mμ) indicative of skeletal rearrangement and were not examined further.

4,5-Benzo-3,3,6,6-tetramethyl-1-oxacycloheptene (XVI).—A solution of 6.0 g. (0.11 mole) of the ditosylate XVb in 50 ml. of tetrahydrofuran was added, with stirring, to a solution of 1.0 g. of lithium aluminum hydride in 20 ml. of the same solvent. After refluxing for 10 hr. the reaction mixture was decomposed with ice and 3 N sulfuric acid, diluted with water, and extracted with ether. After drying and concentration of the ether solution the crude product was chromatographed on 40 g. of basic alumina (Woelm, activity grade 1) and eluted with petroleum ether. The solvent was removed and the residue distilled to give 1.8 g. (77% yield) of slightly impure XVI, b.p. 57–59° (0.4 mm.), whose elemental analysis and infrared and n.m.r. spectra indicated that it was contaminated with significant amounts of I.

Anal. Calcd. for $C_{14}H_{20}O$ (204.30); C, 82.30; H, 9.87; Found: C, 84.01; H, 10.68.

One gram of the above product mixture was rechromatographed on 60 g. of acidic alumina (Woelm, activity grade 1) and the hydrocarbon portion eluted with petroleum ether. The ultraviolet, infrared and n.m.r. spectra of this hydrocarbon were identical with those of o-di-t-butylbenzene (see below). The second major fraction, eluted with ether, gave 0.8 g. of the purified cyclic ether XVI, b.p. 58–60° (0.4 mm.), m.p. 45.5–47° (micro crystals from petroleum ether at −70°), $n^{25}D$ 1.5219; λ^{CS_2} 7.2(m), 7.4(s), 7.7(m), 8.0(w), 8.3(m), 8.9(s), 9.5(m), 9.75(m), 9.9(m), 10.05(m), 11.1(m) and 13.3(vs) μ; λ_{max} 262 and 269 mμ (ϵ 185 and 170, respectively), λ_{min} 259 and 266 mμ (ϵ 175 and 165, respectively). The n.m.r. spectrum showed 12 methyl protons as a single peak at τ 8.68, 4 methylene protons at τ 6.42, and 4 benzenoid protons as an A_2B_2 multiplet centered at τ 2.79.

Anal. Calcd. for $C_{14}H_{20}O$ (204.30): C, 82.30; H, 9.87. Found: C, 82.07; H, 9.68.

C. o-Di-t-butylbenzene (I).—A solution of 16.0 g. (0.03 mole) of the ditosylate XVb in 75 ml. of t-butyl alcohol was added to a solution of potassium n-butyl mercaptide (prepared from 2.5 g. of potassium, 2.9 g. of n-butyl mercaptan and 150 ml. of t-butyl alcohol) in t-butyl alcohol. The mixture was refluxed for 15 hr., cooled, and poured into 500 ml. of 10% sodium carbonate solution. The mixture was extracted with three 75-ml. portions of petroleum ether. The combined extracts were washed three times with 50-ml. portions of water, dried over anhydrous sodium carbonate, and distilled. The oily dithioether XVc [7.2 g. (0.0197 mole), 66% yield] distilled as a colorless oily liquid, b.p. 135–138° (0.4 mm.), λ_{max} 262 mμ (ϵ 211). This was desulfurized directly with 140 g. of freshly prepared W-6 Raney nickel in ethanol with stirring at 45–50°. The mixture was filtered, diluted with 4 l. of water and extracted with five 150-ml. portions of petroleum ether. The combined petroleum ether extracts were dried over anhydrous sodium carbonate and the solvent removed by distillation at atmospheric pressure. The fragrant oily residue was chromatographed over basic alumina (60 g., Woelm, activity grade 1) then over acidic alumina (60 g., Woelm, activity grade 1), and the product eluted with petroleum ether was fractionally distilled through a spinning-band column of 25 theoretical plates. The hydrocarbon I distilled at 66–67° (0.4 mm.) or at 121–122° (10 mm.). Recrystallization from methanol furnished 1.3 g. (35% yield from the dithioether) of colorless tiny needles of I, m.p. 27–28° (lit.[7] 27.5–28.5°), $n^{30}D$ 1.5148 (lit.[7] 1.5149); $\lambda^{CS_2}_{max}$ 7.05(w), 7.2(m), 7.4(s), 8.15(m), 8.4(m), 9.45(s), 9.85(w), 10.6(w), 10.95(w), 11.9(w) and 13.3(vs) μ; λ_{max} 261.5 mμ (ϵ 205) [lit.[8] 261 mμ (ϵ 189)]. The n.m.r. spectrum showed a singlet at τ 8.50 [lit.[7] τ 8.51, 8.67[8]] (18 protons) and an A_2B_2 multiplet at τ 2.6–3.0 (4 benzene protons).

Anal. Calcd. for $C_{14}H_{22}$ (190.32): C, 88.35; H, 11.65. Found: C, 88.53; H, 11.63.

Substitution and Addition Reactions of the Fluoroölefins. V. The Electrophilic Addition of Mercuric Fluoride to Fluoropropenes in Hydrogen Fluoride[1]

By WILLIAM T. MILLER, JR., AND MARK B. FREEDMAN

Experimental results on the addition of HgF_2 to $CF_3CH=CF_2$ and to $CF_3CF=CF_2$ in HF solution are reported. It is shown that the mechanism of addition must involve electrophilic attack on the fluoroölefin by mercury cations. This type mechanism is favored in HF by the resistance of highly fluorinated olefins to protonation, and by the strong solvation and weak nucleophilic reactivity of fluoride ion and weak solvation and strong electrophilic reactivity of metal cations. Attention is directed to electrophilic reactions of π-electron systems as a significant new area of carbon–fluorine chemistry.

Highly fluorinated olefins characteristically react with nucleophiles and resist attack by electrophiles such as strong acids. In fact, electrophilic addition to a perfluoroölefin appears not to have been previously demonstrated. Consequently, it was of considerable interest to find that the addition of mercuric fluoride to 1,1,3,3,3-pentafluoropropene and to hexafluoropropene takes place in hydrogen fluoride solution under conditions which suggest an electrophilic mechanism. Further work has confirmed this view. The present paper presents the experimental results obtained and a discussion of evidence bearing on the mechanism of addition.

The Mercuric Fluoride Addition Reaction.—The formation of bis-(1,1,1,3,3,3-hexafluoroisopropyl)-mercury, $(CF_3CHCF_3)_2Hg$, was first observed in attempting to prepare 1,1,3,3,3-pentafluoropropene from 3,3-dichloro-1,1,3-trifluoropropene by reaction with mercuric oxide and hydrogen fluoride. This result was attributed to the addition of HgF_2 to the first-formed $CF_3=CHCF_3$.[2] In the present work we have confirmed this hypothesis by preparing $(CF_3CHCF_3)_2Hg$ directly from $CF_2=CHCF_3$ and HgF_2 and have also added HgF_2 to $CF_2=CFCF_3$ in HF solution. Most of our work has been carried out with $CF_2=CFCF_3$.

Other workers have also recently reported reactions between mercuric fluoride and fluoroölefins. Krespan has described the addition of HgF_2 in AsF_3 solution to the fluoroethylenes $CF_2=CF_2$, $CF_2=CClF$, $CF_2=CHF$ and $CF_2=CCl_2$ to form the corresponding substituted diethylmercury compounds. The mechanism of addition was indicated as ionic but was not considered further.[3] Goldwhite, Haszeldine and Mukherjee obtained $CF_3CClFHgF$ in moderate yield and CF_3CF_2-HgF in trace amounts from HgF_2 and $CF_2=CClF$ and $CF_2=CF_2$ in the absence of a solvent. The reaction was presumed to be a nucleophilic addition with fluoride ion attack on the CF_2 group.[4] Aldrich, Howard, Linn, Middleton and Sharkey have shown that mercuric fluoride in HF is generally applicable as a reagent for the preparation of secondary and tertiary mercurials from terminal fluoroölefins.[5] A related reaction carried out by Young, Tsoukalas and Dresdner consists of the reversible addition of HgF_2 to $CF_2=NCF_3$ in the absence of a solvent to form $(CF_3NCF_3)_2$-Hg.[6]

The reaction of mercuric fluoride with 1,1,3,3,3-

(1) For a preliminary account of this work, see W. T. Miller, Jr., M. B. Freedman, J. H. Fried and H. F. Koch, *J. Am. Chem. Soc.*, **83**, 4105 (1961). Reference (14) is the preceding paper in this series.

(2) J. H. Fried, Ph.D. Thesis, Cornell University, 1955.

(3) C. G. Krespan, *J. Org. Chem.*, **25**, 105 (1960).

(4) H. Goldwhite, R. N. Haszeldine and R. N. Mukherjee, *J. Chem. Soc.*, 3825 (1961).

(5) P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton and W. H. Sharkey, private communication.

(6) J. A. Young, S. N. Tsoukalas and R. Dresdner, *J. Am. Chem. Soc.*, **80**, 3604 (1958).

pentafluoropropene and with hexafluoropropene takes place readily in HF solution at temperatures below 100° to form $(CF_3CHCF_3)_2Hg$ and bis-(heptafluoroisopropyl)-mercury, $(CF_3CFCF_3)_2Hg$. Yields of up to 80% based on the olefin have been obtained with small quantities of reactants. In the absence of the HF solvent very little reaction took place. Mercuric oxide in HF can also be utilized for the mercuration of CF_2=$CFCF_3$, but gave relatively poor yields, with low HF/HgO ratios, due to the formation of water.[7] Efforts to isolate the intermediate compound heptafluoroisopropylmercuric fluoride, $(CF_3CFCF_3)HgF$, were unsuccessful. Our results suggest that this compound reacted faster than the HgF_2 with CF_2=$CFCF_3$, possibly due to a greater solubility in HF. Reaction of a mixture of HgF_2 and $HgCl_2$ with CF_2=$CFCF_3$ yielded heptafluoroisopropylmercuric chloride, $(CF_3CFCF_3)HgCl$, preferentially. Neither $HgCl_2$ nor $(CF_3CFCF_3)HgCl$ reacted with HF or with CF_2=$CFCF_3$ in HF at moderate temperatures.

The structures of the isopropylmercuric compounds were shown by cleavage with bromine or iodine to the corresponding hexafluoroisopropyl halides. The bis-isopropylmercury compounds were stable to aqueous acids and bases but were readily demercurated by aqueous sodium sulfide. Evidence for complex formation between $(CF_3CFCF_3)_2Hg$ and tertiary amines and between $(CF_3CHCF_3)_2Hg$ and chloride and iodide ions in aqueous solution was obtained by qualitative tests. The formation of complex ions from perfluoroalkylmercury compounds has been observed previously.[8]

Treatment of $(CF_3CFCF_3)HgCl$ with silver oxide in aqueous alcohol yielded hexafluoroisopropylmercuric hydroxide. $(CF_3CFCF_3)HgOH$, a water-soluble basic material which could be reconverted into (CF_3CFCF_3)-HgCl by the action of concentrated aqueous hydrochloric acid. Corresponding reactions have been observed with CF_3HgOH and CF_3CF_2HgOH.[9]

The properties of $(CF_3CFCF_3)_2Hg$ are of special interest. In addition to its unusual stability it is the only perfluoroörganomercury compound so far prepared which is a volatile liquid (b.p. 116°). Its physical properties resemble those of $(CF_3NCF_3)_2Hg$ (b.p. 127°).[6] However, it is very much more stable.

The Electrophilic Reaction Mechanism.—The usefulness of liquid hydrogen fluoride as a solvent for the mercuric fluoride perfluoroölefin reaction depends not only upon the occurrence of the desired reaction and the acid stability of the addition products but also upon the absence of a competing HF addition to the olefin. No CF_3CHFCF_3, which would be formed by the addition of HF to CF_2=$CFCF_3$ as well as by the acid cleavage of the isopropyl mercurials, was found in any of the reaction products.[10] Hexafluoropropene and CF_3CF=$CFCF_3$ have also been shown to be stable to HF at temperatures up to 200° and to HF containing potassium fluoride at 125°.[1,11] Since HF has an H_0 of about −10,[12] carbonium ions, which would be formed by the protonation of perfluoroölefins such as CF_3-$CHFCF_2^+$ and $CF_3CHFCF(CF_3)^+$, are shown to be very strong acids indeed. $H_nF_{n+1}^-$ ions in HF are shown to be very weak nucleophiles.[13]

The observed deactivation of fluoride ion in hydrogen fluoride virtually eliminates nucleophilic reactions with perfluoroölefins in this solvent since fluoride ion is ordinarily the only anion and nucleophile which can be present.[15–18] On the other hand, various cations can exist in relatively high concentrations in HF solution,[16,19] are weakly solvated and can function as strong electrophiles. For example, argentous ion forms stable complexes with aromatic hydrocarbons in HF although only weak interactions are observed in aqueous solutions.[20] Mercuric and other metal cations have also been observed to form complexes with donor type molecules such as acetonitrile even though these are protonated in HF solution.[21] It is largely because of the unusual combinations of properties outlined above that hydrogen fluoride serves as an effective solvent for reactions between metal cations and fluoroölefins.

Mercuric fluoride forms a 0.5% solution in liquid HF at 11.9°[19] and is presumably more soluble at the reaction temperatures of ca. 85°. Unlike the other mercuric halides it has an ionic lattice and is a strong electrolyte.[22] Dissociation is to be expected in HF solution because of the strong solvation of the fluoride ion. Accordingly, we conclude that the addition of mercuric fluoride to perfluoroölefins in HF involves an electrophilic attack on the π-electrons of the olefinic bond by a mercury cation.[23] We suggest the following type mechanistic representation, with the formation of an intermediate cyclic mercurinium ion, which is analogous to earlier proposals for olefin mercuration reactions.[24,25] Concerted reactions are also possible on the basis of the available evidence. The essential point is that while perfluoroölefins are unreactive with the strongly solvated fluoride ion in HF solution, sufficient electrophilic reactivity is developed by the addition of a mercury cation to the double bond to bring about reaction of fluoride ion at carbon. The addition of fluoride ion to the terminal carbon atom is favored sterically and energetically. Extra driving force is derived from the formation of the very stable −CF₃ grouping.[26]

We believe that our results point to a significant and previously unrecognized area of carbon–fluorine chemistry consisting of the electrophilic reactions of π-electron systems.[28] A number of metal ions and com-

enormously with solvation. Very rapid reactions have been observed in solvents such as chloroform and formamide.[14]

(14) W. T. Miller, Jr., J. H. Fried and Harold Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

(15) K. Fredenhagen, *Z. Elektrochem.*, **37**, 684 (1931).

(16) K. Fredenhagen and G. Cadenbach, *Z. phyik. Chem.*, **A146**, 245 (1930).

(17) A. F. Clifford, H. C. Beachell and W. M. Jack, *J. Inorg. Nucl. Chem.*, **5**, 57 (1957).

(18) Complex anions such as BF_4^- and SbF_6^- which can be present in HF^{17} are weaker bases than the $H_nF_{n+1}^-$ ions and are considered unlikely to serve as fluoride nucleophiles.

(19) A. W. Jache and G. H. Cady, *J. Phys. Chem.*, **56**, 1106 (1952).

(20) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **79**, 2495 (1957).

(21) A. F. Clifford and J. Sargent. *ibid.*, **79**, 4041 (1957).

(22) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, p. 322.

(23) Presumably the reactive cationic species consist of mercuric ion, the ion pair HgF^+ and the intermediate ion R_FHg^+.

(24) H. J. Lucas, F. R. Hepner and S. Winstein, *J. Am. Chem. Soc.*, **61**, 3102 (1939).

(25) J. Chatt, *Chem. Revs.*, **48**, 7 (1951).

(26) Additional support for an electrophilic mechanism is provided by the observation that $(CF_3)_2C$=CF_2 is relatively unreactive with the HgF_2/HF reagent.[8] This compound has been shown to react very readily with nucleophilic reagents.[27]

(27) T. J. Brice, J. D. La Zerte, L. J. Hals and W. H. Pearlson, *J. Am. Chem. Soc.*, **75**, 2698 (1953).

(28) Electrophilic reactions can also take place with saturated perhalogen compounds. The substitution of chlorine by fluorine in perhalo compounds by reaction with HgF_2 in HF solution must involve electrophilic attack on halogen by mercury cations. Rearrangement reactions are also brought about by electrophilic catalysts.[29]

(29) W. T. Miller, Jr., E. W. Fager and P. H. Griswold, *J. Am. Chem. Soc.*, **72**, 705 (1950).

(7) Krespan obtained only 5% of $(CF_3CF_2)_2Hg$ from CF_2=CF_2 by reaction with HgF_2 in concentrated aqueous HF.[8]

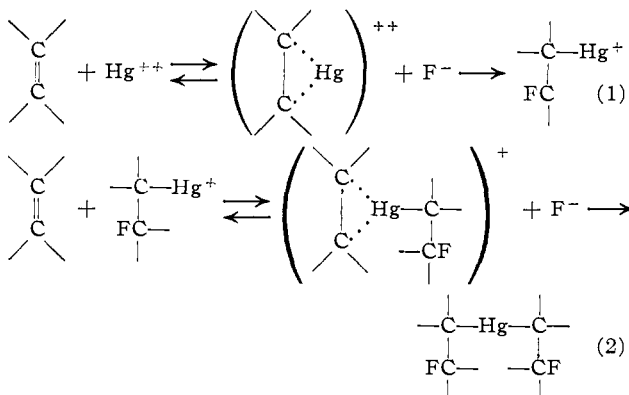(8) H. J. Emeleus and J. J. Lagowski, *J. Chem. Soc.*, 1497 (1959).

(9) J. Banus, H. J. Emeleus and R. N. Haszeldine, *ibid.*, 2948 (1949); 3041 (1950).

(10) CF_3CHFCF_3 was shown to be unreactive with HgF_2 in HF at 80°.

(11) I. L. Knunyants, U. U. Shokina and N. D. Kuleshova, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, **9**, 1693 (1960).

(12) H. H. Hyman, M. Kilpatrick and J. J. Katz, *J. Am. Chem. Soc.*, **79**, 3668 (1957).

(13) The nucleophilicity of fluoride ion toward perfluoroölefins varies

$$\underset{\diagup\;\diagdown}{\overset{\diagdown\;\diagup}{\underset{C}{\overset{C}{\|}}}} + Hg^{++} \rightleftharpoons \left(\overset{\overset{\diagdown\;\diagup}{C}}{\underset{\underset{\diagup\;\diagdown}{C}}{\vdots\; Hg}}\right)^{++} + F^- \longrightarrow \underset{F\overset{|}{C}}{\overset{|}{-C}-Hg^+} \quad (1)$$

$$\underset{\diagup\;\diagdown}{\overset{\diagdown\;\diagup}{\underset{C}{\overset{C}{\|}}}} + \underset{F\overset{|}{C}-}{\overset{|}{-C}-Hg^+} \rightleftharpoons \left(\overset{\overset{\diagdown\;\diagup}{C}}{\underset{\underset{\diagup\;\diagdown}{C}}{\vdots\; Hg-\overset{|}{C}-}}\right)^+ + F^- \longrightarrow \underset{F\overset{|}{C}-\;\;-C\overset{|}{F}}{\overset{|}{-C}-Hg-\overset{|}{C}-} \quad (2)$$

pounds may be expected to exhibit catalytic activity with fluoroölefins or to yield organometallic compounds, as in the present work, by means of electrophilic reactions. A general tendency toward the formation of cyclic intermediates or transition states in which a "full" positive charge is not present on carbon is suggested by the observed great difficulty of forming carbonium ions by the protonation of perfluoroölefins. Conditions suitable for the formation of simple perfluoro carbonium ions in solution are difficult to imagine.

As further examples of electrophilic reactions with perfluoroölefins we can cite the catalytic effect of argentous ion in promoting the addition of HF to $CF_2=CFCF_3$ and to $CF_3CF=CFCF_3$,[1] the catalytic effect of mercuric and argentous ions in promoting reaction between water and $CF_2=CFCF_3$ to form $CF_3CHFC-OOH$,[30] and of argentous ion in promoting reaction of water with $CF_3C\equiv CCF_3$ at room temperature to form $CF_3CH_2COCF_3$.[30] Possibly, the polymerization of $CF_2=CF_2$ brought about by HgF_2[3,4] proceeds by a cationic mechanism.[31]

Experimental

Bis-(heptafluoroisopropyl)-mercury.[32]—A 360-ml. stainless steel bomb was charged with 47 g. (0.20 mole) of HgF_2, 57 g. (2.85 moles) of HF and 42 g. (0.28 mole) of $CF_3CF=CF_2$. Three 0.5″ stainless steel ball bearings were placed in the bomb to increase mixing and it was heated in a rocker shaker for 24 hours at 85 ± 2°. The bomb was vented through a copper tube, packed with sodium fluoride to remove HF; 1.8 g. of $CF_3CF=CF_2$ was recovered in a Dry Ice trap. No CF_3CHFCF_3 could be detected by infrared absorption spectra. The bomb residue was extracted with four 30 ml. portions of CH_2Cl_2 at reflux. During the extraction 12.7 g. of mercury was recovered.[33] Distillation of the combined extracts yielded 51.1 g. (0.095 mole, 68%) of $(CF_3CFCF_3)_2Hg$, b.p. 116–117°. Sublimation of the solid residue gave 3.3 g. (0.0082 mole, 3%) of $(CF_3CFCF_3)HgCl$, m.p. 77–78°.

Yields of $(CF_3CFCF_3)_2Hg$ ranging from 65 to 80% and of $(CF_3CFCF_3)HgCl$ from 1.5 to 6.5% were obtained from a number of closely comparable reactions.

A redistilled sample of $(CF_3CFCF_3)_2Hg$ had the following properties: b.p. 116.6° (740 mm.), f.p. 16.2–16.4°; d^{20}_4 2.5454, $n^{20}D$ 1.3271; mol. wt. 558, 559; Hg 37.1, 37.2; reported[34] b.p. 117°, $n^{25}D$ 1.3244; calculated for $C_6F_{14}Hg$: mol. wt., 539; Hg 37.2. Strong infrared absorption bands were found within the 7–10 μ range at 7.64, 7.82, 8.26, 8.61, 9.13 and 9.29 μ (liquid film).

Mercuric chloride in HF did not react with $CF_3CF=CF_2$ during 24 hours at 86 ± 2°. The reactants were recovered and no HCl could be detected in the vent gases. Similarly, $HgCl_2$ did not appear to react with $(CF_3CFCF_3)_2Hg$ in which it is insoluble on heating at 100 ± 5° for 24 hours.[35]

(30) N. Edelson, Ph.D. Thesis, Cornell University, 1962.

(31) In this connection it is interesting to note that silver nitrate was originally used as a polymerization catalyst for tetrafluoroethylene; R. J. Plunkett, U. S. Patent 2,230,654, Feb. 4, 1941.

(32) The fluoroisopropylmercury compounds are presumed to be highly toxic. Apparatus was rinsed with sodium sulfide solution to remove residues of the fluoroörganomercury compounds.

(33) Some metallic mercury was formed in all cases. It was shown that HgF_2 in HF reacted slowly with the steel bombs utilized.

(34) E. G. Howard and W. J. Middleton, U. S. Patent 2,970,173, Jan. 31, 1961.

(35) This reaction was carried out by R. A. Haggard.

$(CF_3CFCF_3)_2Hg$ was unchanged by heating at 116° for 26 days. It reacted immediately with 0.1 M aqueous sodium sulfide to form black mercuric sulfide; no reaction was observed with 2 M MeONa in MeOH; 2% alcoholic $AgNO_3$ yielded an immediate heavy white precipitate, presumably of a complex salt; 2% aqueous $KMnO_4$ was reduced within 5 min. when added to an acetone solution of the mercurial; 30% pyridine in pentane evolved considerable heat on addition of the mercurial; a 5% solution of bromine in CCl_4 was decolorized within 5 min. at 85°; $AlBr_3$ gave an immediate violent reaction; aluminum powder reacted vigorously to give CF_3CHFCF_3 after hydrolysis suggesting the intermediate formation of a perfluoroisopropyl-aluminum compound.[36a]

$(CF_3CFCF_3)_2Hg$ was soluble in all organic solvents tested, but was qualitatively insoluble in water and in 4.6 M aqueous HCl and in 8.6 M KI solutions at room temperature.

Bis-(1,1,1,3,3,3-hexafluoroisopropyl)-mercury.—Using the procedure described above, 47 g. (0.20 mole) of HgF_2, 45 g. (2.25 moles) of HF and 16 g. (0.12 mole) of $CF_3CH=CF_2$ were heated at 88 ± 2° for 24 hours. On venting, 2.6 g. of $CF_3-CH=CF_2$ was recovered. Extraction with five 40-ml. portions of hot CH_2Cl_2 followed by distillation yielded 16.7 g. (0.048 mole) of $(CF_3CHCF_3)_2Hg$, b.p. 154° (738 mm.), m.p. 38.8–39.0°; reported[2] b.p. 154°, m.p. 38–39°. A C–H infrared absorption band was observed at 3.32 μ with strong bands within the range of 7–10 μ at 7.28, 7.79, 7.91, 8.30, 8.46, 8.62 and 9.33 μ (KBr pellet). Reaction of $(CF_3CHCF_2)_2Hg$ with bromine yielded $CF_3CHBrCF_3$.[1,2]

$(CF_3CHCF_3)_2Hg$ gave an immediate black precipitate of HgS with 0.1 M aqueous sodium sulfide; no reaction was observed with 2 M MeONa in MeOH; 2% alcoholic $AgNO_3$ yielded an immediate, but light, white precipitate; 2% aqueous $KMnO_4$ was not reduced within 5 min. when added to an acetone solution of the mercurial; 30% pyridine in pentane gave no observable reaction; a 5% solution of bromine in CCl_4 was decolorized within 5 min. at 85°; $AlBr_3$ gave a dark color at room temperature and a vigorous reaction on warming.

$(CF_3CHCF_3)_2Hg$ was appreciably soluble in all organic solvents tested but was least soluble in alkanes and CCl_4. It was qualitatively insoluble in water and in aqueous KCl, HCl and KI solutions at room temperature but dissolved in 6 M HCl at 65°. Both $(CF_3CFCF_3)_2Hg$ and $(CF_3CHCF_3)_2Hg$ had pungent irritating odors and were lachrymators.

Perfluoroisopropylmercuric Chloride.—$(CF_3CFCF_3)HgCl$ was first obtained in low yield, 8.5%, from the reaction of 44 g. (0.20 mole) of HgO in 43 g. (2.15 moles) of HF with 35 g. (0.23 mole) of $CF_3CF=CF_2$ at 67 ± 2° for 12 hours. Most of the $CF_3CF=CF_2$, 63%, was recovered unchanged. The chlorine in the product was attributed to reaction of HgF_2 and/or $(CF_3)_2$-CFHgF with the CH_2Cl_2 utilized to extract the product.

$(CF_3CFCF_3)HgCl$ was also obtained as shown above in small amounts as a by-product from the preparation of $(CF_3CFCF_3)_2Hg$ by reaction of HgF_2 with $CF_3CF=CF_2$ in HF. The HgF_2 utilized was found qualitatively to contain some chlorine. It was also shown that the addition of an approximately equimolar amount of $HgCl_2$ to the reactant HgF_2 resulted in the formation of $(CF_3CFCF_3)HgCl$ in high yield. In one instance the use of a relatively large amount of HgF_2, which would favor the formation of $(CF_3CFCF_3)HgF$, led to the production of a disproportionate amount of $(CF_3CFCF_3)HgCl$, 60%.

From the reaction of 68 g. (0.28 mole) of HgF_2, 51 g. (2.55 moles) of HF and 19 g. (0.13 mole) of $CF_3CF=CF_2$ heated at 85 ± 2° for 24 hours was isolated by extraction with CH_2Cl_2 and sublimation of the recovered extract 31.1 g., (0.077 mole, 60%) of $(CF_3CFCF_3)HgCl$, m.p. 77–78°.

From 42 g. (0.155 mole) of $HgCl_2$, 35 g. (0.146 mole) of HgF_2, 52 g. (2.60 moles) of HF and 18 g. (0.12 mole) of $CF_3CF=CF_2$ heated at 82 ± 2° for 25 hours was isolated 26.3 g. (0.065 mole, 54%) of sublimed $(CF_3CFCF_3)HgCl$, m.p. 77°.

Resublimed $(CF_3CFCF_3)HgCl$ was characterized by: m.p. 77.7–78.1°; Hg, 49.6; Cl, 8.6; mol. wt., 399; calculated for C_3F_7HgCl: Hg, 49.5; Cl, 8.8; mol. wt., 405. Especially strong infrared absorption bands were found within the 7–10 μ range at 7.70, 7.83 and 8.30 μ.

$(CF_3CFCF_3)HgCl$ was unchanged by heating at 116° for 26 days. It reacted immediately with 0.1 M sodium sulfide solution to form black HgS; 2% alcoholic $AgNO_3$ yielded an immediate heavy white precipitate; 2 M NaOCH3 in CH_3OH gave a heavy white precipitate; 2% aqueous $KMnO_4$ was very slowly reduced when added to an acetone solution of the mercurial at room temperature; 30% pyridine in pentane evolved slight heat on the addition of the mercurial; a 5% solution of bromine in CCl_4 was decolorized within 5 min. at 85°; $AlBr_3$ reacted vigorously with warming.

$(CF_3CFCF_3)HgCl$ was quite soluble in oxygenated organic solvents but was sparingly soluble in n-pentane, cyclohexane and carbon tetrachloride. It was qualitatively insoluble in water at 25° but was appreciably soluble at 65°. It slowly dissolved

(35a) This reaction was carried out by D. J. Burton.

in 4.6 M aqueous KCl and in 8.6 M KI (a precipitate formed immediately which slowly dissolved) and was soluble in 6 M HCl, but not in 6 M H_2SO_4, at room temperature. $(CF_3CFCF_3)HgCl$ had a characteristic but not unpleasant odor.

No reaction occurred when $(CF_3CFCF_3)HgCl$ was heated with an excess of $CF_3CF{=}CF_2$ either at 138 $\pm$ 2° for 24 hours in the absence of a solvent or in HF at 142 $\pm$ 2°. In the latter case very little, if any, reaction took place with the HF. After heating a mixture of 1.0 g. of $(CF_3CFCF_3)HgCl$, 12 g. of HF and 5 g. of $CF_3CF{=}CF_2$, 0.8 g. of $(CF_3CFCF_3)HgCl$, m.p. 77–78°, was recovered by sublimation.

Heptafluoroisopropylmercuric Hydroxide.—A glass ampule was charged under nitrogen with a slurry of 5.0 g. (0.012 mole) of $(CF_3CFCF_3)HgCl$ and 4.6 g. (0.020 mole) of Ag_2O in 30 ml. of a 1:1 mixture by volume of ethanol and deaerated water. After shaking for 5 hours at room temperature the ampule contents were filtered with a sintered glass filter and the residue washed four times with 20-ml. portions of 1:1 ethanol–water solution. Distillation of the filtrate under reduced pressure yielded 5.0 g. of gray solid residue. After treatment with 2 g. of activated charcoal in ether solution, 2.7 g. (0.007 mole 58%) of $(CF_3CFCF_3)HgOH$ was recovered which contained 52.5% Hg; calculated for C_3F_7HgOH, Hg 51.9%. This material formed a basic solution in water. It did not melt sharply. Noticeable decomposition began at about 254° with the formation of a pale yellow sublimate; at 265° almost complete melting had occurred.

An aqueous solution of 2.6 g. (0.0067 mole) of (CF_3CFCF_3)-HgOH was neutralized to litmus paper with 12 M HCl and 10 drops of excess acid added. Considerable heat was evolved. Extraction with CH_2Cl_2 gave a white crystalline solid which was sublimed to yield 2.4 g. (0.0059 mole) of $(CF_3CFCF_3)HgCl$, m.p. 77–78°, an 88% yield.

Efforts to prepare $(CF_3CFCF_3)HgF$ from $(CF_3CFCF_3)HgOH$ by treatment with 48% aqueous or anhydrous HF yielded a black tarry product from which no pure material could be isolated.

2-Iodoheptafluoropropane.—Reaction of both $(CF_3CFCF_3)_2Hg$ and $(CF_3)_2CFHgCl$ with iodine yielded CF_3CFICF_3. Its formation confirmed the structure of these compounds.

From 97.0 g. (0.18 mole) of $(CF_3CFCF_3)_2Hg$ and 124.5 g. (0.49 mole) of iodine heated in a glass ampule in a rocker shaker at 127 $\pm$ 2° for 24 hours was recovered by distillation 92.2 g. of crude product. Redistillation of this material after treatment with mercury to remove free iodine yielded 84.2 g. (0.284 mole, 79%) of CF_3CFICF_3, b.p. 40.2–40.8° (738 mm.).

Similarly, from 8.9 g. (0.022 mole) of $(CF_3CFCF_3)HgCl$ and 8.7 g. (0.034 mole) of iodine heated in a glass ampule for 10 hours at 132 $\pm$ 2° and 12 hours at 144 $\pm$ 2° was recovered 2.3 g. of easily volatile product. After washing with 5% aqueous sodium thiosulfate, water and drying over $MgSO_4$, 1.9 g. (0.0064 mole) of CF_3CFICF_3, b.p. 40.0–40.5° (743 mm.), was recovered by distillation.

The freshly distilled samples of CF_3CFICF_3, obtained as described above, were pink colored due to the presence of traces of free iodine. Treatment with mercury removed this color, but during distillation and on standing in diffuse light more iodine was formed. An almost completely colorless sample was obtained by treatment with mercury followed by careful redistillation in a dark room in the presence of a low intensity amber light. It had the properties: b.p. 40.6° (740 mm.), f.p. −60.5 to −61.1°, d^{20}_4 2.0990, n^{20}D 1.3283 (mol. wt. calcd. 296, found 302; I calcd. 42.9, found 43.3). Strong infrared absorption bands were observed at 7.81, 8.03, 8.46, 8.91, 10.45, 11.10, 13.31, 14.02 (and 14.10) μ. Since this work was carried out, the properties of CF_3CFICF_3 have been reported as b.p. 38°,[36] b.p. 40°,[37] n^{20}D 1.327[37] with infrared spectra consistent with the above-cited absorption bands.[36,37]

The infrared spectra, freezing points and densities clearly differentiate CF_3CFICF_3 from $CF_3CF_2CF_2I$; f.p. −95.3; d^{20}_4 2.0566,[38] 2.0626.[39]

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Pyridoxine and Pyridoxal Analogs. VI. Electronic Absorption Spectra of Schiff Bases[1]

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The electronic absorption spectra of the amino acid Schiff bases derived from 3-hydroxypyridine-4-aldehyde, 3-hydroxypyridine-2-aldehyde, salicylaldehyde and from the O-methyl derivatives of these aldehydes were obtained from solid state preparations and from their non-aqueous solutions. Analysis of the spectra confirms the presence of two tautomeric forms in the o-hydroxyaldehyde Schiff bases under these conditions. The equilibrium constants, K_x, between the "enol-imine" and the "keto-enamine" species of the two pyridinoid and the benzenoid series of compounds are determined.

In the preceding paper[3] an investigation of the infrared spectra of the amino acid Schiff bases of 3-hydroxypyridine-4-aldehyde (A, R = OH), 3-hydroxypyridine-2-aldehyde (B, R = OH), salicylaldehyde (C, R = OH) and their O-methyl derivatives (A, B, C, R = OCH_3) led to the assignment of the "keto-enamine" structure VIa–VIb to the o-hydroxyaldehyde Schiff bases. Presence of smaller amounts of the tautomeric "hydroxy-imine" species Va–Vb could not be excluded on the basis of the solid state infrared spectra.

The present work deals with an analysis of the electronic absorption spectra of the o-hydroxyaldehyde Schiff bases listed above, with the purpose of obtaining information on the structure of these compounds, and of the analogous pyridoxal derivatives, in solution.

Experimental

Materials.—The amino acid Schiff bases of o-hydroxy- and o-methoxypyridinealdehydes and of salicylaldehyde and o-methoxybenzaldehyde were synthesized as described earlier.[3] The o-hydroxy- and o-methoxypyridinealdehydes were synthesized according to procedures described previously,[4] and were purified by the method described in a subsequent paper.[5] The

spectro grade solvents employed usually required further purification before use. Dioxane and chloroform were purified successfully by a method described by Wohlleben.[6] All measurements in chloroform were carried out immediately after purification of the solvent. Spectro grade methanol was used directly and gave reproducible results.

Absorption Spectra.—The electronic absorption spectra in the visible and ultraviolet regions were recorded with a Cary model 14 spectrophotometer at 20°. For solution measurements a pair of 10-mm. quartz cells were used. Concentration of all compounds was 10^{-4} mole/liter. The solid state spectra were obtained from potassium bromide pellets of 1 mm. thickness, prepared from a mixture obtained by grinding 400 mg. of oven-dried spectro grade KBr with the weighed compound. Concentration of the compounds was adjusted to a level corresponding to 2×10^{-3} mole/liter assuming complete dispersion. The dispersion achieved by repeated regrinding and reprocessing of the pellets resulted in completely transparent and uniform pellets in all cases. All measurements were carried out with a 1-mm. blank potassium bromide pellet in the reference beam and in an atmosphere of dry nitrogen gas. The background absorption due to adsorption of water was almost completely eliminated with these precautions.

Results

Previous work in these laboratories has shown[7] that electronic absorption spectra of pyridine compounds of

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