The hydration of a number of organic ions can be studied without changes in the method of ion production. We have also observed the hydration of negative ions (*i.e.*, $Cl^- \cdot nH_2O$) on irradiation of suitable (chlorinated) compounds in water vapor. Of the metal ions, $Na^+ \cdot nH_2O$ was observed several times in high abundance but as an impurity ion. Special methods would seem necessary for the controlled production of metal ions under the mild conditions required for the study of clustering equilibria.

Appendix

A Test of the Assumption That Clustering Equilibrium Is Achieved. In order to test whether clustering equilibrium is achieved in the ion source, a set of experiments was performed in which the reaction time of the ions was increased by moving the α beam away from the sampling leak. A specially constructed ion source contained a movable collimating slit (1 × 3 mm., wall thickness 1 mm.) placed 5 mm. in front of the sampling leak, causing the α beam not to graze the leak but to pass over it. Since a second laser leak was not available, a single 50-μ diameter leak was used. The experiments were therefore restricted to 1 torr pressure where the disturbance due to cooling of the jet is small. All experiments were done at room temperature. Under these conditions the major ions are I_4 and I_3. The I_4/I_3 ratio measured previously with the laser leak was 1.3. Measurements with the 50-μ leak and the slit in the lowest position gave a higher result, 2.2 ± 0.2. The increase of the ratio, which should be due to cooling of the jet, is not too large and should not affect the significance of the results quoted below. When the slit was successively raised by 1, 1.5, and 2 mm. above the plane of the leak, no change in the I_4/I_3 ratio was observed. This result is in agreement with the equilibrium assumption. For comparison, an experiment was done with ethylene. One of the major ionic reactions in ethylene[3,13] is a polymerization started by $C_2H_4^+$ and leading to the ions $C_4H_8^+$, $C_6H_{12}^+$, etc. This is a dynamic system of successive ion molecule reactions and should show intensity changes with movement of the slit. Drastic changes were indeed observed.[13] Thus with ethylene at 4×10^{-2} torr pressure[14] the major ion is $C_4H_8^+$ followed by $C_6H_{12}^+$ and $C_8H_{16}^+$ in decreasing concentrations. A movement of the slit by 1 mm. caused a shift of intensities to higher mass, the $C_4H_8^+$ ion becoming almost extinct. The rate constant for $C_4H_8^+$ reaction with ethylene is very small ($<5 \times 10^{-12}$ cc. sec.$^{-1}$ molecule^{-1}). Considering also that ethylene was present at a concentration 1/25th that of ammonia we see that the rate of the $C_4H_8^+$ reaction is much lower than the rates that could be expected for the ammonia clustering reactions. The constancy of the ammonia intensity ratios thus must be due to the presence of a clustering equilibrium.

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(13) P. Kebarle, R. M. Haynes, and S. Searles, *J. Chem. Phys.*, to be published.

(14) The ethylene is mixed with 20 torr of Xe in order to produce only $C_2H_4^+$ as primary ethylene ion; see also ref. 3.

Phosphines Containing the CH_3CF_3P Group[1]

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Abstract: Volatile phosphines of the new general type CH_3CF_3PX (where X is a functional group) have been made by various methods, including interconversion. The best approach was through addition of CH_3I to $(CH_3)_2PPCF_3$; the resulting methiodide $(CH_3)_3PPCH_3CF_3{}^+I^-$ was attacked by HCl to form CH_3CF_3PCl. This was converted by NaI to CH_3CF_3PI, and that by PH_3 to CH_3CF_3PH or by Hg to $(CH_3CF_3P)_2$. HCl cleaved the latter to CH_3CF_3PH and CH_3CF_3PCl, with reversal by action of $(CH_3)_3N$. Both CH_3CF_3PH and $(CH_3CF_3P)_2$ form dissociable BH_3 complexes, but BF_3 fails to attach. Ammonolysis or aminolysis of CH_3CF_3PCl led to $H_2NPCH_3CF_3$, $HN(PCH_3CF_3)_2$, $CH_3NHPCH_3CF_3$, $CH_3N(PCH_3CF_3)_2$, and $(CH_3)_2NPCH_3CF_3$, all quantitatively reconvertible by HCl to CH_3CF_3PCl. The related $(CH_3)_2NPCF_3Cl$ also was made. Accurate infrared spectra are presented.

The chemistry of phosphine derivatives containing the $(CH_3)_2P-$ and $(CF_3)_2P-$ groups has shown so many interesting contrasts related to the effect of electronegativity upon the base action *vs.* Lewis acid character of phosphorus, as to justify a full study of phosphines based upon the intermediate group CH_3CF_3P-. Our syntheses and further studies of a series of new volatile compounds of the type CH_3CF_3PX (where X is a chemically active group such as halogen, hydrogen, amino, or phosphino) have shown chemical results mostly confirming the qualitative expectations based upon knowledge of analogous $(CH_3)_2PX$ and $(CF_3)_2PX$ compounds, but unexpected results are possible.

For example, the complex $CH_3CF_3PH \cdot BH_3$ showed the expected poor stability, but unlike $(CH_3)_2PH \cdot BH_3$ or a $(CF_3)_2PH-B_2H_6$ mixture, it formed only H_2 and glassy nonvolatile material on heating in a very small sealed tube; no $(CH_3CF_3PBH_2)_3$ could be found. Only at low partial pressures and with H_2 to stabilize the B_2H_6 was it possible to obtain this ring trimer, in yields up

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[1] Much of this research was supported by the United States Air Force through Contracts AF 33(616)-6913 (KKJ, until Jan. 1961) and AF 33(616)-7810 (JFN, until July 1962), monitored by the Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Later refinements and extensions by ABB were supported by Grants GP-199 and GP-3812 from the National Science Foundation, which also supported the purchase of a Beckman IR7 instrument through Grant G-14665. The contribution of each author is shown by initials.

to 35%. Possibly $(CH_3CF_3PBH_2)_3$ is less stable than higher $CH_3CF_3PBH_2$ polymers—unlike $[(CH_3)_2PBH_2]_3$[2] or $[(CF_3)_2PBH_2]_3$[3]—or perhaps the $CH_3CF_3PH–B_2H_6$ mixture reacts most easily through formation of higher polyboranes leading to resin formation.[4] A fuller account of $(CH_3CF_3PBH_2)_3$ and its consequences is planned for later publication.

The observed chemistry of the $CH_3CF_3P–N$ phosphines was more in accord with expectations. Knowing that $H_2NP(CH_3)_2$ cannot exist (disproportionating instantly to form the P_2N compound, which equilibrates with ammonia and the P_3N compound),[5,6] whereas $H_2NP(CF_3)_2$ is quite stable[7] and requires special or indirect methods for conversion to $HN[P(CF_3)_2]_2$ or $N[P(CF_3)_2]_3$,[8] one might have predicted with some confidence the observed truth that the new compounds $H_2NPCH_3CF_3$ and $HN(PCH_3CF_3)_2$, or $CH_3NHP-CH_3CF_3$ and $CH_3N(PCH_3CF_3)_2$, are readily interconvertible by reaction with CH_3CF_3PCl, HCl, or the appropriate nitrogen base. Disproportionation equilibria involving these pairs might have been expected, but have not been observed. The trisphosphinoamine $N(PCH_3CF_3)_3$, expected to be very difficultly volatile, has not been isolated, but $(CH_3)_2NPCH_3CF_3$ was easily made and proved quite useful in the development of the other CH_3CF_3P compounds.

Unlike $P_2(CF_3)_4$, the diphosphine $(CH_3CF_3P)_2$ is cleavable (quite completely) by dry HCl, but heat (*e.g.*, 1 hr., 50°) is required for a convenient rate, presumably because the phosphorus here is too weakly basic for any fast S_N2 process. This quantitative cleavage to CH_3CF_3PCl and CH_3CF_3PH provides a loss-free synthesis of the latter. Addition of $(CH_3)_3N$ to the product mixture restores the original amount of $(CH_3CF_3P)_2$.

This diphosphine is like $P_2(CF_3)_4$ in its failure to react with BF_3, but differs by reacting easily with BCl_3. However, the process is complex, giving less than half of the expected yield of the cleavage product CH_3CF_3PCl. The adduct $(CH_3CF_3P)_2 \cdot BH_3$ forms easily but is appreciably dissociated below 0°; thus the situation is neatly between the nonexistent $P_2(CF_3)_4 \cdot BH_3$ and the stable $P_2(CH_3)_4 \cdot BH_3$ or $P_2(CH_3)_4 \cdot 2BH_3$.[9]

Experimental Methods

The following sections describe more fully the various aspects of the chemistry of the $CH_3CF_3P–$ unit, as observed by high-vacuum methods. The main working apparatus was a series of U-shaped traps for separations of volatile substances by fractional condensation, usually with Stock-type mercury float-valves serving both as cutoffs and as low-pressure manometers. For mercury-sensitive substances such as CH_3CF_3PI, the cutoffs were halocarbon-greased stopcocks, and a spoon gauge was used as a null manometer. Numerous special devices such as weighing tubes, reaction tubes (either stopcocked or for sealing off), vacuum tube openers, immersible tensimeters, filtering Λ-tubes for purification by crystallization, or infrared cells, were attachable through ground joints and stopcocks. Some of the new compounds developed P–H bonds on contact with hydrocarbon greases, which therefore were usually avoided.

The high-vacuum method made it possible to observe quantitative interconversion reactions, using infrared spectra, volatility data, and molecular weights for identification of all components. Molecular formulas were proved by the weight–volume relationships in such quantitative reactions, providing the equivalent of elementary analyses. The purity of each compound was indicated by excellent conformity to the usual log *P* *vs.* $1/T$ relationship (slight curvature over long ranges); but the melting points of the new compounds usually could not be observed because their irregular molecules formed only glasses at low temperatures.

The Chlorophosphine

Synthesis (KKJ). Our most efficient method for making the chlorophosphine CH_3CF_3PCl began with the addition of CH_3I to the monomer complex $(CH_3)_3PPCF_3$,[10] formed as a thin layer on the inner wall of a stopcocked reaction tube. The addition occurred during a slow warming from −78° toward room temperature. The white solid product, presumed to be the salt $(CH_3)_3P–PCH_3CF_3{}^+I^-$, was treated with HCl in excess, forming CH_3CF_3PCl and a solid, mostly $(CH_3)_3PH^+I^-$. At this point, some 6–10% of the CF_3P units could be recovered as the tetramer–pentamer mixture,[11] and the yield of CH_3CF_3PCl might run as high as 85% of the consumed CF_3P. Typically (JFN), 5.671 mmoles of CF_3P yielded 4.217 mmoles of pure CH_3CF_3PCl; CF_3P recovery, 0.350 mmole. The crude product was exposed to $HgCl_2$ to remove a trace of iodide; then the last trace of HCl could be taken out by a reflux column at −78° or by repeated fractional condensation. More convenient was treatment with a trace of $(CH_3)_2NH$ or its reaction product $(CH_3)_2NPCH_3CF_3$, which a −70° distillation would leave behind. Contact with Apiezon L grease introduced more volatile impurities.

An independent synthesis (KKJ) went through a quantitative conversion of CH_3CF_3PI (which see) to $(CH_3)_2NPCH_3CF_3$. As described in the section on nitrogen-substituted phosphines, this and four other N–P phosphines were cleaved by HCl in quantitative processes with all components conforming to the numerical requirements for single, clean reactions; for example, one yield of CH_3CF_3PCl from $(CH_3)_2NPCH_3CF_3$ was 99.86%. This proof of the formula CH_3CF_3PCl was confirmed by the vapor-phase molecular weight (KKJ, 151.7; JFN, 150.5; calcd., 150.47).

Volatility (KKJ). Table I shows representative equilibrium vapor pressures for highly purified CH_3CF_3PCl, with a well-fitting equation and derived data. Measurements at higher temperatures were not attempted on account of the appreciable reaction of the compound with mercury.

Table I. Volatility of CH_3CF_3PCl
($\log P = 6.1707 + 1.75 \log T - 0.005962T - 1865/T$)
($t_{760} = 51.2°$; Trouton constant = 20.92 e.u.)

Temp., °C.	−37.0	−26.0	−7.2	0.0	10.5	21.0
P_{obsd}, mm.	10.4	21.9	65.5	95.0	157.3	249.4
P_{calcd}, mm.	10.44	21.83	65.5	95.1	157.4	249.4

The Reaction with Mercury (ABB). The reaction of CH_3CF_3PCl with mercury at 25° is slow and self-limiting, forming Hg_2Cl_2 and $(CH_3CF_3P)_2$. Its character was proved by an experiment in which a 6-mmole sample, shaken vigorously with 8 g. of Hg at 45° (27 hr.), was nearly all recovered, but yielded 0.2 mmole of a product whose volatility (4 mm. at 0°), molecular weight (230 ± 2), infrared spectrum, and cleavage by HCl to one each CH_3CF_3PCl and CH_3CF_3PH identified it as the diphosphine $(CH_3CF_3P)_2$. The by-product Hg_2Cl_2 was sublimed away from the mercury and recognized by its behavior toward solvents.

The Iodophosphine

Synthesis by Iodide Exchange (ABB). Sodium iodide was dried *in vacuo* at 180–200° and pulverized under dry nitrogen; this process

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(2) (a) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953); (b) A. B. Burg, *J. Inorg. Nucl. Chem.*, **11**, 258 (1959); (c) R. I. Wagner and F. F. Caserio, *ibid.*, **11**, 259 (1959).

(3) A. B. Burg and G. Brendel, *J. Am. Chem. Soc.*, **80**, 3198 (1958).

(4) A. B. Burg, XVIIth International Congress of Pure and Applied Chemistry," Butterworths, London, 1960, p. 58.

(5) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3871 (1953).

(6) A. B. Burg and P. J. Slota, Jr., *ibid.*, **80**, 1107 (1958).

(7) G. S. Harris, *J. Chem. Soc.*, 512 (1958).

(8) A. B. Burg and J. Heners, *J. Am. Chem. Soc.*, **87**, 3092 (1965).

(9) A. B. Burg, *ibid.*, **83**, 2226 (1961).

(10) A. B. Burg and W. Mahler, *ibid.*, **83**, 2388 (1961).

(11) W. Mahler and A. B. Burg, *ibid.*, **80**, 6161 (1958). These ring compounds have been made more conveniently (KKJ, 1959) by heating CF_3PI_2 with powdered antimony in a sealed tube at 100°. Since SbI_3 is molten at 100°, a fresh antimony surface would always be accessible. The same method applies also to the conversion of $(CF_3)_2PI$ to $P_2(CF_3)_4$.

was repeated until sintering no longer occurred on heating. Then the 1-g. sample was treated with 0.6710 mmole of CH_3CF_3PCl and left in contact for 12 hr. at 25°. The main product was isolated by fractional condensation at −65° and the unused 0.1294 mmole of CH_3CF_3PCl was left with the NaI–NaCl mixture for 16 hr. at 25°. The total yield of the colorless liquid product CH_3CF_3PI was 0.5907 mmole, accounting for 93% of the finally unrecovered 0.6353 mmole of CH_3CF_3PCl. The molecular weight of the product (vapor phase, 24 mm. at 24°) was 242.9 (calcd., 241.9). An experiment equivalent to analysis for iodide was the quantitative conversion to the diphosphine $(CH_3CF_3P)_2$, described in the next main section.

Volatility (ABB). The product CH_3CF_3PI exhibited the volatility behavior expected of a pure substance, as shown in Table II. These data were obtained by means of a mechanically magnified spoon gauge, used as a null instrument.

Table II. Volatility of CH_3CF_3PI
($\log P = 5.8116 + 1.75 \log T - 0.0047T - 2129/T$)
($t_{760} = 102.3$; Trouton constant = 21.36 e.u.)

Temp., °C.	0.00	7.3	13.0	17.7	21.3	22.9
P_{obsd}, mm.	9.95	15.35	20.9	27.7	33.0	35.8
P_{calcd}, mm.	9.95	15.35	21.2	27.3	33.0	35.8

Alternative Syntheses (KKJ). The direct addition of CH_3I to a mixture of the CF_3P tetramer and pentamer[11] gave useful yields of CH_3CF_3PI, but the product usually had an iodine color, and in any case a very critical control of time and temperature was required. The conditions and results of the most successful experiments are shown in Table III. All of these experiments were performed in 10-ml. sealed tubes, so that the proportions of the reactants in the vapor *vs.* liquid phase varied with the amounts employed. Attempts to catalyze the process at 110°, by iodine, mercury, $(CH_3)_2O$, or $(CH_3)_3N$, all led to nil results. In general, it seemed best to employ an excess of CH_3I and to avoid extending the time so far as to cause much decomposition or secondary reaction. A determination of the optimum conditions would require much more experimentation, with little guiding theory. Further experiments by JFN showed no improvement over Table III.

Table III. The CH_3I–$(CF_3P)_n$ Reaction

Reactants mmoles CF₃P units	Reactants mmoles CH_3I	Time, hr.	Temp., °C.	Use of $(CF_3P)_n$, %	Yield,[b] %
7.28	18.45[a]	15	130	(Small)	*Ca.* 50
13.17	26.34	36	110?	16	53
2.83	2.62	2	150	28	31
3.97	7.05	5	148	34	85
10.14	20.30	16	150	100[c]	13

[a] With a trace of I_2, apparently ineffective as a catalyst. [b] Based upon consumed CF_3P units. [c] Much tar formation and a 1.3% yield of CF_3PI_2.

Another method of synthesis, also subject to improvement, was the action of iodine on the tertiary phosphine $CH_3P(CF_3)_2$.[12] During 38 hr. at 196° the reaction consumed 29% of the $CH_3P(CF_3)_2$, giving a 46% yield of CH_3CF_3PI.

The Diphosphine (ABB)

Quantitative Synthesis. A weighed sample of pure CH_3CF_3PI (iodide-exchange product) was shaken with a weighed portion of mercury, introduced through the stopcock of the weighing tube. The volatiles were condensed at the top of the tube by cotton soaked in liquid nitrogen, and the mercury iodides were flame-sublimed in that direction, leaving clean mercury for further reaction. After repetition of the process until the mercury remained clean, the volatile product was distilled off and determined by the loss of weight of the weighing tube. Comparison of the final weight with the sum of the mercury and the empty tube gave a direct determination of the iodine removed from the iodophosphine. The results are described by the following equation with millimole stoichiometry.

$$\begin{array}{lllll} 2CH_3CF_3PI & + \; x\text{Hg} \longrightarrow & (CH_3CF_3P)_2 & + & I_2 \cdot x\text{Hg} \\ 0.5700 & & 0.2829\ (\text{gas}) & & 0.2833 \\ (137.9\ \text{mg.}) & & (65.2\ \text{mg.}) & & (71.9\ \text{mg. I}) \end{array}$$

The product, $(CH_3CF_3P)_2$, was virtually pure as delivered from the weighing tube, except for a negligible trace of more volatile material which probably came from the stopcock system; this was removed by evacuation through a trap at −65°. The molecular weight was determined as 230.5 (calcd., 230.03), confirming the molecular formula already proved by the 99.6% synthesis. The melting range was −58.2 to −57.7°. The volatility–temperature relationship is shown in Table IV.

Table IV. Volatility of $(CH_3CF_3P)_2$
($\log P = 6.2094 + 1.75 \log T - 0.005T - 2323/T$)
($t_{760} = 120.4$; Trouton constant = 21.44 e.u.)

Temp., °C.	0.00	6.70	11.50	16.90	26.30	35.00
P_{obsd}, mm.	4.00	6.22	8.33	11.51	19.44	30.57
P_{calcd}, mm.	4.01	6.19	8.33	11.51	19.44	30.60

Overnight exposure of a small sample of $(CH_3CF_3P)_2$ to Apiezon L grease in an infrared cell caused a 10% formation of CH_3CF_3PH.

Alternative Syntheses (KKJ). Samples having molecular weights near the value 230 calculated for $(CH_3CF_3P)_2$ were made in the year 1959 by two methods. The first was the addition of CH_3Cl to the monomer–complex $(CH_3)_3PPCF_3$. This process proved to be far slower than the CH_3I addition and occurred best at room temperature. Thus the $(CH_3)_3PPCF_3$ could develop its equilibrium with $(CH_3)_3P$ and $(CF_3P)_{4,5}$, with the possibility of adding CH_3Cl during P–P bond formation. While this happened, there was very little addition of CH_3Cl to $(CH_3)_3P$. Thus with the reactants in a sealed tube placed horizontally, 3.15 mmoles of $(CH_3)_3PPCF_3$ absorbed 3.24 mmoles of CH_3Cl (from an excessive sample) during 72 hr. at 25°. Of two products, the more volatile was not easily purified, but its molecular weight (232 ± 5) and volatility (4.4 mm. at 0°) indicated $(CH_3CF_3P)_2$. A less volatile fraction (0.80 mm. at 0° and 10.4 mm. at 53°) might have been a triphosphine. It was destroyed by catalytic action at a stopcock. A fuller study of the whole process is warranted.

The second alternative was the action of CH_3I (3.55 mmoles) during the conversion of CF_3PI_2 (5.34 mmoles) to $(CF_3P)_{4,5}$ by shaking with mercury during 3 weeks at 24°. The volatile products were understood as 2.87 mmoles of CF_3P (as tetramer and pentamer), 1.24 mmoles of $(CH_3)_2PCF_3$, and 0.49 mmole of $(CH_3CF_3P)_2$ (mol. wt. 232). This process also deserves fuller study.

Behavior toward Lewis Acids (ABB). The quantitative cleavage of $(CH_3CF_3P)_2$ by HCl was accomplished by heating the nearly equimolar mixture in a U-tube between mercury valves. After 30 min. at 50°, the mixture was partially resolved and the most and least volatile fractions were heated together as before to complete the process. The products CH_3CF_3PCl and CH_3CF_3PH were separated by repeated fractional condensations using traps at −95, −105, and −196° and reworking the mixed condensate at −105°. The final result is summarized by the following equation with millimole stoichiometry determined by weight of $(CH_3CF_3P)_2$ and gas volumes of the other components.

$$\begin{array}{lllll} (CH_3CF_3P)_2 & + \; \text{HCl} \longrightarrow & CH_3CF_3PCl & + & CH_3CF_3PH \\ 0.2408 & \quad 0.250 & 0.2400 & & 0.2405 \\ & \quad \underline{-0.011} & & & \\ & \quad 0.239 & & & \end{array}$$

The vapor phase molecular weights of the products were respectively 151.4 and 116.3; calcd., 150.47 and 116.04. Their infrared spectra also were recorded accurately, confirming the identity of the CH_3CF_3PCl and so removing any doubt of the validity of the above equation as proof of the molecular formula CH_3CF_3PH.

This cleavage was not appreciably reversible, for the remixed products yielded not a trace of HCl after 1 hr. at 50°. However, with trimethylamine, the quantitative resynthesis was accomplished.

$$\begin{array}{lllll} (CH_3)_3N & + \; CH_3CF_3PCl & + \; CH_3CF_3PH \longrightarrow & & \\ 0.240 & \quad 0.232 & \quad 0.234 & & \\ \underline{-0.013} & & & (CH_3CF_3P)_2 & + \; (CH_3)_3NHCl \\ 0.227 & & & 0.232 & \quad 0.224 \end{array}$$

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[12] R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3651 (1956).

Here all reactants and products were determined by weight except that $(CH_3)_3N$ was measured as a gas. The slightly low consumption of this amine is ascribed in part to a prior slight conversion of CH_3CF_3PCl to $(CH_3CF_3P)_2$ by mercury.

The recovered $(CH_3CF_3P)_2$ was heated with an equimolar portion of BF_3 (5-ml. tube, 12 hr. at 80°) without cleavage; both components were recovered with only slight loss. At a BF_3 pressure of 360 mm., none was absorbed by the liquid diphosphine (at −60 to −30°) except for a slight solubility effect.

With BCl_3 (0.265 mmole) the diphosphine (0.163 mmole) seemed to form a 1:1 adduct during 40 min. at −40°, but the unused BCl_3 contained BF_3 and the exchange products $ClBF_2$ and Cl_2BF, all identified by their infrared spectra.[13] The material trapped at −78° appeared as a sublimable solid with equilibrium pressures 3 mm. at 0°, 5 mm. at 7° (then melting), and 9 mm. at 13°. It developed more BF_3 on standing. Finally it was heated for 12 hr. at 96°, forming an amber-brown resin, a trace of BF_3, and 0.070 mmole of CH_3CF_3PCl, the purity of which was shown by its molecular weight (150.4 ± 1.5) and its infrared spectrum. This unusual reaction deserves fuller study.

An equimolar mixture of $(CH_3CF_3P)_2$ and B_2H_6 showed absorption of the latter during warming from −78 to −50°. The final combining ratio was $1.004BH_3$ per $(CH_3CF_3P)_2$. At −65° the adduct appeared as a glassy liquid, developing mobility upon warming. Its dissociation pressures developed slowly: 1.3 mm. at 0° and 6 mm. at 23°, reverting to nil on long standing at −78°. The relatively high stability of this BH_3 adduct, in contrast to the nonexistent BF_3 adduct, emphasizes the d-orbital ideas discussed by Graham and Stone[14]; indeed, the $P{-}CF_3$ bond would strongly enhance the postulated B–H to P_{3d} π-bond effect, accounting for a relatively good attachment of the BH_3 group.

Methyltrifluoromethylphosphine

Alternative Syntheses. Our most efficient method for making CH_3CF_3PH is the HCl cleavage of $(CH_3CF_3P)_2$ (preceding section): having defined the desired yield, one can begin with about twice as much CH_3CF_3PCl, and finally recover half of this. However, the process involves two heterogeneous steps and might be inconvenient on a large scale.

A fairly good alternative is the action of PH_3 upon CH_3CF_3PI (KKJ)—a method analogous to Harris' synthesis of $(CF_3)_2PH$.[7] In fact, the reaction begins well below room temperature and yields near 70% are easily obtained. For example (ABB), 2.0 mmoles of CH_3CF_3PI and 0.76 mmole of PH_3 gave 1.4 mmoles of CH_3CF_3PH and a golden nonvolatile solid. An attempt (ABB) to perform a similar process with CH_3CF_3PCl and PH_3 was far less successful, for even at temperatures in the range 25–70°, only 10% of the chlorophosphine was used up and only one-third of that appeared as CH_3CF_3PH. Much better was exposure of the PH_3–CH_3CF_3PCl mixture to dry NaI, but this potentially efficient process has not been perfected.

The previously successful method of making a secondary phosphine by the thermal decomposition of an adduct of the type $(CH_3)_2NPR_2\cdot BH_3$[6,15] failed in the present case, for the stable compound $(CH_3)_2NPCH_3CF_3\cdot BH_3$, heated for 96 hr. at 125°, gave less than 0.04% yield of CH_3CF_3PH. The amino groups were accounted for completely as $(CH_3)_2NBH_2$ and $(CH_3)_2NB_2H_5$, but the phosphine units remained in the nonvolatile white solid product.

Of the conceivable methods of making CH_3CF_3PH, the most direct would be addition of CF_3I to CH_3PH_2, excess of which would remove the product HI (KKJ). An exploratory experiment with the analogous addition of CF_3I to $(CH_3)_2PH$ (fast at 0°; complete after 48 hr. at 25°) did indeed give a 90% yield of $(CH_3)_2PCF_3$, which was identified by its known properties (mol. wt. 130.4 *vs.* 130.0 calcd.; volatility 115.2 mm. at 0° *vs.* lit.[12] 117 mm.). However, the relatively weak base character of CH_3PH_2 makes it far less able to attach CF_3I, so that the formation of CH_3CF_3PH by this method seems to be self-limiting and very difficult to repeat. A search for a dependable catalyst might be rewarding.

Volatility (ABB). A sample of CH_3CF_3PH from the action of PH_3 on CH_3CF_3PI was thoroughly purified by fractional condensation; apparent molecular weight 117.0 at 25° and 100 mm. (calculated 116.0). Its infrared spectrum was exactly the same as that of a sample from the cleavage of $(CH_3CF_3P)_2$. Its volatility behavior indicated purity, as shown by the data and equation in Table IV.

Table IV. Volatility of CH_3CF_3PH
($\log P = 5.6349 + 1.75 \log T - 0.00556T - 1586/T$)
($t_{760} = 17.98°$; Trouton constant = 21.06 e.u.)

Temp., °C.	−78.5	−64.16	−49.7	−23.6	0.00	18.09
P_{obsd}, mm.	2.55	8.79	25.6	122.3	374	762
P_{calcd}, mm.	2.58	8.80	25.5	122.3	375	762

The BH_3 Adduct (ABB). A mixture of 0.428 mmole of B_2H_6 and 0.463 mmole of CH_3CF_3PH (volatility sample) showed slow reduction of pressure at −78° and was allowed to equilibrate in a 20-ml. tube at 22°. The excess B_2H_6 was distilled off at −78° and measured as 0.196 mmole. Thus the formula of the adduct was $CH_3CF_3PH\cdot 1.006BH_3$.

This adduct was liquid at −78° and did not dissociate appreciably during distillation through the vacuum line at 22°: neither component passed through an evacuated trap at −78°. Its liquid–vapor equilibrium pressures were measured as 4.4 mm. at 0°, 9.7 mm. at 11.3°, and 17.5 mm. at 22.0°, giving the equation $\log P = 8.696 - 2197/T$ (calculated values respectively 4.5, 9.4, and 17.9 mm.). This equation gives the normal boiling point as 105° and the Trouton constant as 26.6 e.u. The latter value suggested some vapor phase dissociation, and this was confirmed by the sudden cooling of an equilibrated sample from 22 to 0°; it first registered 10 mm. pressure at 0°, and then slowly approached the true value, 4.5 mm.

Nitrogen-Substituted Phosphines

Syntheses. The following quantitatively monitored processes represent the syntheses of six new N–P phosphines. Each quantity (given in millimoles) was determined by gas volume measurement except where weight is indicated.

$$\underset{0.510}{CH_3CF_3PCl} + \underset{\begin{array}{r}1.406\\-0.473\\\hline 0.933\end{array}}{NH_3} \longrightarrow \underset{0.278}{H_2NPCH_3CF_3} + \underset{0.0914}{HN(PCH_3CF_3)_2} + \underset{(30.3\text{ mg.})}{\text{nonvolatiles}} \qquad (1)$$

$$\underset{2.132}{CH_3CF_3PCl} + \underset{\begin{array}{r}3.612\\-0.567\\\hline 3.045\end{array}}{NH_3} \longrightarrow \underset{0.145}{H_2NPCH_3CF_3} + \underset{0.787}{HN(PCH_3CF_3)_2} + \underset{\ldots}{(NH_4Cl)} \qquad (2)$$

$$\underset{\begin{array}{r}0.930\\-0.251\\\hline 0.679\end{array}}{CH_3CF_3PCl} + \underset{1.247}{CH_3NH_2} \longrightarrow \underset{0.441}{CH_3NHPCH_3CF_3} + \underset{0.097}{CH_3N(PCH_3CF_3)_2} + \underset{46.3\text{ mg.}}{\text{nonvolatiles}} \qquad (3)$$

$$\underset{\begin{array}{r}0.944\\-0.738\\\hline 0.206\end{array}}{CH_3CF_3PCl} + \underset{0.410}{2CH_3NH_2} \longrightarrow \underset{0.205}{CH_3NHPCH_3CF_3} + \underset{\ldots}{\text{nonvolatiles}} \qquad (4)$$

$$\underset{\begin{array}{r}0.7072\\-0.6737\\\hline 0.0335\end{array}}{CH_3CF_3PCl} + \underset{\begin{array}{r}0.170\\-0.018\\\hline 0.152\end{array}}{3CH_3NHPCH_3CF_3} \xrightarrow{100°} \underset{\substack{0.060\\(15.6\text{ mg.})}}{2CH_3N(PCH_3CF_3)_2} + \underset{(3.8\text{ mg.})}{\text{nonvolatiles}} \qquad (5)$$

$$4.30(CH_3)_3PPCH_3CF_3{}^+I^- + 4.16HCl \longrightarrow (\text{volatile product});$$
$$(\text{volatile product}) + \underset{\text{excess}}{(CH_3)_2NH} \longrightarrow \underset{1.97}{(CH_3)_2NPCH_3CF_3} + \text{nonvolatiles} \qquad (6)$$

$$\underset{0.929}{CH_3CF_3PI} + \underset{\begin{array}{r}2.208\\-0.348\\\hline 1.860\end{array}}{2(CH_3)_2NH} \longrightarrow \underset{0.925}{(CH_3)_2NPCH_3CF_3} + \underset{0.930\text{ (wt.)}}{(CH_3)_2NH_2I} \qquad (7)$$

$$\underset{0.879}{CF_3PCl_2} + \underset{\begin{array}{r}1.846\\-0.072\\\hline 1.774\end{array}}{2(CH_3)_2NH} \longrightarrow \underset{0.850}{(CH_3)_2NPCF_3Cl} + \underset{\ldots}{\text{nonvolatiles}} \qquad (8)$$

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(13) L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.*, **24**, 245 (1956).

(14) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 170 (1956).

(15) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **82**, 2148 (1960).

Table V. Data Confirming the Molecular Formulas of Six N–P Phosphines

Formula	Mol. wt. Obsd.	Mol. wt. Calcd.	Sample, mmole	HCl used Obsd.	HCl used Calcd.	Product Obsd.	Product Calcd.	N^+Cl^- salt Obsd.	N^+Cl^- salt Calcd.	Done by
						CH_3CF_3PCl				
$H_2NPCH_3CF_3$	131.3	131.0	0.1744	0.350	0.349	0.175	0.174	0.172[a]	0.174	ABB
$HN(PCH_3CF_3)_2$	244.6	245.0	0.742	2.202	2.226	1.452	1.484	0.749[b]	0.742	JFN
$CH_3NHPCH_3CF_3$	145.6	145.1	0.932	1.896	1.864	0.930	0.932	0.941[a]	0.932	JFN
$CH_3N(PCH_3CF_3)_2$	260.9	259.1	0.163	0.491	0.489	0.311	0.326	...	...	JFN
$(CH_3)_2NPCH_3CF_3$	160.5	159.1	0.647	1.295	1.294	0.645	0.647	0.64[a] 0.67[b]	0.647	KKJ
						CF_3PCl_2				
$(CH_3)_2NPCF_3Cl$	180.7	179.5	0.484	(not detnd.)		0.484	0.484	0.50[b]	0.484	KKJ

[a] Determined by weight. [b] Determined by Cl^- titration.

These processes usually occurred during slow warming from −78° or lower, in small stopcock-closed vertical reaction tubes. Often the less-volatile reactant was condensed in a thin, wide layer on the inner wall of the tube, permitting any heterogeneous reaction to occur more smoothly.

Equation 1 (ABB) illustrates the observation that the ammonolysis of CH_3CF_3PCl always produces some $HN(PCH_3CF_3)_2$ even when ammonia is present in excess. This result would suggest disproportionation of $H_2NPCH_3CF_3$ toward equilibrium with ammonia and $HN(PCH_3CF_3)_2$; however, a pure sample of $H_2NPCH_3CF_3$ failed to form any of either of these products during a week at 40° and 10 min. at 70°. Hence the formation of $HN(PCH_3CF_3)_2$ here probably was due to a localized excess of CH_3CF_3PCl and a favoring mechanism.

Equation 2 (JFN) was planned to favor the formation of $HN(PCH_3CF_3)_2$. Since the reaction mixture was allowed to stand for 12 hr. at 25°, the presence of unused ammonia means that its action on $HN(PCH_3CF_3)_2$ to form $H_2NPCH_3CF_3$ is slow; less probable would be an approach toward equilibrium in the disproportionation of $H_2NPCH_3CF_3$.

Equations 3 (JFN) and 4 (ABB) illustrate the effect of varying the procedure when CH_3N–P phosphines are sought. In process 3 there were no special precautions to avoid local heating effects, and some $CH_3N(PCH_3CF_3)_2$ was obtained. But in process 4, which employed a far larger excess of CH_3CF_3PCl, there was more uniform contact and slower heating, leading only to $CH_3NHPCH_3CF_3$. Then process 5 (ABB), wherein the reaction mixture cooled from 100 to 40° during 16 hr., showed clearly the heat requirement for partial conversion of $CH_3NHPCH_3CF_3$ to $CH_3N(PCH_3CF_3)_2$ in the presence of excess CH_3CF_3PCl. With a moderate excess of CH_3NH_2, a fully monitored quantitative synthesis of $CH_3NHPCH_3CF_3$ was obtained by JFN: $0.942CH_3CF_3PCl$ and $1.888CH_3NH_2$ formed $0.941CH_3NH_3Cl$ and $0.932 CH_3NHPCH_3CF_3$, fully establishing the formula of the latter product. For the purification of this compound, it was necessary to employ a −78° reflux column to remove the excess amine, which apparently tended to cling through weak hydrogen bonding.

Process 6 (KKJ) represents the original synthesis of $(CH_3)_2NPCH_3CF_3$ by forming $(CH_3)_3PPCF_3$ from $(CH_3)_2P$ and $(CF_3P)_4$, adding CH_3I, treating with HCl, and acting with $(CH_3)_2NH$ upon a volatile product which only later was recognized to be nearly pure CH_3CF_3PCl. Equation 7 (KKJ) represents the quantitative synthesis of the same aminophosphine from CH_3CF_3PI obtained by the syntheses described in Table III. This also was the first step in the proof of the formula CH_3CF_3PI, independently of the synthesis by halide exchange.

Equation 8 (KKJ) describes the nearly quantitative synthesis of $(CH_3)_2NPCF_3Cl$, which was tried with $Zn(CH_3)_2$ in an early attempt to make $(CH_3)_2NPCH_3CF_3$. That attempt did not succeed, possibly on account of Zn–P complex formation, but $(CH_3)_2NPCF_3Cl$ seems worthy of description in its own right.

Proofs of Molecular Formulas. All six of these N–P phosphines were cleaved by dry HCl (present in excess and measured back), quantitatively yielding the corresponding chlorophosphines, as shown in Table V. Here again, the reactions occurred in stopcocked tubes attached to the high-vacuum line; and the millimole quantities were determined by gas volume measurements unless otherwise indicated. The molecular weights were determined by vapor density measurements.

Volatility Data. Beyond the data of Table V, the purity of each of the six N–P phosphines was further indicated by its excellent conformity to a Nernst approximation equation (type, $\log P = C + 1.75 \log T - BT - A/T$) with reasonable values for the three parameters and derived constants, as shown in Table VI. This table shows also for each compound the fractional condensation conditions used for purification: first the temperature for trapping out any less volatile impurities and then the temperature of the trap through which the more volatile materials would be removed. The accuracy with which the equations implied by Table VI describe reality is shown by the examples of actual data in Table VII.

Table VI. Volatility Constants for Six N–P Phosphines

Formula	Nernst constants A	Nernst constants 10^6B	Nernst constants C	Norm. B.p., °C.	Trouton const., e.u.	Purif. temp., °C.
$H_2NPCH_3CF_3$	2307	7663	7.6722	79.1	21.1	−60, −78
$HN(PCH_3CF_3)_2$	2467	4595	6.1401	142.8	21.9	−35, −50
$CH_3NHPCH_3CF_3$	2088	5000	5.9405	92.1	21.1	−50, −78
$CH_3N(PCH_3CF_3)_2$	2356	3540	5.1870	164.9	21.0	−30, −45
$(CH_3)_2NPCH_3CF_3$	2109	5000	5.9119	98.9	21.0	−45, −78
$(CH_3)_2NPCF_3Cl$	2134	3800	5.3231	115.0	22.0	−35, −45

Table VII. Volatility Data for Six N–P Phosphines

	$H_2NPCH_3CF_3$ (ABB)					
Temp., °C.	−35.7	−7.0	0.00	12.6	17.5	20.9
P_{obsd}, mm.	1.97	16.16	24.95	51.3	65.8	78.2
P_{calcd}, mm.	1.97	16.17	24.95	51.0	65.9	78.2
	$HN(PCH_3CF_3)_2$ (JFN)					
Temp., °C.	0.00	5.5	15.0	38.9	51.6	66.6
P_{obsd}, mm.	1.31	1.94	3.60	14.60	28.1	55.9
P_{calcd}, mm.	1.31	1.94	3.62	14.64	28.0	55.9
	$CH_3NHPCH_3CF_3$ (JFN)					
Temp., °C.	−23.8	0.0	11.5	20.0	27.0	34.0
P_{obsd}, mm.	3.43	15.6	30.2	46.9	65.9	90.9
P_{calcd}, mm.	3.37	15.6	30.0	46.8	65.9	91.2
	$CH_3N(PCH_3CF_3)_2$ (JFN)					
Temp., °C.	9.9	22.0	31.7	39.5	47.8	60.0
P_{obsd}, mm.	1.42	2.90	5.37	8.14	12.5	22.4
P_{calcd}, mm.	1.42	3.03	5.33	8.15	12.5	22.4
	$(CH_3)_2NPCH_3CF_3$ (KKJ)					
Temp., °C.	0.0	10.5	20.0	24.8	41.5	64.5
P_{obsd}, mm.	12.3	22.4	37.1	47.3	101.8	252.3
P_{calcd}, mm	12.3	22.4	37.1	47.2	101.7	252.6
	$(CH_3)_2NPCF_3Cl$ (KKJ)					
Temp., °C.	0.00	5.4	34.6	50.2	69.7	74.9
P_{obsd}, mm.	5.47	7.61	37.50	77.06	170.8	207.7
P_{calcd}, mm.	5.45	7.63	37.50	77.06	170.8	207.6

Infrared Spectra

The significant frequencies (cm.$^{-1}$) of vapor phase infrared absorption observed for our ten new phosphines are listed for com-

Table VIII. Vapor Phase Infrared Spectra of Ten Phosphines

Group mode	CH_3CF_3PH	CH_3CF_3PCl	CH_3CF_3PI	$(CH_3CF_3P)_2$	$H_2NPCH_3CF_3$	$HN(PCH_3CF_3)_2$	$CH_3NHPCH_3CF_3$	$CH_3N(PCH_3CF_3)_2$	$(CH_3)_2NPCH_3$-CF_3	$(CH_3)_2NPCF_3$-Cl
N–H or P–H stretching	. . . R(nil) 2329Q(2.7) 2320P(2.3)	. . .	. . .	. . .	3496(3.4) 3391(1.1)	3385(0.8) 3341(0.6)	3498(0.26) 3460(0.86) 3400(0.39)	. . .	. . .	. . .
C—H stretching	3012sh(0.24) 3003R(0.27) 2994Q(0.30) 2986–91P(0.1) 2946R(0.35) 2929Q(0.52) 2933P(0.36) 2845(0.10)	3010R(0.097) 3000Q(0.102) 2993P(0.095) 2964(0.01) 2929(0.124) 2924(0.124) 2844(0.01) 2822(0.04)	. . . 2928(0.42) . . .	3002(0.45) 2934(0.90) 2835(0.22)	2995(0.8) 2988(0.9) 2925(0.63) 2832(0.20)	2991(0.8) 2924(0.46) 2820(0.07)	2995R(1.52) 2988Q(1.93) · · · P(nil) 2960(2.05) 2934(2.07) 2905(1.7) 2828(1.57)	3000(1.0) 2988(1.03) 2960(0.90) 2927(1.14) 2906sh(0.6) 2831(0.6)	3007sh(w) 2995(0.9) 2989(1.25) 2929(1.5) 2908(2.6) 2861(0.9) 2817(1.5) 2812sh(w)	2865(ms) 2720(ms)
N–H or P–H bending	1003R(0.80) 998Q(0.95) 994P(0.87)	. . .	. . .	. . .	1571(2.5)	(Too weak)	1570(0.30)	. . .	. . .	. . .
CH_3 deformations	1440R(0.70) 1434Q(0.85) 1427P(0.73) 1310R(0.27) 1303Q(0.35) 1294P(0.26) 1265(0.23)	1456sh(0.03) 1423(1.15) 1355(0.04) 1297(0.59) 1279(0.25) 1268(0.28)	1421(2.0) 1314(0.24) 1298R(0.89) 1294Q(1.1) 1291P(0.94) 1260(0.5)	1430(2.8) 1378(0.09) 1302(0.62) 1287(0.52) 1275(0.49)	1433R(1.1) 1427Q(1.5) 1420P(1.0) 1306R(0.67) 1299Q(0.82) 1293P(0.49) 1265(0.25)	1427(2.1) 1303(1.3) 1292sh(0.9) 1264(2.2)	1484(0.48) 1466R(0.54) 1460Q(0.66) 1456P(0.55) 1429(1.6) 1384(1.3) 1300m(0.90) 1265(0.43)	1425(2.92) 1300(1.66) 1265(0.84)	1477(0.10) 1469(0.07) 1460(0.61) 1454(0.24) 1428(0.77) 1279(2.6)	1480(m) 1460(m) 1290(ms)
C–F stretching	1189(13) 1183(24) 1175(20) 1141(68) 1137(55)	1181(17) 1160(25) 1132(22) 1126(22)	1169.5(64) 1157(70) 1121(70) 1118(70)	1141(61) 1125(58)	1194R(15) 1188Q(26) 1182P(19) 1135(28) 1124(34) 1115(33)	1186(27) 1138(32) 1123(33)	1181(19) 1133sh(23) 1121(36) 1114(31)	1177(27) 1128sh(50) 1120m(54)	1176(20) 1116(46) 1106sh(–)	1177(vs) 1137(vs) 1109sh(m)
CH_3 or NH_2 rocking or wagging, or P–N–P stretch	· · · R(nil) 900Q(2.1) · · · P(nil) 848R(3.0) 842Q(3.5) · · · P(nil)	906R(1.3) 901Q(2.55) 895P(1.4) 880R(2.0) 873Q(2.5) 869P(1.6)	903R(4.1) 900Q(6.7) 897P(4.3) 882R(7.1) 878Q(8.1) 875P(7.7)	902R(3.4) 888Q(4.9) 874P(2.5) 841–55(0.4)	894R(2.6) 889Q(4.1) 883P(3.1) 870sh(1.9) 845d(2.4)	917(12) 885(3.2) 871(7.2) 820(0.22)	891R(4.5) 885Q(4.9) 882P(3.8) 847(0.3) 827(0.17)	917sh(3.2) 899(9.6) 874(5.0) 847(14.4)	916(2.9) 880(3.4) 874(3.4)	890(vw) 865(w) 849(vw)
CF_3 symmetric deformation	748R(0.33) 742.5Q(0.50) 737.5P(0.48)	748R(0.23) 742Q(0.37) 737P(0.18)	742R(1.7) 739Q(1.8) 736P(1.75)	741R(1.53) 738Q(1.58) 735P(1.51)	(Not seen)	752(0.46) 735(0.61)	777m(1.60) 736(0.44)	733.5(0.72)	777(0.30)	733(w)
P–CH_3 stretching	698R(0.82) 691Q(0.98) 685P(0.65)	700d(1.7)	692(4.4)	695(1.2)	702(1.8)	702(2.5)	700.5(1.1)	702(2.26)	718(1.36)	690(ms)
CF_3 asymmetric deformation	539sh(0.24) 531R(0.28) 522Q(0.36) 518P(0.28)	545–7R(—) 516Q(5.6) 540P(—)	540(0.7) 518(0.4)–?	538(0.16)	574(0.72) 564(0.71) 546(1.0) 539(1.06)	546.5(2.05)	544.5(1.1) 535(1.03)–? 515(1.23)–?	543(0.7)	542(0.45)	. . .
P–N, P–Cl, or P–I stretching	. . .	519–22R(—) 516Q(1.4) 510–13P(—)	390(10)	. . .	998.5(1.8)	. . .	989(0.21)	. . .	988(8.1)	990(s)
P–CF_3 stretching	427R(1.2) 421Q(1.5) 415P(1.0)	425.3(0.39)	423(8.5) 418(9)	422.3(3.0)	431(3.0)	441(0.88) 431(0.77)	441(1.25)	453.5(2.22) 425sh(0.4)	451(1.32)	. . .
N–P–C characteristic	. . .	. . .	. . .	. . .	487(0.9) 393(1.8)	489(1.1) 385(0.27)	496(1.0) 388(1.4)	487(0.18) 381(1.5)	485(0.27) 377(0.8)	. . . . . .
P–CF_3 rocking or wagging	317(0.26)	329.5(0.39)	327(0.5)	320(0.5)	327m(2.4) 299(1.9) 245(1.3) 238(1.3)	342(1.2)	324R(0.60) 319Q(0.65) 313P(0.55)	346(0.85)	. . .	. . .

parison in Table VIII. For $(CH_3)_2NPCF_3Cl$ the instrument was the Perkin-Elmer Infracord (KKJ), but for the nine others the Beckman IR7 was employed with NaCl or CsI optics (ABB). Calibrations based upon known fine-structure peaks brought the uncertainty down to 0.5 cm.$^{-1}$ in the range below 800 cm.$^{-1}$ or to 1 cm.$^{-1}$ at higher frequencies, for all sufficiently well-defined peaks. However, some absorption maxima were broader than that (usually multiplets lacking resolution) and some P and R branches for the simpler compounds appeared as shoulders for which the significant frequencies could not be closely defined. The relative intensity of absorption, defined as $k = (100/PL) \log I_0/I$ for pressure of vapor P at 25° and path L (both in cm.) is shown in parentheses after each frequency. The k value represents the actual chart record of absorption at the indicated frequency, implying overestimation of the intrinsic intensity of any weak band superposed upon a branch of a stronger band; but the method does offer empirical reproducibility.

The "Group mode" column of Table VIII describes the vibrational modes to be expected in each frequency range, but the listed frequencies may often include unassigned minor peaks, or overtones enhanced by Fermi resonance. This effect makes specific identification difficult in some ranges; for example, sometimes the C–H stretching in the CH_3CF_3P unit has such low intensity that overtones and combinations are not to be sorted out. However, greater intensity does not necessarily identify C–H stretching in the $N-CH_3$ unit.

Methyl group rocking and wagging are fairly clear for the simpler compounds, but asymmetric P–N–P stretching can appear in the same region, and even symmetric P–N–P stretching might intrude if the P–N–P bond angle is sufficiently narrow. Or a peak at 527.5 (1.9) for $HN(PCH_3CF_3)_2$ and another at 585 (0.2) for $CH_3N(PCH_3CF_3)$ might be assigned to that mode. Rocking and wagging of the NH_2 group in $H_2NPCH_3CF_3$ were not clearly recognized, but could be confused with the similar CH_3 motions.

The $N-CH_3$ stretching mode might be expected in the range 1000–1100 cm.$^{-1}$ but was not to be found in that range for $CH_3NHPCH_3CF_3$. One might be tempted to assign it to a peak at 1080 (3.4) for $CH_3N(PCH_3CF_3)_2$, one at 1067 (0.7) for $(CH_3)_2NPCH_3CF_3$, and one at 1063 (m) for $(CH_3)_2NPCF_3Cl$, except that a Fermi-resonating overtone of CF_3 asymmetric deformation often is seen as just such a peak or shoulder, riding on the P branch of a C–F stretching band. Thus for CH_3CF_3PCl we find 1030 (0.06); or for CH_3CF_3PI, 1080 sh (1.4), 1074 (1.1), and 1013 (0.16); or for $(CH_3CF_3P)_2$, 1081 sh (1.1).

The five $N-PCH_3CF_3$ compounds have a common feature which is not immediately explained: peaks near 390 and 490 cm.$^{-1}$. These might represent some kind of coupled $N-P-CH_3$ vibration. Even less intelligible are the sigmoid absorptions shown by $CH_3NHPCH_3CF_3$, located roughly at 626 (0.32) and 593 (0.42). These may be related to the unassigned peaks 656 (0.80) for $(CH_3)_2NPCH_3CF_3$, 607 (0.24) and 585 (0.20) for $CH_3N(PCH_3CF_3)_2$, and 623 (0.83) and 648 sh (0.63) for $H_2NPCH_3CF_3$.

Still other peaks not included in Table VIII, and mostly assignable to overtones and combinations, are listed with intensities as follows (cm.$^{-1}$).

CH_3CF_3PH: 2267 (0.14), 1984 (0.07), 1923R (0.030), 1917Q (0.033), 1912P (0.030), 1871 (0.09).

CH_3CF_3PCl: 2343 (0.07), 2314 (0.12), 2240 (0.10), 2175–99 (0.27).

CH_3CF_3PI: 2328 (0.7), 2322 (0.5), 2216 (0.14), 1229 (0.2), 1213 (0.2), 841 (0.15), 794 (0.27), 776 (0.16).

$(CH_3CF_3P)_2$: 2335–2260 (sh, 0.18), 2243 (0.34), 2205 (0.14), 1017 (0.11).

$H_2NPCH_3CF_3$: 2440–20 (0.03), 2320–05 (0.12), 2279 (0.19), 2250 (0.11), 2225 (0.07).

$HN(PCH_3CF_3)_2$: 2355–2220 with maximum at 2260 (0.15), 960 (0.24).

$CH_3NHPCH_3CF_3$: 3344 (0.02), 2775 (0.17), 2758 (0.12), 2300 (0.13), 2244 (0.13), 2178 (0.09), 1995 (0.05), 1912 (0.05), 1850 (0.06).

$(CH_3)_2NPCH_3CF_3$: 2475 (0.07), 2383 (0.04), 2327 (0.04), 2293 (0.04), 2229 (0.04).

Some of the peaks of Table VIII were seen as closely spaced doublets or unresolved multiplets, and accordingly are marked d or m. Other abbreviations, such as sh for shoulder or parenthetical intensity estimates such as vw, w, m, ms, s, or vs, have the usual meanings.

Studies of Silicon–Nitrogen Compounds. The Base-Catalyzed Elimination of Silane from Trisilylamine[1,2]

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Abstract: The reactions of bases with trisilylamine have been studied, and it has been found that a reaction takes place in the liquid phase. Silane is always formed in these reactions, and under certain conditions N,N′,N″-trisilylcyclotrisilazane can be prepared. Kinetic studies and reactions utilizing labeled compounds have been carried out, and it has been shown that the elimination of silane from trisilylamine is base catalyzed and probably an intermolecular reaction.

Trisilylamine, $(SiH_3)_3N$, the only silylamine isolated from the reaction of excess silyl chloride with ammonia,[4,5] is a planar molecule[6] and exhibits very weakly basic properties.[5,7–9] These properties have been attributed to the partial double bond character of the silicon–nitrogen bond which results from the interaction between the electron pair of the nitrogen and the empty d orbitals of the silicon.[10–12]

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(4) A. Stock and C. Somieski, *Ber.*, **54**, 740 (1921).

(5) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 30.

(6) K. Hedburg, *J. Am. Chem. Soc.*, **77**, 6491 (1955).

(7) A. G. MacDiarmid, *Advan. Inorg. Chem. Radiochem.*, **3**, 207 (1961).

(8) A. B. Burg and E. S. Kuljian, *J. Am. Chem. Soc.*, **72**, 3103 (1950).

(9) S. Sujishi and S. Witz, *ibid.*, **76**, 4631 (1954).