system) the possibility that the rearrangements were caused by pyrolysis can be dismissed. It is probable that, as suggested earlier,[2] the rearrangements proceed through the interaction of the nonbonding p-orbital electrons on the fluorine atom with vacant d orbitals on the phosphorus. In the present case the transfer of fluorine to a distant phosphorus atom also appears to occur in transitions such as

$$(CF_3)_2PP(CF_3)_2^+ \longrightarrow CF_3PCF_2^+ + (CF_3)_2PF$$

which may indicate that the fluorine atoms of a CF_3 group attached to one phosphorus can interact with the d orbitals of the distant phosphorus atom.

Finally, this work should act as a warning that fluorocarbon derivatives are not solely characterized by normal bond breaking in the mass spectrometer since rearrangement of fluorine atoms can occur readily in phosphorus and arsenic compounds. Similar rearrangements may be anticipated in other fluorocarbon nonmetal and metal derivatives.

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Synthesis and Characterization of the Alkylhydridotrifluorophosphoranes CH_3PF_3H and $C_2H_5PF_3H^1$

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The compounds CH_3PF_3H and $C_2H_5PF_3H$ have been prepared by the reaction of the respective alkyltetrafluorophosphorane with trimethyltin hydride. These compounds are considerably more stable than HPF_4 and H_2PF_3 and may be manipulated and stored in Pyrex apparatus without decomposition. Infrared spectra and ^1H and ^{19}F nmr spectra at low temperatures confirm an equatorial-substituted trigonal-bipyramidal geometry for both alkylhydridofluorophosphoranes. At room temperature the nmr spectra indicate a substantial averaging of axial and equatorial fluorine atom environments owing to intramolecular exchange processes.

Ivanova and Kirsanov reported in 1961 the synthesis of three arylhydridotrifluorophosphoranes, $ArPF_3H$ (Ar = *p*-chlorophenyl, *p*-tolyl, and phenyl), by the oxidative reaction of KHF_2 with the respective aryldichlorophosphine.[2] The same reaction with alkyldichlorophosphines is reported in a patent[3] to yield alkylhydridotrifluorophosphoranes *in situ*. These products were not characterized, however, but were allowed to react with secondary amines giving a series of compounds of the general formula $RPF_2(NR'_2)H$ (R = CH_3, C_2H_5; R′ = CH_3, C_2H_5, *n*-C_4H_9). We wish now to report the synthesis and characterization of CH_3PF_3H and $C_2H_5PF_3H$ as relatively stable entities from the exchange reactions of CH_3PF_4 and $C_2H_5PF_4$, respectively, with $(CH_3)_3SnH$. These reactions are analogous to the reaction which we have recently reported for the preparation of HPF_4 and H_2PF_3.[4]

Evidence is also presented for the formation of $(CH_3)_2NPF_3H$ from the exchange reaction between $(CH_3)_2NPF_4$ and $(CH_3)_3SnH$. This compound could not be obtained in pure form, however.

Synthesis

A Pyrex-glass vacuum system of standard construction was used in this work. Stopcocks were greased with Apiezon-N grease. Quantities of volatile materials were measured in a calibrated volume on the line. Substances of low volatility were weighed in an ampoule and then transferred to the line.

Methyl- and ethyltetrafluorophosphoranes were prepared by the reaction of PF_5 and the respective tetraalkyltin compounds.[5] These starting materials were shown to be pure by comparison of observed vapor pressures with similar data for samples known to be pure. The vapor pressure data for pure CH_3PF_4 and $C_2H_5PF_4$, previously unreported, are given in Table I. Dimethylaminotetrafluorophosphorane was prepared by the method reported by Demitras, Kent, and MacDiarmid;[6,7] purity was verified by vapor pressure measurements (obsd, 40 mm at 0°; lit.,[8] 40 mm).

Trimethyltin hydride and triethyltin hydride were prepared from lithium aluminum hydride and the respective trialkyltin chloride or bromide.[9,10] Purity was ascertained by comparison of vapor pressures of samples with known values ($(CH_3)_3SnH$:

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TABLE I

PHYSICAL DATA FOR CH_3PF_4, $C_2H_5PF_4$, CH_3PF_3H, AND $C_2H_5PF_3H$

	P, mm			P, mm	
Temp, °C	Obsd	Calcd	Temp, °C	Obsd	Calcd
$CH_3PF_4(1)$[a]			$C_2H_5PF_4(1)$[c]		
−69.5[b]	5.2	5.2	−46.2	13.7	13.5
−63.2[b]	9.7	9.9	−37.4	24.0	24.0
−58.7[b]	15.4	15.2	−31.2	35.1	35.1
−45.7	39.0	39.4	−28.2	40.3	42.0
−41.9	50.2	50.2	−23.9	54.5	52.5
−38.1	94.0	93.4	$C_2H_5PF_3H(1)$[e]		
−24.1	134.4	140.8			
			−32.9	10.6	10.6
$CH_3PF_3H(1)$[d]			−29.8	13.2	13.0
−45.5	11.1	11.2	−26.9	16.1	15.7
−37.1	20.5	19.9	−26.4	16.3	16.2
−31.1	29.0	29.3	−22.4	19.5	20.9
−22.4	49.1	49.7	0	77.3	74.3
0	167	166	11.4	128.9	131.3

[a] Liquid: $\log P(\mathrm{mm}) = (-1448.9/T) + 7.9765$; solid: $\log P(\mathrm{mm}) = (-1880.8/T) + 6.7870$. Mp −52° (lit.[6] −50°); bp 11.7° (extrapolated) (lit.[6] 10–12°). $\Delta H_{\mathrm{vap}} = 6.6$ kcal/mole; Trouton's constant = 23.2 cal/mole deg. [b] Solid CH_3PF_4. [c] $\log P(\mathrm{mm}) = (-1522.8/T) + 7.8408$. Mp −70°; bp 33.9° (extrapolated) (lit.[6] 34–34.5°). $\Delta H_{\mathrm{vap}} = 7.0$ kcal/mole; Trouton's constant = 22.7 cal/mole deg. [d] $\log P(\mathrm{mm}) = (-1602.0/T) + 8.0866$. Bp 34.6° (extrapolated). $\Delta H_{\mathrm{vap}} = 7.3$ kcal/mole; Trouton's constant = 23.8 cal/mole deg. [e] $\log P(\mathrm{mm}) = (-1685.5/T) + 8.0425$. Bp 53.4° (extrapolated). $\Delta H_{\mathrm{vap}} = 7.7$ kcal/mole; Trouton's constant = 23.6 cal/mole deg.

70 mm at 0°; lit.,[11] 71 mm; $(C_2H_5)_3SnH$: 8 mm at 24.5°; lit.,[12] 8.3 mm). Tributyltin hydride was a commercial sample.[13]

Infrared spectra were recorded on a Perkin-Elmer Model 421 grating spectrophotometer for the region 4000–600 cm^{-1}; below 600 cm^{-1} data were obtained from a Beckman IR-10. Pyrex-glass cells of 10-cm length were used. In contrast to observation with HPF_4 and H_2PF_3,[4] very little decomposition of the samples occurred in the cell.

The Reaction of Trimethyltin Hydride and Methyltetrafluorophosphorane.—Trimethyltin hydride (26.6 mmoles) and CH_3PF_4 (26.6 mmoles) were condensed together in a 1-l. reaction bulb. On warming to room temperature a white solid slowly formed. After 1 hr the volatile products of this reaction were transferred to the vacuum system. Only a very small amount of noncondensable gas was present.

The volatile products were fractionated through a series of traps maintained at −64, −96, −112, and −196°. The −96 and −112° traps collected a total of 21.8 mmoles of the product CH_3PF_3H (82% yield). Vapor density measurements at 112 mm and 23° gave a moleculr weight of 104.7 (calcd for CH_4PF_3, 104.0). A small amount of material remained in the −64° trap. A gas-phase infrared spectrum of this fraction showed a P═O stretching band at 1360 cm^{-1}, similar to that found for $HPOF_2$[3] (1375 cm^{-1}). Although this compound was not characterized because of the small quantity of material involved, we believe it to be $CH_3PO(F)H$. The infrared spectra of the small amount of material which collected in the −196° trap corresponded with that of a mixture of SiF_4 and CH_3PH_2.[14,15]

The white, solid product obtained in this reaction was not examined in detail. Although it was primarily $(CH_3)_3SnF$, some phosphorus was always retained in the solid. The solid behaved in a manner similar to that of other solids observed in exchange reactions of PF_5;[3,4] it fumed slightly in air, evolving HF, and absorbed small quantities of gaseous NH_3.

If excess trimethyltin hydride was present, a second reaction occurred between this reagent and CH_3PF_3H. When a 250-ml reaction bulb containing 7.2 mmoles of CH_3PF_4 and 13.3 mmoles of $(CH_3)_3SnH$ was warmed to room temperature, the expected white solid accompanying the formation of CH_3PF_3H was observed. After 10 min a second noticeable solid formation occurred as the sides of the reaction bulb suddenly clouded over. When 30 min had elapsed, the bulb was opened to the line and the volatile components were collected at −196°. In contrast to the 1:1 reaction described above, this reaction produced a large amount of noncondensable gas which was removed by pumping through the collection trap. Fractionation of the volatile condensable products through −64, −112, and −196° traps produced less than 0.5 mmole of the P═O-containing compound in the −64° trap and 3.8 mmoles of CH_3PF_3H in the −112° trap. The −196° trap contained 2.6 mmoles of gaseous products. An infrared spectrum showed that this was predominantly CH_3PH_2 containing a trace of SiF_4.[12,13]

Infrared spectrum (cm^{-1}) of CH_3PF_3H (at 120 mm pressure, and at 10 mm for reported structure of very intense absorptions): 3090 vw, 3040 vw, 3005 vw, 2995 vw, 2635 vw, 2570 w, 2560 w, 2460 s, 2445 s, 2435 s, 1500 b, vw, 1432 m, 1418 m, 1388 sh, 1375 s, 1372 s, 1367 sh, 1360 sh, 1320 vs, b, 1292 sh, 1283 sh, 975 vs, b, 873 vs, 864 sh, 855 vs, 842 sh, 837 vs, 832 sh, 825 vs, 812 vs, 775 vs, b, 730 w, 697 w, 667 w, 605 s, 595 s, 465 vs, b.

The Reaction of Trimethyltin Hydride and Ethyltetrafluorophosphorane.—The reaction of $C_2H_5PF_4$ with $(CH_3)_3SnH$ was carried out using the same procedure as described above for the CH_3PF_4 reaction. On warming of a 500-ml reaction bulb containing 16.5 mmoles of $C_2H_5PF_4$ and 17.0 mmoles of $(CH_3)_3SnH$ to room temperature, a white solid was observed to form. After 30 min small amounts of yellow solid were discoloring the solid. The bulb was opened to the line and the volatile products condensed at −196°. There was no noncondensable gas. The volatile products were then fractionated through −22.4, −64, −96, and −196° traps. Small amounts of white solid appeared in the −22 and −64° traps but were not investigated. The −196° trap also collected a trace amount of gas which was discarded. A total of 13.8 mmoles (83% yield) of the product $C_2H_5PF_3H$ collected in the −96° trap. Vapor density measurements led to an observed molecular weight of 119.4 (calcd for $C_2H_6PF_3$, 118.0).

Infrared spectrum (cm^{-1}) (at 100 mm pressure, and at 8 mm for reported structures of very intense absorptions): 2995 s, 2970 s, 2900 s, 2555 w, 2430 s, 1470 s, 1425 m, 1365 m, 1285 m, 1245 m, 1026 vs, 1031 vs, 998 s, sh, 935 sh, 927 vs, 923 sh, 920 sh, 825 sh, 820 sh, 815 sh, 785 s, b, 675 w, 666 w, 592 s, 525 s, 470 vs, b, 310 s.

The Reaction of Trialkytin Hydrides with Dimethylaminotetrafluorophosphorane.—Equimolar amounts (10.0 mmoles) of $(CH_3)_2NPF_4$ and $(CH_3)_3SnH$ were condensed in a 250-ml reaction bulb at −196°. As the contents warmed to room temperature, a white solid formed. Volatile components were transferred to the line and several fractionations were attempted. However, it was found impossible to obtain a pure fraction of $(CH_3)_2NPF_3H$. The gas-phase infrared spectrum always showed a mixture of starting materials and $(CH_3)_2NPF_2$ in addition to the desired P–H-containing species (P–H band at 2455 cm^{-1}). The absorptions were so complex in the P–F region below 1000 cm^{-1} that the definite assignment of bands to PF_3 groups was difficult. However, by noting changes in band intensity with increased concentration of hydride, it appeared that the phosphorus hydride was present as $(CH_3)_2NPF_3H$.

The reactions of $(CH_3)_2NPF_4$ with two hydrides of lower volatility, $(C_2H_5)_3SnH$ and $(n\text{-}C_4H_9)_3SnH$, were investigated in order to avoid some of the separation problems which occurred with the complex mixture from the $(CH_3)_3SnH$–$(CH_3)_2NPF_4$ reaction. Triethyltin hydride (32 mmoles) was transferred as a liquid from an ampoule attached to the side of a 250-ml reaction

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bulb in which was contained 18 mmoles of $(CH_3)_2NPF_4$. The bulb was gently agitated for about 15 min to ensure complete mixing and then opened to the line. Volatile products were condensed into a −196° trap and then fractionated through −22.4, −78, and −196° traps. The excess hydride remained in the −22.4° trap. The −196° fraction measured less than 0.1 mmole and was discarded. The −78° fraction was a mixture and several fractionations could not purify it. A gas-phase infrared spectrum showed a peak at 2455 cm^{-1}, as in the case of the product mixture from the trimethyltin hydride reaction, again indicative of a P–H species. This spectrum also showed peaks for $(CH_3)_2NPF_2$ but there did not seem to be a noticeable amount of $(CH_3)_2NPF_4$. The relative intensity of the infrared bands suggested about a 50:50 mixture of $(CH_3)_2NPF_3H$ and $(CH_3)_2NPF_2$. Vapor density measurements indicated a molecular weight of 123 (calcd for $(CH_3)_2NPF_2$, 113; for $(CH_3)_2NPF_3H$, 133). As the samples stood at room temperature either within the vacuum line or in the infrared cells, a yellow solid formed and the P–H stretching mode absorption band steadily decreased in intensity. At the same time molecular weight determinations on the volatile contents slowly decreased.

Similar results were obtained for the products of the reaction of tributyltin hydride and $(CH_3)_2NPF_4$. If a large excess of either hydride was used, complete reduction of the phosphorane occurred and $(CH_3)_2NPF_2$ was the only condensable product identified.

Characterization

Vapor Pressure Studies.—After several refractionations, center cuts of the major fractions were used for vapor pressure studies. Purity was checked by measuring pressures in two different volumes and for different fractions of the sample being studied. During measurements, pressures were rechecked at −45 and −64° to be sure decomposition was not occurring. The linear equations reported were obtained from a least-squares treatment of the data. Table I lists the thermodynamic data obtained for CH_3PF_3H and $C_2H_5PF_3H$.

Mass Spectrographic Studies.—Mass spectrographic studies using a 70-ev source were run on both RPF_4 and RPF_3H compounds ($R = CH_3, C_2H_5$). In agreement with the data for HPF_4 and H_2PF_3[4] no parent ion could be seen for any of these substances. For the alkyltetrafluorophosphoranes the ion of major abundance was PF_4^+, probably formed in a process $RPF_4 + e \rightarrow PF_4^+ + R + e$, though the presence of relatively low intensity RPF_3^+ ions showed that the alternative process $RPF_4 + e \rightarrow RPF_3^+ + F\cdot + e$ (or F^-) did occur. For RPF_3H compounds the three related fragmentation patterns leading to RPF_3^+, HPF_3^+, and RPF_2H^+ all were seen to occur. Likewise in the mass spectra of HPF_4 and H_2PF_3[4] both PF_4^+ and HPF_3^+, and HPF_3^+ and $H_2PF_2^+$, respectively, were observed as primary peaks.

The data from this study and related studies will be presented at a later time.

Nmr Spectra.—Proton and ^{19}F nmr spectra of CH_3PF_3H and $C_2H_5PF_3H$ were run at several temperatures between −60 and +39°. The neat liquid samples were contained in Pyrex-glass tubes (5-mm o.d.) to which a small amount of NaF was added.[4] The ^{19}F nmr spectra were obtained on a Varian HR-60 spectrometer at 56.4 Mc; the ^1H spectra, on a Varian A-60A at 60 Mc. Table II lists the observed coupling constants and chemical shifts for CH_3PF_3H and $C_2H_5PF_3H$ as the neat liquids at −60°.

TABLE II

NMR DATA ON LIQUID CH_3PF_3H AND $C_2H_5PF_3$ AT −60°

	Chemical shift, ppm	
	CH_3PF_3H	$C_2H_5PF_3H$
$F_{ax}{}^a$	+14.4	+25.3
$F_{eq}{}^a$	+95.9	+98.9
$H_{P-H}{}^b$	+7.1	+7.4
$H_{CH_3}{}^b$	+1.7	+1.5
$H_{CH_2}{}^b$	...	+0.5
	Coupling constants,[c] cps	
	CH_3PF_3H	$C_2H_5PF_3H$
$J_{P-F_{ax}}$	(795)	(810)
$J_{P-F_{eq}}$	(965)	(976)
J_{P-H_P}	850	862
J_{P-HCH_3}	18	26.4
J_{P-HCH_2}	...	18.5
$J_{F_{ax}-H_P}$	120 (115)	121 (118.5)
$J_{F_{ax}-HCH_3}$	13 (12)	1.3
$J_{F_{ax}-HCH_2}$	...	(95)
$J_{F_{eq}-H_P}$	30 (26)	30 (28.7)
$J_{F_{eq}-HCH_3}$	4 (not resolved)	Not observed
$J_{F_{eq}-HCH_2}$	...	3.3 (4.4)
$J_{F_{ax}-F_{eq}}$	(19)	(22.7)
$J_{H_P-HCH_3}$	1.8	Not observed
$J_{H_P-HCH_2}$	...	1
$J_{HCH_3-HCH_2}$	...	7.5

[a] Relative to external CF_3COOH. [b] Relative to external $(CH_3)_4Si$. [c] Values obtained from the ^{19}F spectra are given in parentheses.

Discussion

The synthesis of alkylhydridotrifluorophosphoranes from trimethyltin hydride and alkyltetrafluorophosphoranes parallels the reaction we recently reported for the synthesis of HPF_4 and H_2PF_3.[4] This exchange reaction was somewhat slower, however, and could be run equally well with reagents in the liquid or gaseous state. This contrasts to the synthesis of HPF_4 and H_2PF_3 in which the reaction in a condensed phase gave very little of the desired products.

In the presence of excess trimethyltin hydride alkylhydridotrifluorophosphoranes were further reduced to phosphines. If 2:1 $R_3SnH:R'PF_4$ ratios were chosen, good yields of the phosphines $R'PH_2$ were obtained. This parallels our reported observations on the formation of phosphine from $(CH_3)_3SnH$ and PF_5 in a ratio greater than 2:1.

In contrast to the properties of HPF_4 or H_2PF_3, the alkylhydridotrifluorophosphoranes were relatively stable. Methylhydridotrifluorophosphorane could be handled without decomposition in a Pyrex line, and it could be stored in Pyrex ampoules at −10° without rapid decomposition.

Though we were able to observe $(CH_3)_2NPF_3H$ as a product of the reaction of $(CH_3)_2NPF_4$ and R_3SnH, we were never able to obtain this substance pure. The product mixture from this reaction contained $(CH_3)_2NPF_3H$ and either $(CH_3)_2NPF_4$ or $(CH_3)_2NPF_2$, the latter impurity always arising when an excess of the tin hydride was used. None of these substances was separable. The formation of $(CH_3)_2NPF_2$ from excess R_3SnH and $(CH_3)_2NPF_4$ is rather surprising, since the analogous reaction of alkyltetrafluorophosphorane leads to alkylphosphines.

The compound $(CH_3)_2NPF_3H$ is relatively unstable. One can observe this decomposition of a sample in a gas infrared cell over several minutes by the diminution of intensity of the γ_{P-H} band at 2455 cm^{-1}.

The characteristic P–H stretching frequency was observed at 2445 cm^{-1} for CH_3PF_3H and at 2430 cm^{-1} for $C_2H_5PF_3H$. These positions compare favorably to the values for HPF_4 (2465 cm^{-1}) and H_2PF_3 (2465, 2445 cm^{-1}). In the same region of the spectra of CH_3-PF_3H and $C_2H_5PF_3H$ a second band of considerably lower intensity was observed at 2565 and 2555 cm^{-1}, respectively. Analogous absorptions in HPF_4 and H_2PF_3 were tentatively assigned to a combination band.

The complexity of the spectra of the two compounds below 1000 cm^{-1} made assignments of these bands difficult, but in their over-all pattern a number of similarities with spectra of dialkyltrifluorophosphoranes could be seen.

Proceeding on the basis of an assumed equatorial-substituted trigonal-bipyramidal geometry, we found the low-temperature (−60°) ^{19}F and ^1H nmr spectra quite easy to interpret. For CH_3PF_3H the ^{19}F spectrum[16] consisted of two sets of resonances corresponding to axial and equatorial fluorine environments. Each set of resonances was a widely spaced doublet corresponding to spin–spin coupling of the fluorine atom with the phosphorus nuclear spin of $^1/_2$. For the equatorial fluorine resonance each component of the doublet was split into a pair of overlapping triplets owing to the couplings $J_{F_{eq}-H}$ (30 cps) and $J_{F_{eq}-F_{ax}}$ (19 cps). The axial fluorine resonance appeared as two doublets ($J_{P-F_{ax}}$, $J_{H-F_{ax}}$). There was additional structure observed also on each component of this multiplet which could be ascribed to overlapping 1,3,3,1 quartets ($J_{CH_3-F_{ax}}$, $J_{F_{eq}-F_{aq}}$).

The fluorine nmr spectrum at −60° for $C_2H_5PF_3H$ was rather similar to that for CH_3PF_3H. The only difference that arises is that coupling of both axial and equatorial fluorines to the methylene protons of the ethyl group is resolvable.

In the proton spectrum of CH_3PF_3H at −60° the resonances are sharp, and all possible coupling values could be observed. The single hydrogen atom bonded to phosphorus occurred as two groups of resonances separated by 850 cps (J_{P-H}). Each group of resonances (see Figure 1) consisted of a triplet of doublets ($J_{F_{ax}-H}$, $J_{F_{eq}-H}$), with further quartet structure visible on each peak (J_{CH_3-H}). The methyl proton resonance (Figure 2) was complex because it too showed all of the couplings expected. However, it is not difficult to break up this pattern, which is based on first-order couplings only, with a knowledge of some of the coupling constant values. One sees two overlapping sets of peaks (J_{P-CH_3} = 30 cps); each set of peaks involves a triplet ($J_{F_{ax}-CH_3}$ = 18 cps) of doublets ($J_{F_{eq}-CH_3}$ = 4 cps). Each component of the whole pattern is then split into a doublet (J_{CH_3-H} = 1.8 cps).

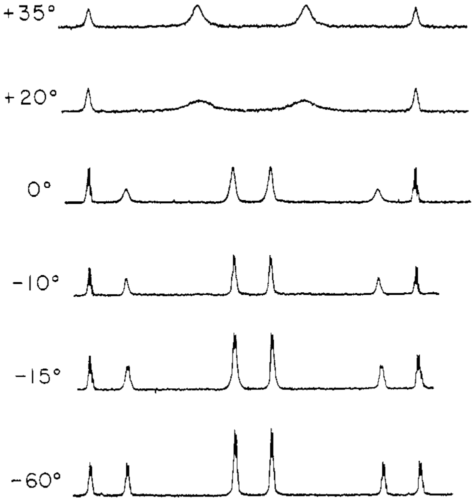

Figure 1.—Upfield half of the P–H pmr resonance in CH_3PF_3H at several temperatures.

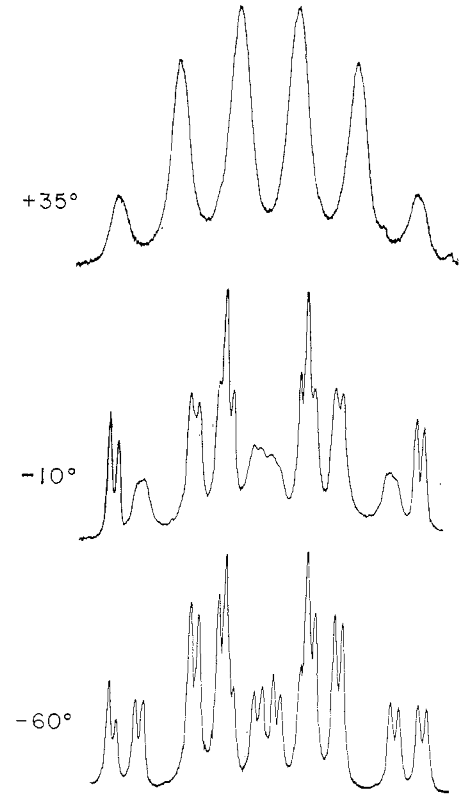

Figure 2.—Methyl pmr resonance in CH_3PF_3H at several temperatures.

The proton spectrum of $C_2H_5PF_3H$ at −60° was in most respects similar to that of CH_3PF_3H, with the exception that it is the methylene group which couples with phosphorus, axial and equatorial fluorines, and hydrogen. In addition $J_{CH_2-CH_3}$ and a small $J_{F_{ax}-CH_3}$ were observed. This resulted in a much more complex $-CH_2-$ proton resonance.

In both values of the fluorine chemical shifts and in the coupling constants $J_{P-F_{ax}}$, $J_{P-F_{eq}}$, $J_{F_{ax}-F_{eq}}$, $J_{F_{ax}-CH_n}$,

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(16) S. G. Pierce, Ph.D. Thesis, University of Wisconsin, 1967.

and $J_{F_{eq}-CH_n-}$, the spectra of CH_3PF_3H and $C_2H_5PF_3H$ observed correspond closely to those reported for other R_2PF_3 compounds (R = alkyl, aryl).[6] This lends further support to our assumed geometry for the RPF_3H systems.

At higher temperatures one could early see the effect of an intermolecular exchange process which at high enough temperatures leads to nmr equivalence of the axial and equatorial fluorines. In the ^{19}F nmr spectra of both CH_3PF_3H and $C_2H_5PF_3H$, this led to a gradual broadening of the resonances and loss of resolution. However, even at room temperature two broad doublets ($J_{P-F_{av}}$) corresponding to equatorial and axial fluorines were still observable, which suggests that equilibration is occurring at an intermediate rate with respect to the nmr time scale. The proton spectra for these two compounds proved much more interesting, however. The change observed for the upfield half of the hydrogen doublet in CH_3PF_3H as the temperature is raised from −60° to +39° is reproduced in Figure 1. At the higher temperature the proton resonance is a 1:3:3:1 quartet, due to coupling with the three equivalent fluorines. The methyl group proton is also considerably simplified at the higher temperature (Figure 2). The simple six-line pattern (1:3:4:4:3:1) evolves as two overlapping quartets ($J_{F_{av}-CH_3}$ = 9 cps; J_{P-CH_3} = 18 cps). All of the lines are somewhat broad at this temperature so that the smaller CH_3–H coupling of 1.8 cps, observable at lower temperatures, is not resolved.

Professor Cornwell of this department is continuing the study of the nmr spectra of these compounds.

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The Reaction of 1,1-Dimethylhydrazine with Gaseous Chloramine

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The reaction of 1,1-dimethylhydrazine with chloramine or a mixture of chloramine and ammonia yields 2,2-dimethyltriazanium chloride, $[(CH_3)_2N(NH_2)_2]^+Cl^-$. The sole solid by-product in this reaction is ammonium chloride, apparently formed by the decomposition of chloramine on the solid reaction product and possibly also by catalytic decomposition of chloramine by dimethylhydrazine. The dependence of the formation of 2,2-dimethyltriazanium chloride upon temperature, concentration, and reaction time has been investigated. Hydrogen-1 nmr and infrared spectroscopic evidence for the structure is given.

The recently discovered reactions of 2-dialkylamino-1,3,2-dioxophospholanes with a gaseous mixture of chloramine and excess ammonia[1] produced by the gas-phase chlorination of ammonia,[2] yielding 2,2-dialkytriazanium chlorides, led us to consider the reaction of 1,1-dialkylhydrazines with chloramine. Chloramination should yield the dialkyltriazanium chlorides in accordance with the equation

$$R_2N\text{-}NH_2 + NH_2Cl \longrightarrow [R_2N(NH_2)_2]^+Cl^-$$

It had previously been shown[3] that triazanium ion or triazane is a probable intermediate in the decomposition of hydrazine by chloramine in liquid ammonia and that the initial step in this process is probably represented by the equation

$$NH_2NH_2 + NH_2Cl \longrightarrow NH_2NH_2NH_2^+ + Cl^-$$

Triazanium salts with one or two unsubstituted amino groups, produced by amination of the corresponding hydrazines with hydroxylamine-O-sulfonic acid[4] or with 2-acyloxazirides,[5] were reported recently.

Since it has been shown that trialkylamines, ammonia, and chloramine combine to form trialkylhydrazinium chlorides,[6] it might be expected that the reaction of a dialkylhydrazine, chloramine, and ammonia would yield dialkyltriazanium chloride in an analogous manner. This communication reports the results of the study of the chloramination of 1,1-dimethylhydrazine. An account is also given of an attempt to isolate the postulated[3] triazanium chloride from the chloramine–hydrazine reaction mixture.

Experimental Section

Materials.—1,1-Dimethylhydrazine was obtained from Eastman Organic Chemicals, refluxed over potassium hydroxide, and distilled. Diethyl ether (anhydrous, Baker Analyzed reagent) was used as obtained. Anhydrous hydrazine was obtained from Matheson Coleman and Bell and used as obtained.

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