

CONTRIBUTION FROM ROHM AND HAAS COMPANY,
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The μ -Oxo-difluorophosphines $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$, $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$, and $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$

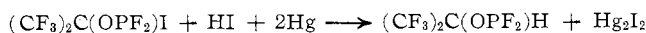
BY MAX LUSTIG AND W. E. HILL

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The reactions between hexafluoroacetone and difluoroiodophosphine, PF_2I , and difluorobromophosphine, PF_2Br , yield the addition compounds 2-iodo-2-(μ -oxo-difluorophosphine)hexafluoropropane, $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$, and 2-bromo-2-(μ -oxo-difluorophosphine)hexafluoropropane, $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$, respectively. The former addition compound reacts with mercury in the presence of hydrogen iodide to give 2-hydrido-2-(μ -oxo-difluorophosphine)hexafluoropropane, $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$. Some physical and chemical properties of these three new compounds have been examined.

Some recent communications have appeared describing the formation of dioxophospholanes by reaction of hexafluoroacetone (HFA) with alkyl and aryl phosphites and phosphines.^{1,2} We wish to report that the reaction of the halophosphine PF_2I or PF_2Br with HFA does not yield the corresponding dioxophospholane, but yields $(\text{CF}_3)_2\text{C}(\text{POF}_2)\text{I}$ or $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ according to the reversible reaction $(\text{CF}_3)_2\text{CO} + \text{PF}_2\text{X} \rightarrow (\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{X}$, where $\text{X} = \text{I}$ or Br . The formation of these addition compounds may be explained by a route similar to that described for the interaction of HFA with phosphites and phosphines,^{1,2} involving the 1,3-dipolar intermediate $(\text{CF}_3)_2\text{C}^--\text{O}^+-\text{PF}_2\text{X}$, which can rearrange to give the 2-halo derivative by transfer of a positive halogen from the phosphorus to the carbon atom. At room temperature the 2-iodo addition compound slowly decomposes to the reactants PF_2I and HFA, although the former reactant is identified by its decomposition products.³ Consequently, the extent of the equilibrium could not be measured, but the equilibrium involving $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ has been examined (see Experimental Section). A similar dissociation is observed in the case of the hexafluoroacetone-triphenylphosphine addition compound.² Under the conditions employed for the reactions of PF_3 , PF_2Cl , and POF_2Br , respectively, with HFA, no products were observed.

Since difluorophosphine, HPF_2 , can be prepared by the reaction of PF_2I , HI , and mercury,⁴ it was speculated that $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ might behave in a similar manner. Indeed, the corresponding hydrido derivative, $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$, was likewise prepared by the reaction



Experimental Section

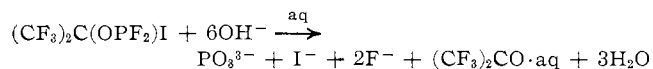
Reagents.—The hexafluoroacetone was obtained from the General Chemical Division, Allied Chemical Co. The PF_2Cl ³ and PF_2I ^{3,5} were prepared and purified by the known methods. The PF_2Br and POF_2Br were synthesized in a similar manner

involving the addition of HBr to $\text{PF}_2\text{N}(\text{CH}_3)_2$ and $\text{POF}_2\text{N}(\text{CH}_3)_2$, respectively. Purification of the PF_2Br was accomplished by passing it through traps maintained at -95 and -126° . The -126° trap held the PF_2Br . The fluorophosphoryl bromide was purified by passing it through cold traps at -80 and -126° . It was retained in the latter trap. The PF_3 , HCl , HBr , and HI were procured from the Mathieson Co., Inc. The HBr and HI were purified by passing the respective gases through a trap set at -95° and collecting them in another at -196° .

Apparatus and General Procedure.—A standard Pyrex vacuum apparatus was used for transfer and purification of gaseous materials. Infrared spectra in the 4000 – 200-cm^{-1} region were taken with a Perkin-Elmer 521 spectrophotometer using a 10-cm path length gas cell with CsBr windows at pressures of ~ 15 mm. The mass spectra were obtained with a Consolidated Engineering Corp. Model 61-620 spectrometer at an ionization potential of 100 ev. The ^{19}F and ^1H nmr spectra were taken with a Varian Model V4310 spectrometer operating at 40 Mc, and the ^{31}P spectra were obtained at 12.8 Mc. Samples were generally measured at ambient temperature in 5-mm o.d. Pyrex tubes using CCl_3F as an internal standard for fluorine spectra and TMS and H_3PO_4 as external standards for the ^1H and ^{31}P spectra, respectively.

Preparation of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$.—In a typical experiment HFA (2.48 mmoles) and excess PF_2I (3.64 mmoles) were combined in a 100-ml Pyrex bulb at -196° . The reaction bulb was warmed slowly to room temperature over a 1-hr period and then allowed to stand for another 3.5 hr. The products were passed slowly through traps set at -95 and -196° . The -95° trap retained 1.76 mmoles of pure $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ (66.3% yield) while the -196° trap held PF_3 (1.03 mmoles), PF_2OPF_2 (0.13 mmole), PF_2I (trace amount), and HFA (0.62 mmole). A yellow solid⁶ remained in the reactor.

Reactions of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$. A. With Alkaline Solution.—The compound reacts rapidly with dilute aqueous base at 60° in accordance with the equation



B. With HI and Mercury.—To prepare $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$, 1.28 mmoles each of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ and HI were placed into a 100-ml bulb containing excess Hg (1.0 ml) at -196° . The bulb was allowed to warm slowly to ambient temperature and then the mixture was stirred for 2 hr. The products were then passed through traps maintained at -95 , -126 , and -196° . The latter contained PF_3 (0.120 mmole) and HFA (0.439 mmole); the -126° trap contained $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ (0.701 mmole, 59.8% yield) while the -95° trap held unreacted $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ (0.128 mmole) and traces of unidentified substance(s).

Preparation of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$.—Into a 100-ml Pyrex reactor were distilled 2.80 mmoles each of HFA and PF_2Br while the vessel was held at -196° . The mixture was allowed to warm to room temperature and stand for 39 hr at room temperature (*ca.* 24°). After this time, infrared spectral analysis showed no

(1) F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tetrahedron Letters*, 2151 (1966).

(2) R. F. Stockel, *ibid.*, 2833 (1966).

(3) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

(4) R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1339 (1965).

(5) R. W. Rudolph, J. G. Morse, and R. W. Parry, *ibid.*, **5**, 1464 (1966).

change in the relative intensities of the bands owing to the equilibrium mixture of gaseous compounds. The mixture was rectified by slow passage through traps set at -95 and -126° . The former contained 0.72 mmole of pure $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ (25.7% yield). The two reactants were retained at -126° . Alternately, to establish the reversibility of this reaction, 2.80 mmoles of purified $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ were allowed to stand for 18 hr at the same temperature in the same bulb when infrared analysis again indicated a state of constant composition. The total quantity of the gas was measured by its pressure-volume-temperature relationship and a sample of the gaseous mixture was analyzed by its mass spectrum for per cent composition. The mixture contained 0.75 mmole of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ (corresponding to 26.8% association) and 2.0 mmoles each of HFA and PF_2Br .

Attempted Synthesis of Other μ -Oxo Phosphorus Fluoride Compounds.—The following pairs (4.65 mmoles of each member) were placed into separate 500-ml Pyrex bulb reactors: PF_3Cl and HFA, PF_3 and HFA, and POF_2Br and HFA. There was no indication of product formation in any of the bulbs at room temperature, at 50° , and at 100° .

Analyses.—Carbon analyses were performed by conventional combustion using MgO in the combustion tube. Total fluorine was determined by reduction with lithium in *n*-propylamine followed by distillation of the fluoride as H_2SiF_6 and titration with thorium nitrate. The hydrolyzable fluorine was determined by alkaline hydrolysis followed by distillation and titration. Iodine was determined as iodate after oxidation of the hydrolyzed $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ with bromine water in dilute H_2SO_4 solution; bromine was determined as Br^- by titration of the hydrolyzed $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ with $\text{Hg}(\text{NO}_3)_2$. The phosphorus in the difluorophosphine compounds was analyzed as phosphate after oxidation with nitric acid. *Anal.* Calcd for $\text{C}_6\text{F}_8\text{IOP}$: C, 9.94; I, 35.06; P, 8.59; solution F^- , 10.50. Found: C, 10.01; I, 35.3; P, 8.6; solution F^- , 9.4. Calcd for $\text{C}_6\text{F}_8\text{HOP}$: C, 15.25; F, 64.40; P, 13.12. Found: C, 14.83; F, 64.5; P, 13.7. Calcd for $\text{C}_6\text{F}_8\text{BrOP}$: C, 11.43; Br, 25.37; F, 48.25; P, 9.83; solution F^- , 12.06. Found: C, 10.50; Br, 25.8; F, 50.6; P, 10.5; solution F^- , 11.8.

Physical Properties. A. Molecular Weights.—The molecular weights were determined by vapor density measurements assuming perfect gas behavior. The molecular weight found for $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ is 357.4 g/gram molecular volume (calcd 361.9), that for $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ is 310.5 (calcd 314.9), and that for $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ is 233.8 (calcd 236.0).

B. Melting Points.—The melting points were observed visually by placing samples in 5-mm o.d. Pyrex tubes which were submerged in a cold pentane bath which warmed at a rate of $0.25^\circ/\text{min}$. The melting point of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ is $-98.4 \pm 0.6^\circ$ and that of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ is $-90 \pm 2^\circ$.

C. Vapor Pressures.—These were measured at various temperatures and at constant volume by use of a gauge similar to that described by Foord.⁶ Owing to the instability of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$, vapor pressures could not be measured to its boiling point; however, some of the data are given [T ($^\circ\text{C}$), P (mm)]: (13.1, 48.5; 19.6, 68.0; 21.9, 77.2; 26.3, 97.0; 31.7, 126.8; 38.2, 172.3; 44.8, 229.0; 55.3, 356.0;⁷ 60.4, 437.4⁷). The measurements for $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ are: (-46.8 , 12.4; -25.1 , 45.2; -15.1 , 80.0; -8.2 , 111.8; -1.7 , 161.5; 0.9, 186.4; 10.4, 280.3; 13.0, 340.9). The extrapolated boiling point of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ is $74.4 \pm 0.9^\circ$ while that of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ is $30.7 \pm 0.2^\circ$. The vapor pressure data for the iodo compound follow the equation $\log P(\text{mm}) = 8.451 - (1.936/T)$, and the measurements on the hydrido derivative correspond to $\log P(\text{mm}) = 7.767 - (1.505/T)$. The molar heat of vaporization and Trouton constant for $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ are 8.860 kcal and 25.40 eu, respectively, and the corresponding values for $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ are 6.887 kcal and 22.86 eu.

D. Infrared Spectra.—The infrared spectrum of $(\text{CF}_3)_2\text{C}$

$(\text{OPF}_2)\text{I}$ shows bands at 2500 (w, sharp, pqr), 1295 (vs), 1252 (vs, complex), 1172 (m), 1136 (vs), 1101 (sh), 955 (ms), 890 (s), 872 (s), 850 (s), 824 (s), 735 (m), 711 (ms, complex), 605 (m), 549 (w), 510 (m), and 404 (w, complex) cm^{-1} . That of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ is similar and shows bands at 1298 (vs), 1258 (vs, broad), 1219 (sh), 1176 (m), 1189 (vs), 1102 (w), 962 (s), 919 (s), 877 (s), 854 (s), 820 (s), 738 (m), and 714 (s) cm^{-1} . Although specific assignments for the bands in the spectra of the above two compounds cannot be made, absorptions are observed in regions assigned to C-F, C-O-P, and P-F stretching motions.⁸ The spectrum of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ exhibits frequencies at 2975 (w, sharp), 1760 (w, broad), 1370 (s), 1300 (vs), 1268 (ms), 1240 (vs), 1215 (vs), 1176 (m), 1117 (s), 1905 (s), 1028 (m), 901 (ms), 878 (s), 825 (s, doublet), and 380 (w) cm^{-1} . This spectrum also shows bands in the regions associated with C-F, C-O-P, and P-F as well as with C-H stretching motions. The absorption at 2975 cm^{-1} is assigned to a tertiary C-H stretching motion.⁷

E. Nmr Spectra.—The ^{19}F nmr spectrum of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)$ has an absorption due to the two CF_3 groups centered at ϕ 74.5 and due to the PF_2 group at ϕ 46.9. The former is split into a doublet ($J = 8$ cps) from the interaction of the ^{31}P nucleus and each member of the doublet is further divided into triplets ($J = 0.9$ cps) *via* coupling with the two fluorine atoms bound to the phosphorus. The resonance centered at ϕ 46.9 is split into a doublet ($J = 1384$ cps) by coupling with the ^{31}P atom and each member of the doublet is further split into multiplets which were not well resolved. The spectrum of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ has absorptions due to the two CF_3 groups centered at ϕ 77.8 and due to the PF_2 group at ϕ 45.9. The former is split into a doublet ($J = 12$ cps) due to the interaction of the ^{31}P nucleus, and each member of the doublet is further divided into triplets ($J = 1.6$ cps) due to the two fluorine atoms bonded to the phosphorus. The resonance centered at ϕ 45.9 is split into a doublet ($J = 1384$ cps) due to coupling with the ^{31}P nucleus and each member of the doublet is further split into septuplets ($J = 1.6$ cps). The ^{19}F spectrum of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ has some similarity to those above. The resonance of the two identical CF_3 groups is located at ϕ 75.5 which is a gross triplet ($J \cong 5$ cps). This triplet shows further splitting ($J \cong 1$ cps). Homodecoupling and heterodecoupling (irradiation of the proton) lead to ambiguous results, but they indicated that there is considerable interaction between the CF_3 fluorine nuclei and the other nuclei. The resonance for the fluorine atoms bound to the phosphorus is centered at ϕ 50.5 and is split into a doublet ($J = 1344$ cps). Each member of the doublet is also split into a complex multiplet. The ^{31}P spectrum shows a triplet ($J = 1325$ cps) which is subsplit ($J \cong 7$ cps). The proton resonance shows septet or nonet splitting ($J = 5$ cps) that is centered at -186 cps. Irradiation of the CF_3 group fluorines changed the proton multiplet into a doublet ($J = 10$ cps) due to the interaction between the ^{31}P and ^1H nuclei. The area ratio of the fluorine atoms bound to carbon to those attached to phosphorus in $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{I}$ was measured to be 3.2:1.0 and in $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{Br}$ to be 3.1:1.0 while the C-F to P-F ratio in $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ was found to be 3.3:1.0.

The nmr spectra of $(\text{CF}_3)_2\text{C}(\text{OPF}_2)\text{H}$ can be interpreted in the following manner. The gross triplet of the CF_3 group can be caused by interaction between it and two different nuclei of spin $1/2$ and having coupling constants approaching 5 cps. The proton multiplet shows $J_{\text{F}_3\text{H}} = 5$ cps. If it can be assumed that $J_{\text{F}_3\text{P}} \cong 4$ cps, the CF_3 group triplet in the ^{19}F spectrum is roughly consistent with such splitting constants. The subsplitting observed in both the CF_3 and PF_2 fluorine resonance is presumably due to the $J_{\text{F}_3\text{F}_2}$ interaction. The doublet in the proton spectrum which arises from irradiation of the CF_3 group indicates that $J_{\text{HP}} = 10$ cps.⁹ The nonet of peaks in the proton spectrum is consistent with the J_{HP} and $J_{\text{F}_3\text{H}}$ values. The ^{19}F and ^{31}P spectra indicated $J_{\text{F}_3\text{P}}$ values of 1344 and 1324 cps, respectively.

(8) L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd ed, Methuen and Co., Ltd., London, 1959.

(9) This value is more accurate than the 7 cps value measured in the ^{31}P spectrum.

(6) S. G. Foord, *J. Sci. Instr.*, **11**, 126 (1934).

(7) These values are questionable owing to decomposition of the sample.

It is assumed that $J_{F,H} \cong 0$, since no further splittings of the proton and PF_2 group fluorine nuclear resonances are observed. There was little change in the field position of the proton when measured at -40° indicating it is not acidic and is bonded to a carbon rather than to the oxygen atom.

F. Mass Spectra.—The mass spectrum of $(CF_3)_2C(OPF_2)I$ was obtained with the cycloid tube at room temperature and the following are the absorptions observed, given as mass number (species) and relative abundance: 12 (C^+), 1.2; 25 (CF_2^+ , PF_2^+), 0.7; 28 (CO^+), 0.3; 31 (CF^+ , P^+), 9.0; 47 (COF^+ , PO^+), 1.6; 50 (CF_2^+ , PF^+), 12.6; 63.5 (I^{2+}), 1.6; 66 (COF_2^+ , POF^+), 0.8; 69 (CF_3^+ , PF_2^+), 100.0; 78 ($C_2F_2O_2^+$, $COPF^+$), 2.5; 85 (POF_2^+), 5.3; 88 (PF_3^+), 4.3; 97 ($C_2F_3O^+$, CF_2OP^+), 23.4; 100 ($C_2F_4^+$), 1.1; 119 ($C_2F_5^+$), 1.1; 127 (I^+), 5.5; 128 ($C_3F_4O^+$, $C_2F_3OP^+$), 1.1; 147 ($C_3F_5O^+$, $C_2F_4OP^+$), 10.4; 166 ($C_3F_6O^+$, $C_2F_5OP^+$), 1.0; 177 (CF_2I^+ , PFI^+), 1.6; 196 (CF_3I^+ , PF_2I^+), 14.4; 235 ($C_3F_8OP^+$), 2.3 The spectral pattern for $(CF_3)_2C(OPF_2)Br$ is: 12 (C^+), 0.9; 28 (CO^+), 1.2; 31 (CF^+ , P^+), 8.8; 47 (COF^+ , PO^+), 1.1; 50 (CF_2^+ , PF^+), 12.2; 66 (COF_2^+ , POF^+), 0.4; 69 (CF_3^+ , PF_2^+), 100.0; 78 ($C_2F_2O^+$, $COPF^+$), 2.1; 79 ($^{79}Br^+$), 1.6; 81 ($^{81}Br^+$), 1.6; 85 (POF_2^+), 2.6; 88 (PF_3^+), 1.6; 97 ($C_2F_3O^+$, CF_2OP^+), 21.2; 100 ($C_2F_4^+$), 0.5; 119 ($C_2F_5^+$), 0.9; 129 ($CF_2^{79}Br^+$), 2.0; 131 ($CF_2^{81}Br^+$), 2.1; 147 ($C_3F_5O^+$, $C_2F_4OP^+$),

13.8; 148 ($CF_3^{79}Br^+$, $PF_2^{79}Br^+$), 6.4; 150 ($CF_3^{81}Br^+$, $PF_2^{81}Br^+$), 6.0; 166 ($C_3F_6O^+$, $C_2F_5OP^+$), 0.4; 179 ($C_2F_4^{79}Br^+$), 0.5; 181 ($C_2F_4^{81}Br^+$), 0.5; 207 ($C_3F_4^{79}BrO^+$), 0.5; 209 ($C_3F_4^{81}BrO^+$), 0.5; 235 ($C_3F_8OP^+$), 1.6. The pattern for $(CF_3)_2C(OPF_2)H$ has many similar features to those listed above and shows a large number of hydrogen-containing species: 12 (C^+), 0.4; 28 (CO^+), 1.0; 29 (HCO^+), 32.9; 31 (CF^+ , P^+), 7.4; 47 (COF^+ , PO^+), 2.4; 50 (CF_2^+ , PF^+), 6.2; 51 (HCF_2^+ , HPF^+), 40.7; 63 ($HC_2F_2^+$), 1.5; 66 (COF_2^+ , POF^+), 0.4; 69 (CF_3^+ , PF_2^+), 100.0; 78 ($C_2F_2O^+$, $COPF^+$), 1.5; 79 ($HC_2F_3O^+$, $HCOPF^+$), 33.6; 82 ($HC_2F_3^+$), 2.0; 85 (POF_2^+), 1.6; 89 (HPF_3^+), 1.7; 93 ($C_3F_3^+$), 0.6; 97 ($C_2F_3O^+$, CF_2OP^+), 0.9; 101 ($HC_2F_4^+$), 10.7; 113 ($HC_3F_4^+$), 4.8; 128 ($C_3F_4O^+$, $C_2F_3OP^+$), 1.6; 129 ($HC_3F_4O^+$, HC_2OP^+), 9.3; 132 ($HC_3F_5^+$), 10.6; 147 ($C_3F_5O^+$, $C_2F_4OP^+$), 0.8; 167 ($HC_3F_6O^+$, $HC_2F_5OP^+$), 6.4; 217 ($HC_3F_7OP^+$), 1.2; 236 ($HC_3F_8OP^+$), 2.8.

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A Study of the Fragmentation of Trifluoromethylarsenic Compounds in the Mass Spectrometer

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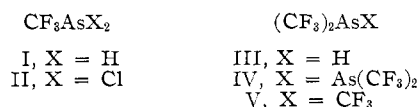
The mass spectra of some trifluoromethylarsenic compounds have been examined. In addition to the products of normal fragmentation, rearranged fluorocarbon ions and species containing As-F bonds were observed in all the spectra.

Introduction

The migration, under electron impact, of groups or atoms other than hydrogen has received wide attention recently,¹ although the only relevant discussion of inorganic systems is a report of the mass spectra of perhalogeno aromatic phosphines, where the formation of rearranged fluorocarbon ions with elimination of PF_2 and PF_3 as neutral species was observed.^{1a} A study of some trifluoromethyl derivatives of arsenic is described in this paper. Previous work in this field has been carried out by Cullen and Frost,² who measured the ionization potentials of some perfluoroarsines, and by Cowley, Burg, and Cullen,³ who have reported a partial mass spectrum of the novel cyclic compound, $(CF_3As)_4$.

Results and Discussion

The mass spectra of compounds I-V have been examined; in each case, rearrangement ions containing



As-F bonds have been found. The spectra are shown in Table I, while some metastable ions observed in the spectra, together with their assignments, are listed in Table II.

The initial breakdown of the dihydro compound I can be represented by the scheme shown in Figure 1, where an asterisk indicates that the appropriate metastable ion was observed. Normal fragmentation occurs by loss of H, F, or CF_3H from the molecular ion, followed by stepwise degradation of the ions so formed. However, the parent and some of the fragment ions can also lose fluorocarbon fragments containing CF or CF_2 groups, resulting in the formation of rearranged ions containing As-F bonds. For example, loss of CFH_2 and CF_2H_2 from $CF_3AsH_2^+$ gives AsF_2^+ (m/e 113, 1.9%)⁴ and AsF^+ (m/e 94, 7.0%), respectively. While the corresponding metastable peak was not observed, $AsFH^+$ (m/e 95, 3.7%) probably arises from the molecular ion by loss of CF_2H as a neutral fragment. The formation of rearranged fluorocarbon ions

(3) A. H. Cowley, A. B. Burg, and W. R. Cullen, *J. Am. Chem. Soc.*, **88**, 3178 (1966).

(1) (a) J. M. Miller, *J. Chem. Soc., Sect. A*, in press; (b) J. H. Bowie, S. O. Lawesson, J. Ø. Madson, G. Schroll, and D. H. Williams, *J. Chem. Soc., Sect. B*, 951 (1966), and references therein.

(2) W. R. Cullen and D. C. Frost, *Can. J. Chem.*, **40**, 390 (1962).

(4) Intensities are expressed relative to the total ionization, defined as ΣI_n where n refers to all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.