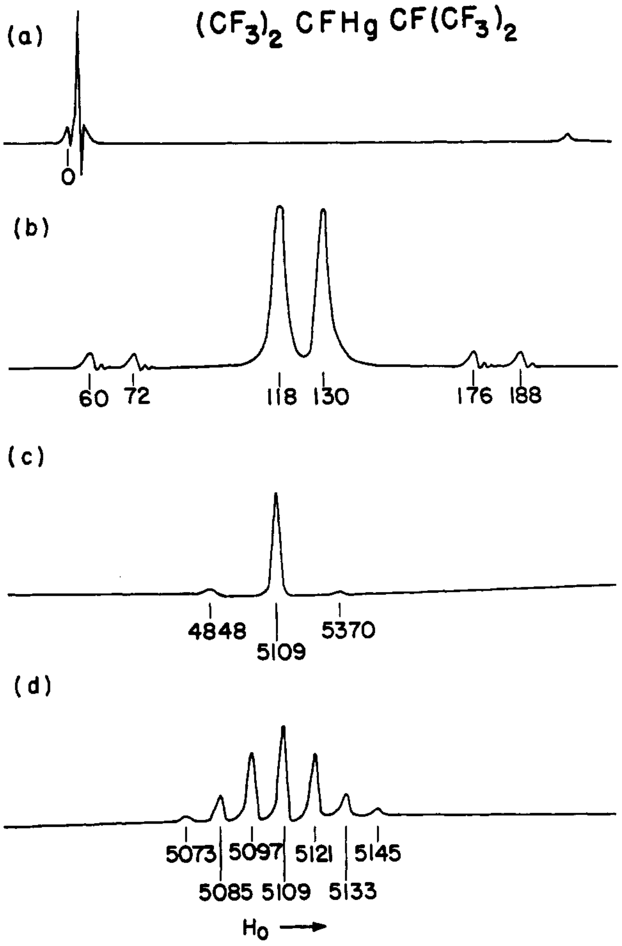

Fig. 1.—Fluorine magnetic resonance spectrum of bis(perfluoromethylethyl)mercury at (a) low resolution and (b), (c), and (d) high resolution (see ref. 6).

Although bis(perfluoroisopropyl)mercury is not hydrolyzed by boiling water, it reacts with water at 200° in a sealed vessel to give 2H-heptafluoropropane and bis(perfluoroisopropylmercury)oxide. As shown in the following chart, the mercurial is also reduced by aqueous sodium sulfide, aqueous sodium stannite, and potassium iodide in boiling water. These reactions take a somewhat different course with certain fluoromercurials. For example, 1H-heptafluoro-2-butene and 1H-heptafluoro-3-butene are obtained by reactions of bis(1H - 1 - trifluoromethylpentafluoropropyl)mercury with aqueous sodium sulfide (see p. 186, col. 1).

Derivatives.—Secondary perfluoroalkyl mercurials react with halogens typically[1c] to form perfluoro-*sec*-alkyl iodides and bromides, the other product being a

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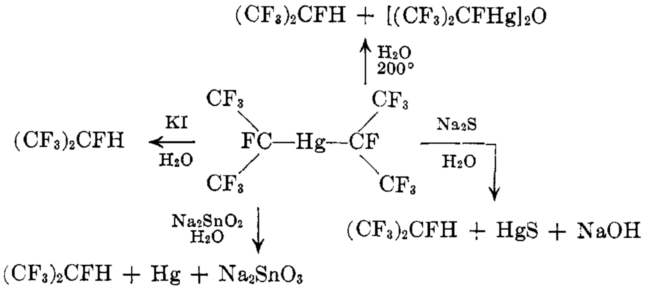
[5] R. E. Dessey, T. J. Flautt, H. H. Jaffe, and G. F. Reynolds, *J. Chem. Phys.*, **30**, 1422 (1959).

[6] 1,2-Difluorotetrachloroethane was used as a reference compound. The spectra were measured as a 40% solution in acetonitrile on a 40-Mc. Varian high resolution nuclear magnetic resonance spectrometer at 10,000 gauss.

[7] E. S. Gould, "Mechanism and Structure in Organic Chemistry, Henry Holt and Co., New York, N. Y., 1959, pp. 217–218; C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 70–90.

[8] C. S. Marvel and H. O. Calvery, *J. Am. Chem. Soc.*, **45**, 820 (1923).

[9] R. D. Chambers, W. K. R. Musgrave, and J. Savory, *J. Chem. Soc.* 3779 (1961); *ibid.*, 1993 (1962).



mercuric halide. Bis(perfluoro-*t*-butyl)mercury reacts with bromine to give perfluoro-*t*-butyl bromide, but its reaction with iodine is capricious. On one occasion, a product was obtained that almost certainly was perfluoro-*t*-butyl iodide. However, numerous attempts to repeat iodine cleavage of the tertiary mercurial failed.

The development of an easy method for obtaining secondary and tertiary perfluoroalkyl halides opens new possibilities for synthesis of many branched-chain derivatives. We have used the halides to prepare nitroso compounds. Ultraviolet irradiation of heptafluoro-2-iodopropane and nitric oxide[10] gave heptafluoro-2-nitrosopropane,[11] a blue gas boiling at −8 to −6°, in 53% yields. A tertiary nitroso compound, tris(trifluoromethyl)nitrosomethane,[11] has also been synthesized. This compound was obtained by irradiating perfluorobutyl bromide in the presence of nitric oxide. It is a blue liquid boiling at 23–24° and freezing at 0°.

Experimental

Bis(perfluoroisopropyl)mercury (I).[12]—Mercuric fluoride[13] (240 g., 1.01 moles), 70 g. of anhydrous hydrogen fluoride, and 300 g. (2 moles) of hexafluoropropylene were heated in a bomb[14] at 110° for 12 hr. The bomb was cooled and vented. The product was poured into a polyethylene bottle, which was loosely capped and set aside in a hood to allow excess hydrogen fluoride to evaporate. Traces of hydrogen fluoride were removed by stirring the product with sodium fluoride powder; alternatively the hydrogen fluoride was extracted with water and the product then dried with phosphorus pentoxide. Distillation of the product gave 323 g. (60%) of bis(perfluoroisopropyl)mercury, b.p. 115–116°, m.p. 20–21°, n^{25}_D 1.3244, d^{25}_4 2.5301. The mercury compound must be dry before distillation; otherwise an azeotrope, b.p. 90°, containing approximately 4.3% water results.

Anal. Calcd. for $C_6F_{14}Hg$: F, 49.38; Hg, 37.24. Found: F, 48.77; Hg, 37.13.

Perfluoroisopropylmercury Chloride.[12]—Bis(perfluoroisopropyl)mercury (135 g., 0.25 mole) and 29 g. (0.25 mole) of thiophosgene were heated in a bomb at 200° for 5 hr. The bomb was cooled and vented, and the black, fuming liquid was distilled. In addition to recovered starting materials, there was obtained 32.9 g. (32%) of perfluoroisopropylmercury chloride, b.p. 173–178°. The mercury compound crystallized from cyclohexane as colorless needles, m.p. 77.0–78.3°.

This compound was also obtained as a by-product in the preparation of bis(perfluoroisopropyl)mercury. (The mercuric fluoride[13] used in this work contained chloride as an impurity.)

Anal. Calcd. for C_3ClF_7Hg: Cl, 8.75; F, 32.83; Hg, 49.52. Found: Cl, 9.09; F, 32.01; Hg, 48.96.

4H-Heptafluoro-1-butene.—Into a solution of 163 g. (4.06 moles) of sodium hydroxide (98%) in 800 ml. of methanol was dropped with stirring 1 kg. (4.06 moles) of 5H-octafluorovaleric acid. The solution was evaporated to dryness in evaporating dishes on a steam bath to give 1068 g. of salt. The salt was pyrolyzed in a flask in a Wood's metal bath at 250–280°; vapors were led into a solid carbon dioxide–acetone-cooled trap. Distillation gave 543 g. (73%) of 4H-heptafluoro-1-butene, b.p. 21°.

The assignment of the double bond to the 1-position was based on the infrared spectrum of the compound, which showed absorption at 5.58 μ, indicative of an olefinic bond substituted with three fluorine atoms.[15]

Bis(3H-1-trifluoromethylpentafluoropropyl)mercury (II).[12]—A mixture of 72 g. (0.3 mole) of mercuric fluoride,[13] 100 g. (0.55 mole) of 4H-heptafluoro-1-butene, and 100 g. of anhydrous hydrogen fluoride was placed in a bomb[14] and heated at 120° for 12 hr. After the hydrogen fluoride evaporated, the clear remaining liquid was washed with dilute aqueous sodium bicarbonate, dried under anhydrous calcium chloride, and distilled, b.p. 172.5–173°, weight 120 g. (73%). This material solidified at 0° and had a density of 2.44 g./ml.

Anal. Calcd. for $C_8H_2F_{16}Hg$: F, 50.3; Hg, 33.3. Found: F, 49.4; Hg, 32.5.

5-Chloroheptafluoro-1-butene.—The sodium salt of 5-chloroperfluorovaleric acid was pyrolyzed at 340°. 5-Chloroheptafluoro-1-butene, b.p. 34°, was obtained in 76% yield.

Anal. Calcd. for C_4ClF_7: Cl, 16.38; F, 61.4. Found: Cl, 16.77; F, 61.3.

Bis(3-chloro - 1 - trifluoromethylpentafluoropropyl)mercury (III.)[12]—A mixture of 36 g. (0.15 mole) of mercuric fluoride,[13] 56 g. (0.26 mole) of 4-chloroöctafluorobutene, and 100 g. of hydrogen fluoride was heated in a bomb[14] at 120° for 13 hr. The product was worked up as described for bis(3H-trifluoromethylpentafluoropropyl)mercury (II). In addition to 20 g. of mercury, there was obtained 8.6 g. (5%) of a liquid, b.p. 85–97° (20 mm.), m.p. −10°, density 2.42 g./ml.

Anal. Calcd. for $C_8F_{16}Cl_2Hg$: Cl, 10.5; Hg, 30.1. Found: Cl, 10.5; Hg, 30.4.

Bis(9H-1-trifluoromethylheptadecafluorononyl)mercury (IV).[16]—1H-Nonadecafluoro-9-decene, b.p. 73–74° (32 mm.), n^{26}_D 1.300, was prepared by pyrolysis of sodium 10H-perfluorodecanoate. Bis(9H - 1 -trifluoromethylheptadecafluorononyl)mercury, m.p. 100–101°, was prepared from the fluoroölefin as described in the previous examples.

Anal. Calcd. for $C_{20}H_2F_{40}Hg$: F, 63.2. Found: F, 62.9.

Bis(perfluoro-*t*-butyl)mercury (V).[12]—Mercuric fluoride,[13] (10 g.), 50 g. of anhydrous hydrogen fluoride, and 89 g. of a mixture of gases containing 17.3% perfluoroisobutylene,[17] 76.4% perfluorocyclobutane, and 6.0% perfluoromethylcyclobutane were heated in a bomb[14] at 200° for 12 hr. The bomb was allowed to cool to room temperature. The gases were removed and detoxified by bubbling them through 20% methanolic potassium hydroxide. The solid residue was triturated with dilute nitric acid to dissolve unchanged mercuric fluoride, washed with water, and dried over sulfuric acid. There was obtained 7.37 g. (33%) of white solid, which sublimed to give large crystals, m.p. 65–66°.

Anal. Calcd. for $C_8F_{18}Hg$: Hg, 31.42. Found: Hg, 31.20.

Bis(1,1-dichloro-2,2,2-trifluoroethyl)mercury.[12]—A mixture of 133 g. (1 mole) of 1,1-dichloro-2,2-difluoroethylene, 120 g. (0.5 mole) of mercuric fluoride, and 100 g. of anhydrous hydrogen fluoride was heated at 100° for 12 hr. in a bomb.[14] The product was a gray, granular solid that was recrystallized from chloroform to give 150 g. of bis(1,1-dichloro-2,2,2-trifluoroethyl)mercury as fine white needles, m.p. 180–185°. A second crop of crystals, 24 g., was obtained by evaporation of the filtrate of the first recrystallization. Total yield was 174 g. (69%). The fluorine n.m.r. spectrum of a chloroform solution contained a single unsplit absorption band flanked by two smaller satellite bands.

Anal. Calcd. for $C_4F_6Cl_4Hg$: Cl, 28.1. Found: Cl, 26.8.

Heptafluoro-2-iodopropane.—Bis(perfluoroisopropyl)mercury (540 g., 1 mole) and 510 g. (2 moles) of iodine were heated in a bomb at 200° for 8 hr. The bomb was chilled in an ice bath and vented. The chilled product was filtered; the use of a solid carbon dioxide trap in the suction system prevented large losses of

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[10] Haszeldine has prepared CF_3NO from trifluoroiodomethane and nitric oxide. R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953); J. Banus, *ibid.* 3755 (1953); J. Jander and R. N. Haszeldine, *ibid.*, 912 (1954).

[11] I. L. Knunyants, E. G. Bykhovskaya, V. N. Frosin, and Ya. M. Kisel, *Dokl. Akad Nauk SSSR*, **132**, 123 (1960).

[12] The mercury compounds are volatile and their vapors are toxic.

[13] A technical grade supplied by the Harshaw Chemical Co. was used.

[14] "Hastelloy" (trademark of the Haynes Stellite Div. of Union Carbide Co., Kokomo, Ind.) was more satisfactory than stainless steel.

[15] D. G. Weiblen has briefly reviewed the infrared spectra of fluoroolefins in "Fluorine Chemistry," Vol. II, J. H. Simons, ed., Academic Press, Inc., New York, N. Y., 1954, pp. 453, 454. Terminal perfluoroolefins absorb at 5.56–5.58 μ.

[16] This compound was prepared by Dr. Donald Hummel of the Jackson Laboratory of the Du Pont Co.

[17] Perfluoroisobutylene is extremely toxic. It should be used only where ventilation is good enough to assure its concentration will not rise above 1–2 p.p.m. if the bomb is accidently discharged.

product. There was obtained 454 g. of the crude product, which on distillation yielded 439 g. (74%) of pale pink 2-iodoheptafluoropropane, b.p. 40°; reported, 40.0°.[18] It was protected from light and heat during storage.

The assignment of structure was supported by the n.m.r. spectrum. Two fluorine peaks were present in the ratio of 6:1. The larger peak was split into a doublet, and the smaller peak was split into seven peaks.

Anal. Calcd. for C_3F_7I: C, 12.18; F, 44.95; I, 42.89. Found: C, 12.63, 12.23; F, 44.60; I, 42.49.

2-Bromoheptafluoropropane.—Bis(perfluoroisopropyl)mercury (162 g., 0.30 mole) and 96 g. (0.60 mole) of bromine were heated in a bomb at 200° for 4 hr. The bomb was cooled to about 50°, and the gases were condensed into a solid carbon dioxide–acetone-cooled trap. Distillation gave 102 g. (68%) of heptafluoro-2-bromopropane,[9] b.p. 14–18°.

Anal. Calcd. for C_3F_7Br: F, 53.43; Br, 32.10. Found: F, 53.42, 53.27; Br, 31.83, 31.77.

Pyrolysis of Bis(perfluoroisopropyl)mercury. Tetradecafluoro-2,3-dimethylbutane.—Although the pyrolysis could be carried out in a bomb at 350°, better yields were obtained by passing the vapors through a hot tube. A Pyrex tube (25 mm. o.d.) was packed for 100 mm. of its length with quartz chips. The packed zone was maintained at 498°, and 50 g. of bis(perfluoroisopropyl)-mercury was dropped through at the rate of 9 ml. per hr. with a nitrogen flow of 9 l./hr. The products were collected in a trap cooled with ice followed by one cooled with solid carbon dioxide–acetone. There was obtained 13.5 g. (27%) of mercury and 17.7 g. (57%) of perfluoro-2,3-dimethylbutane, b.p. 60–61°; reported, 60.0°.[9] The n.m.r. spectrum supported the assigned structure.

Anal. Calcd. for C_6F_{14}: C, 21.32; F, 78.68. Found: C, 21.47; F, 78.23.

2H-Heptafluoropropane.—A. A three-necked flask was equipped with dropping funnel, stirrer, and reflux condenser connected to a solid carbon dioxide–acetone-cooled trap. The reducing agent, (a) 16.6 g. (0.1 mole) of potassium iodide dissolved in 100 ml. of boiling water or (b) 30 g. (0.12 mole) of sodium sulfide nonahydrate dissolved in 50 ml. of water, was placed in the flask and 27 g. (0.05 mole) of bis(perfluoroisopropyl)mercury was added dropwise with stirring. There were collected, respectively, (a) 12.1 g. (71%) and (b) 13.3 g. (78%) of crude product in the trap. Distillation of the latter product afforded 10.3 g. (60%) of 2H-heptafluoropropane, b.p. −8 to −7°. Gas chromatographic analysis (see below) of the distilled product indicated that it was 99% pure.

B. Bis(perfluoroisopropyl)mercury (13.5 g., 0.025 mole) was dissolved in 100 ml. of absolute ethanol. Then, 2.3 g. (0.1 mole) of sodium was added portionwise with ice-bath cooling over a period of about 4 hr. During addition, gases evolved were collected in a trap cooled with solid carbon dioxide and acetone. The reaction mixture was slowly diluted with water to a volume of about 300 ml. and warmed until gas evolution ceased. The 2H-heptafluoropropane in the trap weighed 5.1 g. (60% yield). Its infrared spectrum was identical with that published.[19] Mass spectral data established that the product was 93–96% 2H-heptafluoropropane. Vapor phase chromatography on a column of the ethyl ester[20] of "Kel F" acid 8114[21] supported on 40–60 mesh firebrick indicated the 2H-heptafluoropropane to be approximately 97% pure.

Perfluoro-*t*-butyl Bromide.—Four 50-ml. Carius tubes each were filled with 12.3 g. (0.0194 mole) of bis(nonafluoro-*t*-butyl)-mercury and 2 ml. (6.20 g., 0.0387 mole) of bromine. The tubes were sealed under a nitrogen atmosphere and heated at 300° for 8 hr. The contents of the tubes were sublimed into a cold trap. The trap was allowed to warm to room temperature, and the product was blown by a stream of nitrogen through a gas washing bottle containing 10% sodium carbonate solution, then through a calcium chloride tower, and finally into another cold trap. There was obtained a total of 27.6 g. (60%) of a volatile white solid. The product did not give a black mercuric sulfide precipitate with sodium sulfide solution and therefore was free of starting material. The sulfide solution did turn yellow, however, which suggested the possibility of oxidation of the sulfide to polysulfide by the nonafluoro-*t*-butyl bromide. The n.m.r. spectrum of the product in ether solution showed a single peak with no splitting. A sample in ether solution was analyzed *via* gas chromatography on the diglyceride of ω-trifluorohexanoic acid.[22] Only one peak besides the ether peak was found. A sample of the bromide in an evacuated sealed capillary (totally immersed in an oil bath) melted at 55.5–57.5°.

Anal. Calcd. for C_4F_9Br: F, 56.58; Br, 26.73. Found: F, 56.58, 56.82; Br, 26.54, 26.43.

Hydrolysis of Bis(perfluoroisopropyl)mercury. Bis(perfluoroisopropylmercury) Oxide.—Bis(perfluoroisopropyl)mercury (54 g.) and 10 ml. of water were heated in a bomb at 200° for 12 hr. The resulting crude solid (29 g.) was recrystallized from ether to give white crystals, m.p. 292–295°. The infrared spectrum (KBr) was blank from 2–7 μ; the n.m.r. spectrum in hexadeuteroacetone showed no proton resonance absorption, but the fluorine spectrum of the compound was characteristic of the $(CF_3)_2CFHg$— group. These facts indicated the structure $[(CF_3)_2CFHg]_2O$, which was confirmed by the analytical data.

Anal. Calcd. for $C_6F_{14}Hg_2O$: F, 35.22; Hg, 53.13. Found: F, 34.97; Hg, 53.36.

When this compound was dissolved in ethereal hydrogen chloride solution, a white solid was obtained. After crystallization from benzene and sublimation, the solid was identified as perfluoroisopropylmercury chloride by means of mixed melting point determination and comparison of its solution infrared spectrum with that of an authentic sample.

2H-Heptafluoropropane was expected as the by-product of the hydrolysis reaction and its formation was verified by collecting the off-gases from the bomb and examining them by gas chromatography. The retention time of the main component peak (90%) was the same as that of 2H-heptafluoropropane.

Heptafluoro-2-nitrosopropane.—A quartz, spiral mercury resonance lamp was placed inside a 22-l., two-necked glass flask fitted with a side-arm stopcock. The whole system was mounted on a mechanical shaker. Five kilograms of metallic mercury was poured into the flask. The flask was evacuated to less than 1-mm. pressure with an oil pump. Then, 134 g. (0.45 mole) of heptafluoro-2-iodopropane was allowed to vaporize into the flask (the pressure increased to 338 mm.), and 265 mm. of nitric oxide was admitted. Shaking was started, and the mixture was irradiated 3 hr. An additional 156 mm. of nitric oxide was admitted, and the system was irradiated 11 hr. At the end of this time, the pressure in the flask had decreased by a total of 367 mm. The gases were slightly green because of nitrogen dioxide, which was reduced to nitric oxide by shaking the system with the lamp extinguished. The blue gas was pumped from the reaction flask and was caught in a series of liquid nitrogen traps. The product was distilled to give 49.5 g. (55%) of heptafluoro-2-nitrosopropane, b.p. −8 to −6°. The n.m.r. spectrum was characteristic of the perfluoroisopropyl group.

Anal. Calcd. for C_3F_7NO: F, 66.83. Found: F, 66.78, 66.84.

Tris(trifluoromethyl)nitrosomethane.—The equipment described above was used. The flask was charged with 2.5 kg. of mercury. Into the evacuated flask was vaporized 21.5 g. (0.072 mole) of nonafluoro-*t*-butyl bromide. Then, 61 mm. (0.072 mole) of nitric oxide was admitted, and shaking was started. After 15 min. of shaking to scavenge nitrogen dioxide, the system was irradiated for 6 hr.

The gases were pumped into a series of three liquid nitrogen traps. The product in the traps was blown by a stream of nitrogen through a column of mercury to remove traces of NO_2 and caught again in a cold trap. The product was distilled through an ice–water-cooled condenser to give 8.4 g. (37%) of a deep blue liquid, b.p. 23–25°, f.p. *ca.* 0°. The n.m.r. spectrum of the product showed a single fluorine resonance peak with no splitting, as is expected for the perfluoro-*t*-butyl group. Gas chromatographic analysis using the ethyl ester[20] of "Kel-F" acid 8114[21] supported on firebrick showed that the product was 95% tris(trifluoromethyl)nitrosomethane.

Anal. Calcd. for C_4F_9NO: F, 68.64. Found: F, 68.02.

Solubility of Mercuric Fluoride in Anhydrous Hydrogen Fluoride.—The solubility was demonstrated qualitatively. A sample

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(18) (a) R. D. Chambers, W. K. R. Musgrave, and J. Savory, *Proc. Chem. Soc.*, 113 (1961); (b) M. Hauptschein and M. Braid, *J. Am. Chem. Soc.*, **83**, 2382 (1961).

(19) Ref. 13, pp. 459, 472.

(20) T. M. Reed, III, *Anal. Chem.*, **30**, 221 (1958).

(21) This acid is available from the Minnesota Mining and Manufacturing Co.

(22) J. F. Harris and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961).

(23) Trademark for Du Pont tetrafluoroethylene resin.

of mercuric fluoride was sealed in a closely woven Teflon[23] cloth bag. After it was found that shaking the bag in a bottle did not allow the solid to pass through the interstices of the cloth, the bag was then shaken with anhydrous hydrogen fluoride in a sealed vessel at 100° for 2 hr. The vessel was cooled, the Teflon bag was removed, and the anhydrous hydrogen fluoride was allowed to evaporate to give almost a complete recovery of the mercuric fluoride.

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Friedelin and Related Compounds. VI.[1] Azahomofriedelanes

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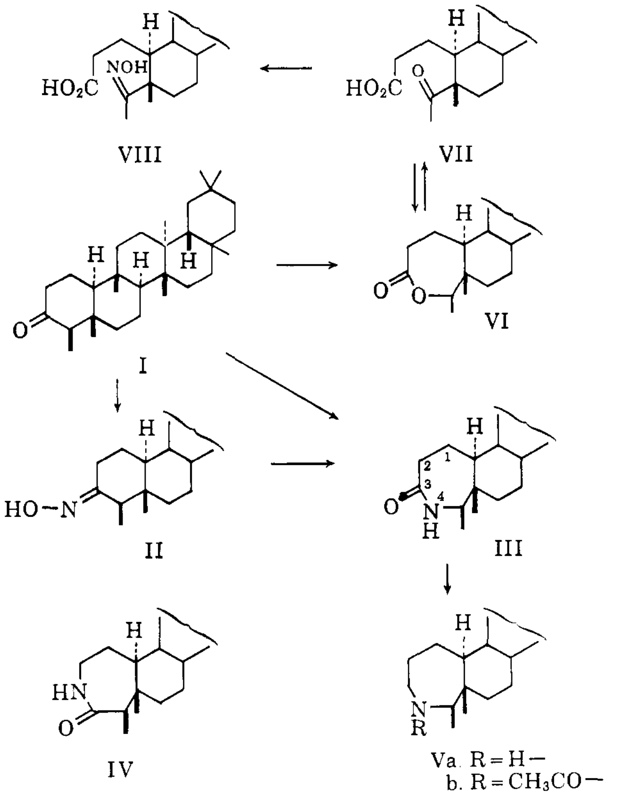
The structure of the product obtained by the Beckmann rearrangement of friedelin oxime (II) and Schmidt reaction of friedelin (I) has been established as 4-aza-A-homofriedelan-3-one (III) by its conversion to the friedelin lactone (VI) by the action of dinitrogen tetroxide.

Considerable work, much of which is reviewed in recent studies,[2-4] has been done on the preparation of azasteroids. The introduction of a nitrogen atom into the steroid ring A to yield the appropriate A-homolactam[3-5] is conveniently accomplished by the Beckmann rearrangement[6] of the easily available 3-ketoximes. Attention has also turned recently to the products obtained by Beckmann rearrangement of the 3-ketoximes[7,8] obtained from triterpenoids (β-amyrin, allobetulin) of the familiar dimethylcyclohexanol ring A structure.

The pentacyclic triterpenoid ketone, friedelin (I), provides a third type of ring A 3-ketone structure. The subjection of friedelin oxime to the action of phosphorus pentachloride in chloroform solution, typical conditions for rearrangement, was reported in 1935 by Drake and Shrader,[9] who established that the product was an "isomeric substance which is no longer an oxime." Their reluctance to formulate this product as a lactam can be attributed to their failure to hydrolyze it under a range of vigorous acid and base conditions or convert it to friedelin or a known derivative. The ready accessibility of friedelin oxime (II) as recently described,[10] has prompted the reinvestigation of this transformation.

Treatment of the oxime (II) with phosphorus pentachloride in chloroform solution gave a product with melting point in agreement with that previously reported,[9] although further purification was effected by chromatographic treatment. The same major product was isolated by the action of *p*-toluenesulfonyl chloride on the oxime in pyridine solution. The infrared spectrum of the product was consonant with an unstrained lactam structure, as expected from a normal Beckmann rearrangement, of which 4-aza-A-homofriedelan-3-one (III) and 3-aza-A-homofriedelan-4-one (IV) are the obvious possibilities. A distinction in favor of III is made on the evidence presented below. Chemical evidence for the presence of the lactam function in III was obtained by reduction with lithium aluminum hydride to give a secondary amine, $C_{30}H_{53}N$, formulated as Va. This yielded, on heating with acetic anhydride, an amide (Vb) whose infrared spectrum lacked an —NH— stretching signal.

Efforts to establish that the lactam had structure (III) by oxidation of the α-methylene group (absent in IV) to yield an α-ketolactam were unsuccessful, unchanged starting material being recovered in high yield after attempted oxidation with selenium dioxide under a variety of conditions[11] and with chromium trioxide in pyridine solution.[12]



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