Dehydrofluorination of Amine Metalloid Fluorides. II.[1a] The Reaction of Phosphorus Pentafluoride with Primary Amines[1b]

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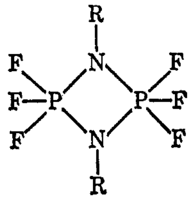
Phosphorus pentafluoride is shown to react with primary amines to give a variety of products depending upon the amine, solvent, and reaction conditions. An adduct was isolated from aniline, 2,6-dimethylaniline, and *n*-propylamine but could not be isolated from 2,6-diethylaniline or isopropylamine under the mildest conditions employed (0–10°) in heptane or benzene. Disproportionation of the adduct from aniline and *n*-propylamine in the presence of phosphorus pentafluoride gave the corresponding amine hexafluorophosphate salt and diazadiphosphetidine. Disproportionation of the adduct from more hindered amines such as 2,4-dimethylaniline, 2,6-dimethylaniline, and 2,6-diethylaniline gave the corresponding amine hexafluorophosphate salt and aminophosphorus tetrafluoride. Addition of triethylamine (or other tertiary amine) to the reaction of primary amines with phosphorus pentafluoride causes formation of diazadiphosphetidines from hindered as well as unhindered amines, with formation of the tertiary amine hexafluorophosphate salt. The infrared and ^{19}F nmr spectra are discussed for certain of the products. Dehydrofluorination of ammonia–phosphorus pentafluoride with triethylamine or diisopropylethylamine–phosphorus pentafluoride gives small yields of phosphonitrilic fluorides but the major product is an incompletely dehydrofluorinated oil.

This paper reports that portion of a general study of the dehydrofluorination of metalloid fluoride–amine systems involving the reactions of phosphorus pentafluoride with primary amines. Phosphorus pentafluoride is known to be a strong Lewis acid and thus to form adducts with Lewis bases.[2] These adducts are generally less stable than the corresponding boron trifluoride adducts possibly because of crowding around the phosphorus atom in the hexacoordinated state. The literature on phosphorus pentafluoride, as thoroughly reviewed by Schmutzler,[3,4] contains very little on the reaction of phosphorus pentafluoride and primary amines in marked contrast to the well-studied reactions of primary amines with phosphorus pentachloride.[5] Several primary amine adducts of phosphorus pentafluoride were reported[6] as curing agents for epoxy resins but synthetic and structural details are lacking. Phosphorus pentafluoride has been reported recently[7] to react with secondary amines according to eq 1. Tertiary amines form adducts with

$$R_2NH + PF_5 \longrightarrow R_2NPF_4 \text{ or } (R_2N)_2PF_3 + R_2NH_2{}^+PF_6{}^- \quad (1)$$

phosphorus pentafluoride but these are often highly dissociated.[2]

Our research shows that phosphorus pentafluoride reacts with primary amines (at times in the presence of a tertiary amine) to give 2,2,2,4,4,4-hexafluoro-2,2,4,4-tetrahydro-1,3-diorgano-1,3,2,4-diazadiphosphetidines (I), hereafter termed the cyclic dimer for simplicity, aminophosphorus tetrafluorides (II), and amine hexafluorophosphate salts (III), depending upon reaction conditions described later. There were indications that products such as $(RNH)_nPF_{5-n}$ and $RNH_3{}^+PF_5NHR^-$ may be formed but these were not characterized. The cyclic dimer (R = Ph) was also formed by dehydrofluorination of aniline–phosphorus pentafluoride with the adduct of boron trifluoride and diisopropylethylamine.



I

$RNHPF_4$

II

$RNH_3{}^+PF_6{}^-$

III

Amine hexafluorophosphate salts are well known, although there are surprisingly few reports of such salts of primary amines. There are no reports of primary aminophosphorus tetrafluorides in the literature. The cyclic dimer is well known for the corresponding phosphorus chlorine compounds[5] and there have been scattered reports of the fluorinated cyclic dimer. The fluorinated cyclic dimer has been prepared previously by (1) the reaction of phosphorus pentafluoride with heptamethyldisilazane,[8] (2) the fluorination of the chlorinated dimer,[9] or (3) the reaction of trimethylamine, methylamine, and phosphorus pentafluoride.[9] Procedure 3, which is analogous to our reactions using triethylamine, has not appeared in the published literature and became known to us after our research was completed.[4]

Results

A.—The reaction of phosphorus pentafluoride with primary amines is not so straightforward as the reaction of boron trifluoride with primary amines. Whereas boron trifluoride and amines almost invariably give the simple adduct,[10] the product isolated from the reaction of phosphorus pentafluoride and primary amines depends upon the amine and reaction conditions employed.

Isolation of the adduct required the proper combination of reaction time, temperature, and poor solvent for

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[1] (a) J. J. Harris and B. Rudner, *J. Amer. Chem. Soc.*, **90**, 515 (1968), is considered part I. (b) J. J. Harris and B. Rudner, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 25L. (c) To whom inquiries should be addressed.

[2] E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nucl. Chem.*, **16**, 52 (1960).

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[8] R. Schmutzler, *Chem. Comm.*, 19 (1965).

[9] P. Haasemann, Ph.D. Dissertation, Technische Hochschule, Stuttgart, Germany, 1963.

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the adduct, rapid addition of phosphorus pentafluoride, and/or less than stoichiometric quantities of phosphorus pentafluoride. The reaction with aniline was studied in some detail. At 6° the adduct was formed with very little side reaction upon either slow or rapid addition of phosphorus pentafluoride to the reaction mixture. However, at 25° rapid addition of phosphorus pentafluoride was necessary to minimize reaction of the adduct with excess aniline. Reaction of the adduct with aniline is postulated to occur according to eq 2 and 3.

$$RNH_2\cdot PF_5 + RNH_2 \longrightarrow RNH_3^+RNHPF_5^- \tag{2}$$

$$3RNH_2\cdot PF_5 + RNH_2 \longrightarrow 2RNH_3^+PF_6^- + (RNH)_2PF_3 \tag{3}$$

The aniline adduct could not be isolated when a marked deficiency of phosphorus pentafluoride was added and if the mixture was stirred several hours before work-up. Similarly the isolated aniline adduct was shown to react at 25° with excess aniline. The aniline adduct was similarly reactive when stirred at 25° in phosphorus pentafluoride which appeared to catalyze its disproportionation according to eq 4.

$$6RNH_2\cdot PF_5 \xrightarrow{PF_5} (RNPF_3)_2 + 4RNH_3^+PF_6^- \tag{4}$$

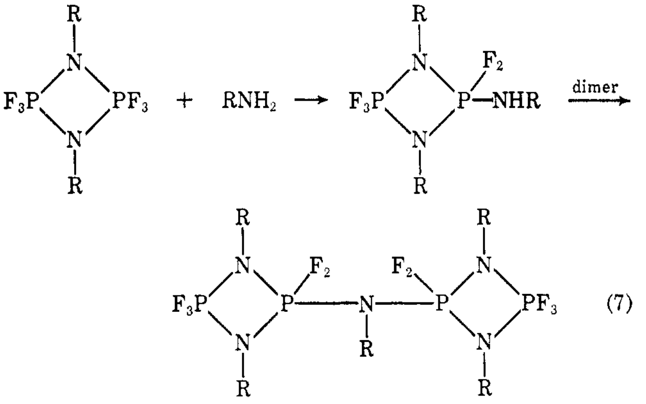
n-Propylamine also reacted according to eq 4 in excess phosphorus pentafluoride. The impure adduct was isolated when a stoichiometric quantity of phosphorus pentafluoride was used. Side reactions according to eq 2 and 3 were indicated. No adduct was isolated from the isopropylamine; reactivity according to eq 2 or 3 was indicated.

The hindered amines 2,6-diethyl- or 2,6-dimethylaniline reacted in a more straightforward manner. Although no adduct could be isolated from 2,6-diethylaniline, a product postulated to be the adduct was formed from 2,6-dimethylaniline by using a deficiency of phosphorus pentafluoride, a poor solvent for the adduct (heptane), and a short reaction time, and immediate separation of the adduct. Both amines reacted with either an excess or a deficiency of phosphorus pentafluoride according to eq 5. The adduct from these highly hindered amines then is not reactive toward excess amine, probably because of steric effects. Cyclic dimer is not formed even when the reaction mixture is refluxed for several hours. Failure to isolate the cyclic dimer does not arise from steric instability of the cyclic dimer since the cyclic dimers are formed in high yield in presence of tertiary amines as described later. Consequently, the lack of cyclic dimer formation must indicate an inability of the intermediate anilinophosphorus pentafluoride to react with itself or with adduct to form cyclic dimer.

$$2RNH_2 + 2PF_5 \longrightarrow RNH_3^+PF_6^- + RNHPF_4 \tag{5}$$

B.—Mixtures of primary amines and tertiary amines (usually triethylamine) in benzene react with phosphorus pentafluoride according to eq 6. The reaction, as indicated by isolation of triethylammonium hexafluorophosphate and soluble dehydrofluorination product, is almost quantitative. Small quantities of partially dehydrofluorinated product $RNHPF_4$ were found at times. The cyclic dimer is formed from all primary amines investigated even those with high steric requirements. Unhindered primary amine phosphorus pentafluoride adducts give, in nearly quantitative conversion, approximately equal quantities of cyclic dimer and higher condensation products. By contrast, the hindered 2,6-diethylaniline gives nearly quantitative yield of cyclic dimer. The greater yield of cyclic dimer from the sterically hindered amines reflects either the greater steric resistance to the formation of larger rings or linear chains or steric resistance to the condensation of the cyclic dimer with excess amine according to eq 7. Thus cyclic dimer (R = Ph) was shown to react with aniline to give higher condensation products. By contrast the cyclic dimer from 2,6-diethylaniline was recovered unchanged after being refluxed in benzene with excess 2,6-diethylaniline.

$$2RNH_2 + 4Et_3N + 6PF_5 \longrightarrow (RNPF_3)_2 + 4Et_3NH^+PF_6^- \tag{6}$$

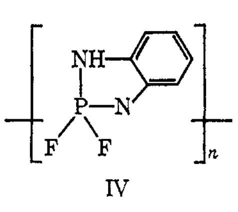


(7)

A detailed study of the efficiency of different tertiary amines was not made. Triethylamine was used in most instances. The relatively low melting point of the by-product triethylammonium hexafluorophosphate was a disadvantage in some instances since the salt served as a solvent for the dehyrofluorination product. In this respect diisopropylethylamine, which forms a much higher melting salt, gave much less trouble. Presumably other tertiary or secondary amines would function as the dehydrofluorinating agent.

C.—Dehydrofluorination was caused by amine complexes of other metalloid fluorides. Thus aniline phosphorus pentafluoride is dehydrofluorinated by the adduct of diisopropylethylamine boron trifluoride to give the cyclic dimer and other dehydrofluorination products.

D.—An attempt to dehydrofluorinate the *o*-phenylenediamine phosphorus pentafluoride adduct with triethylamine phosphorus pentafluoride, to give phosphobenzimidazole derivatives of type IV analogous to borabenzimidazole derivatives, was not successful. Although dehydrofluorination occurred, no well-defined aromatic products could be isolated.



IV

E.—Dehydrofluorination of ammonia–phosphorus pentafluoride with either the triethylamine or diisopropylethylamine adducts of phosphorus pentafluoride gives somewhat variable results. At times small yields of phosphonitrilic fluorides $(NPF_2)_n$ are obtained. However, the main product is an oil not readily separated from the by-product $Et_3NH^+PF_6$ salt. This oil had strong absorption at 1280–1250 and at 910–930 cm^{-1}. The oil likely contained incompletely dehydrofluorinated NH_3–PF_5 products, perhaps of the type $-\!(NHPF_3)\!-$. Since intermediate products of the type NH_2PF_4 may be volatile, more vigorous reactions in sealed systems is indicated.

Discussion

In summary the reaction of phosphorus pentafluoride with primary amines is relatively complex, particularly for nonhindered amines. The complexity of the reactions as described is probably due at least in part to the manner in which the reactions were run since the phosphorus pentafluoride was added to the amine, meaning that excess amine was present during most of the reaction. The reaction products from aniline, *e.g.*, adduct or cyclic dimer, were shown to be reactive to excess aniline. Similar reactivity of other primary amines such as *n*-propylamine was indicated. Thus revising the experimental setup so that primary amine is not present with the reaction products should give more straightforward results. Thus amine might be added slowly to a solution of the phosphorus pentafluoride–tetrahydrofuran adduct (or other suitable source of phosphorus pentafluoride).

No attempt was made to prepare and identify products of the type $(RNH)_nPF_{5-n}$. However products of this type were indicated to be present in reactions involving nonhindered amines such as aniline. Previous research[7] with secondary amines had indicated substitutions on the phosphorus of only one and two amino groups. The less hindered primary amines may give higher substitution and should be a fruitful area for further study.

Properties

A. 2,2,2,4,4,4-Hexafluoro-2,2,4,4-tetrahydro-1,3-organo-1,3,2,4-diazadiphosphetidine (Cyclic Dimer).—The cyclic dimers $(RNPF_3)_2$ were solids (except where R = *n*-propyl) sufficiently volatile to be purified by sublimation at reduced pressure. Sublimation of 2,6-disubstituted phenyl derivatives left negligible residue, but less hindered phenyl derivatives left resinous materials of higher molecular weight. The more hindered derivatives were thus more resistant to rearrangement to higher molecular weight products. This is consistent with the greater yields of cyclic dimer, compared with higher molecular weight resinous products, isolated from the preparations from 2,6-disubstituted anilines. The cyclic dimers in which R is aromatic could also be purified readily by recrystallization from dried aromatic solvents, such as benzene, in which they were only sparingly soluble at room temperature. The solubility of the products in polar solvents such as tetrahydrofuran was greater, but these were not used for crystallization because of their tendency to pick up moisture which reacts with the cyclic dimer. The compounds reported, except for the more volatile R = *n*-propyl one, did not fume and could be handled in air. However, exposure to air had to be brief since the products were attacked by atmospheric moisture. Analytical samples were handled under nitrogen. The melting points and volatilities are indicated in Table I.

Table I
Melting Point and Volatility of Cyclic Dimers $(RNPF_3)_2$

No.	R	Mp, °C	Sublimation temperature[a] or bp, °C (mm)
1	C_6H_5	198–205	Sublimes at 110–130 (0.4)
2	2,4-$Me_2C_6H_3$	164–168	Sublimes at 140–150 (0.4)
3	2,6-$Me_2C_6H_3$	255–257	Sublimes at 130 (0.05)
4	2,6-$Et_2C_6H_3$	151–152	Sublimes at 125 (0.025)
5	*n*-C_3H_7	4–7	Boils at 41 (4)
			Boils at 70–72 (21)
6	*t*-C_4H_9	70–72	Sublimes at 70 (4)

[a] The sublimation temperature refers to the bath temperature.

The chemical reactivity of the cyclic dimers was not studied in detail. However, the steric requirements of the organic group affected their stability. Thus cyclic dimer (R = Ph) reacted with aniline to form higher condensation products while cyclic dimer (R = 2,6-$Et_2C_6H_3$) did not react with excess 2,6-diethylaniline.

B. Aminophosphorus Tetrafluorides.—The aminophosphorus tetrafluorides $(RNHPF_4)$ had about the same volatility as the parent amine. Except where R is 2,6-diethylphenyl or 2,6-dimethylphenyl they decomposed to cyclic dimer (and other products) and amine hexafluorophosphate too rapidly for satisfactory analysis to be obtained. Small amounts of a product believed to be anilinophosphorus tetrafluoride were formed in the reaction with aniline, but this product was not characterized except by its infrared spectrum and is not included in Table II. The aminophosphorus tetrafluorides were readily soluble in aromatic or aliphatic hydrocarbon solvents and did not fume in air, except where R = *i*-C_3H_7. However, they were hydrolyzed slowly and exposure to atmospheric moisture was minimized. Properties are listed in Table II.

Table II
Melting Point and Volatility of Aminophosphorus Tetrafluorides $(RNHPF_4)$

No.	R	Mp, °C	Sublimation temperature[a] or bp, °C (mm)
1	2,4-$Me_2C_6H_3$	32–34	Boils at 42–44 (0.5)
2	2,6-$Me_2C_6H_3$	60–62	Sublimes at 60 (0.5)
3	2,6-$Et_2C_6H_3$	15–17	Boils at 63 (0.5)
4	*i*-C_3H_7		Boils at 37 (750)

[a] Sublimation temperature refers to bath temperature.

C. Adducts and Salts.—Several amine–phosphorus pentafluoride adducts were prepared as intermediates during the course of the investigation. The amine–phosphorus pentafluoride adducts were of somewhat limited stability and their isolation where bulky amines were used was not possible. Although the adducts were not well characterized and analyses were obtained in only a few instances, their identification as adducts is believed to be adequate, based on (1) the infrared spectra of the products as discussed in that section and (2) the stoichiometry of the reaction system. The adduct was considered to be formed only if no other products were present except unreacted amine and both amine and adduct were present in the correct weight ratio. Disproportionation of the adduct yields salt and dehydrofluorination products; hence the absence of these indicates the adduct formed has not reacted further. The primary amine adducts were slightly soluble to somewhat soluble in aromatic solvents. They did not fume in the atmosphere but did decompose; thus they could not be stored in glass because of severe etching.

The stability of the adducts which could be isolated was dependent upon the method of preparation and purity. A well-washed adduct of aniline (a) could be partially recovered after 6 hr of reflux in benzene and was only slightly decomposed on several days' storage while a sample (b) prepared in excess phosphorus pentafluoride decomposed in 2 days to salt and cyclic dimer. The adducts rearranged upon heating. The aniline adduct (b), for example, gave salt and cyclic dimer, when heated to 120° at reduced pressure. However, another sample of the aniline adduct (a) gave salt and a product postulated to be $PhNHPF_4$ when heated. Similarly the adduct from *n*-propylamine formed salt and dehydrofluorination products when heated.

A number of amine hexafluorophosphates were isolated as by-products during these reactions. These salts were not completely characterized by analysis although they were analyzed for the PF_6^- group by the Nitron reagent. The characterization as salts is warranted by these analyses and the following points: (1) infrared analysis as described in a following section, (2) solubility in water and insolubility in hydrocarbon, and (3) stoichiometry of the reaction. The salt was considered to be formed only if a corresponding quantity of characterized dehydrofluorination products was isolated. Their physical properties are given in Table III.

TABLE III

PROPERTIES OF AMINE–PHOSPHORUS PENTAFLUORIDE ADDUCTS AND AMINE HEXAFLUOROPHOSPHATE SALTS

No.	Amine	Adduct	Salt
1	$C_6H_5NH_2$	Mp 175–210° dec	Mp 250°, sublimes at 220° (1 atm); 140–160°(0.5 mm)
2	$2,4\text{-}Me_2C_6H_3NH_2$	Not isolated	Mp 194–198°
3	$2,6\text{-}Me_2C_6H_3NH_2$	Discolors at 200°, mp 235–240° dec	Mp 207°, sublimes at 160–180 (0.5 mm)
4	$2,6\text{-}Et_2C_6H_3NH_2$	Unstable	Mp 152–172°
5	$o\text{-}C_6H_4(NH_2)_2$	Mp 126–140°	
6	$n\text{-}C_3H_7NH_2$	Mp 110–120°, very hygroscopic	Mp 187–183°
7	Et_3N	Unstable	Mp 85–88°
8	$i\text{-}Pr_2EtN$	Unstable	Mp 195–204°
9	$i\text{-}PrNH_2$	Unstable	Mp 165–172°

^{19}F Nmr spectra.—The preference of compounds of the type $(RNPX_3)_n$ to exist as dimers rather than as trimers or tetramers as found, for example, for the phosphonitrilic compounds, raises interesting questions about the cyclic bonding orbitals used by the phosphorus atom. Formation of the cyclic phosphorus–nitrogen bonds from one axial and one equatorial bond from the ordinary pentacovalent phosphorus trigonal bipyramid would give a strain-free N–P–N bond angle of 90°. The three fluorine atoms should be at two equatorial and one axial positions and be readily distinguished by ^{19}F nmr analysis. Similarly, formation of the cyclic bonds from two equatorial phosphorus orbitals (which would introduce considerable strain) would leave one equatorially and two axially substituted fluorines, again distinguished by ^{19}F nmr spectroscopy. The analogous dimer $(MeNPCl_3)_2$ has the former configuration.[11] However, the cyclic dimers examined had only a single ^{19}F band indicating that the phosphorus fluorine bonding orbitals are being rapidly equilibrated. The phosphorus fluorine coupling constants for the cyclic dimers are shown in Table IV.

TABLE IV

P–F COUPLING CONSTANTS FOR DIMERS $(RNPF_3)_2$

R	P–F, cps
$n\text{-}C_3H_7$	897.2
C_6H_5	918.2
$2,4\text{-}Me_2C_6H_3$	914.0
$2,6\text{-}Me_2C_6H_3$	900

The coupling constants are intermediate between the normal equatorial phosphorus–fluorine[12] coupling constant of 950–990 cps and the normal axial coupling constant found near 800 cps. Thus it is reasonable to expect that a rapid equilibration of the phosphorus–fluorine bonding orbitals is occurring. The figures above are similar to that reported at 25° for the aliphatic cyclic compound $(CH_2)_4PF_3$, 915 cps.[13] In this instance rapid equilibration of the bonding orbitals was postulated to explain the fluorine equivalence.

The ^{19}F spectra of $2,6\text{-}Et_2C_6H_3NHPF_4$ contained three doublets, one twice as intense as the other two. The more intense set was spaced at 940 cps while the weaker doublets were spaced at 730 cps. The more intense set at 940 cps indicates two equivalent equatorial fluorine atoms. The weaker doublets at 730 cps indicate that the axial fluorines are not equivalent. It may be that the axial fluorine atoms are rendered slightly nonequivalent by the geometry of the 2,6-diethylanilino group attached to the phosphorus atom since rotation may be somewhat hindered. A satisfactory spectrum of $2,6\text{-}Me_2C_6H_3NHPF_4$ was not obtained because of insufficient solubility at room temperature.

Infrared Spectra.—The spectra were run in halocarbon from 5000 to 1330 cm^{-1} and from 1330 to 625 cm^{-1} in Nujol for crystalline products and on neat film for liquid products on a Beckman IR-5A calibrated with polystyrene film.

The varying products, *i.e.*, $R_3NH^+PF_6^-$, $RNH_2\text{–}PF_5$, $RNHPF_4$, and $(RNPF_3)_2$, reported here have infrared spectra which are quite useful in characterizing the products formed. The most significant bands were those in the NH and P–F regions as discussed for each class of compound in the following paragraphs.

The major infrared bands of the cyclic dimer are shown in Table V. The most important indication of dehydrofluorination to the cyclic dimer was the complete absence of bands in the 3200-cm^{-1} region which would indicate presence of NH bonds. All the cyclic dimers contained four very strong absorptions, two

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[11] L. G. Hoard and R. A. Jacobson, *J. Chem. Soc., Ser. A*, 1203 (1966).

[12] R. Schmutzler, *ibid.*, 4551 (1964).

[13] E. L. Mutterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

TABLE V

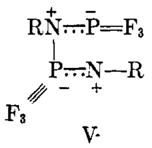
MAJOR INFRARED BANDS[a] OF CYCLIC DIMERS $(RNPF_3)_2$

R					
Phenyl	2,4-Dimethylphenyl	2,6-Dimethylphenyl	2,6-Diethylphenyl	*n*-Propyl	*t*-Butyl
1590 m					
1490 ms	1500 ms	1470 ms	1460 m		
1280 s	1282 d, s	1270 ms	1265 ms	1282 m	1245 ms
	1235 ms	1230 ms	1220 ms	1220 s	1190 ms
				1175 ms	
	1136 ms	1112 ms	1115 ms	1160 m	1136 m
1080 s	1070 ms	1071 ms	1075 ms	1050 m	1052 m
		1040 ms	1030 m		
962 s	967 s	978 m	975 m	975 s	941 s
911 s	919 s	932 s	942 s	922 s	917 s
			928 s	876 ms	
826 s	824 s	830 ms	830 s	841 s	840 ms
793 s	775 s	792 s	800 s	799 s	807 s
		781 s	777 s	781 ms	
754 m		732 m	747 ms		736 ms
693 m	722 m	718 m	713 ms		

[a] Absorptions are given in cm^{-1}; carbon–hydrogen absorptions at 2800 and 1420 cm^{-1} have been omitted.

between 980 and 910 cm^{-1} and two between 850 and 790 cm^{-1}. The absorptions are undoubtedly associated with the phosphorus–fluorine and perhaps the phosphorus–nitrogen bonds. Detailed analysis of the spectra is not attempted here, but it should be noted that the highest of these bands, near 980 cm^{-1}, is at somewhat higher frequency than the upper limit of 940 cm^{-1} reported for the phosphorus–fluorine absorptions in a large number of pentacovalent phosphorus fluorine compounds.[14] These authors did not include the pentacovalent but tetracoordinated phosphonitrilic fluorides which have phosphorus–fluorine absorptions at 980 cm^{-1}.[15] If the cyclic dimers follow the absorption patterns of other pentacovalent, pentacoordinated phosphorus compounds, the phosphorus–nitrogen ring frequency is probably near 980 cm^{-1}. However, the infrared spectrum of $(MeNPCl_3)_2$ shows only a single strong band, previously suggested[16] to be the phosphorus–nitrogen ring vibration, located at 847 cm^{-1}, in the region from 980 to 790 cm^{-1}. Thus one might assign the phosphorus–nitrogen ring frequency in the compounds reported here to the band found near 830 cm^{-1}. Since this frequency is in the absorption region of phosphorus–fluorine bonds, extensive coupling would be expected; so it may not be meaningful to consider separate phosphorus–nitrogen and fluorine–phosphorus absorptions for this system.

Assignment of the ring phosphorus–nitrogen vibrations to strong bands appearing at somewhat higher frequencies is possible, if one would accept the premise that the ring bond strength is considerably influenced by the ability of the nitrogen atom to donate its electrons to the ring. This premise would seem to be established[17] by the effect of amine base strength on dimer formation and stability and reported delocalization of the nitrogen lone pair for $(Cl_3PNMe)_2$,[16] but is contradictory to findings that there is no delocalization of the nitrogen atom lone pair for $(F_3PNMe)_2$.[8] From the effect of base strength on dimer stability we would assign the phosphorus–nitrogen ring vibrations to a very strong absorption at 1220 for N-propyl, to 1135 for N-*t*-butyl whose ring strength might be weakened by steric factors, and to bands in the 1110–1075-cm^{-1} region for the N-aromatic derivatives where the nitrogen atom should be much less basic. These latter assignments are somewhat intermediate between absorptions expected for complete double-bond character as in the phosphonitrilic fluorides[18] which have ring frequencies at 1287–1439 cm^{-1} and that expected for phosphorus–nitrogen single bonds[19] and are thus reasonable since one might expect significant contributions from structures such as V. In addition to the bands mentioned above, a strong



V.

doublet at 1230 and 1270 cm^{-1} was found in the case when R was 2,4-dimethylphenyl, 2,6-dimethylphenyl, and 2,6-diethylphenyl.

The aminophosphorus tetrafluorides were readily characterized by their lack of absorption in the NH_2 region near 1600, coupled with a sharp absorption near 3350 cm^{-1}, characteristic of a single N–H bond. The 3350-cm^{-1} band in the 2,4-dimethylphenyl and 2,6-diethylphenyl derivatives appeared as a very sharp doublet (readily distinguishable from the much broader NH_2 doublet in the same region). Since the compounds were indicated to be pure by vpc, the splitting must be caused by positional isomerization of the NH group with respect to the remainder of the molecule, which is caused perhaps by restriction of the phenyl group rotation by its *ortho* substituent. The aromatic aminophosphorus tetrafluorides had absorption bands in common at 1260, 1040, and 940 and a very intense band at 860 cm^{-1}. The isopropyl derivative had bands at 1110 and 940 and a very strong band at 860 cm^{-1}. The 1260-cm^{-1} band is probably derived from phenyl nitrogen stretching vibrations, whereas bands at 940 cm^{-1} and 860 are derived from phosphorus fluorine vibrations. However, the band at 1040 cm^{-1} (or 1110 cm^{-1} for the isopropyl derivative) seems to be of too high frequency to be derived from the phosphorus–fluorine vibrations and would most likely be assigned to the nitrogen–phosphorus vibration. Assignment of the band to this bond indicates considerable double-bond character to the nitrogen phosphorus bond. The double-bond character would be sensitive to the basicity of the amine, since more strongly basic amines should increase the double-bond character of the nitrogen–phosphorus bond. Thus the absorption frequency changes from 1040 (for aromatic compounds) to 1110 cm^{-1} (for an aliphatic product). The principal absorption bands are shown in Table VI.

The infrared spectra of the amine hexafluorophosphate salts had several distinctive characteristics. The most important band was a very strong absorption at 860–810 cm^{-1} which, upon sample dilution, gave a

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(16) A. C. Chapman, W. S. Holmes, N. L. Paddock, and H. T. Searle, *ibid.*, 1825 (1961).

(17) I. N. Zhmurooa and B. S. Drach, *Zh. Obshch. Khim.*, **39**, 1441 (1964).

(18) A. C. Chapman, N. L. Paddock, D. H. Paine, H. T. Searle, and D. R. Smith, *J. Chem. Soc.*, 3608 (1960).

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TABLE VI

MAJOR INFRARED BANDS[a] OF AMINOPHOSPHORUS TETRAFLUORIDE

Amine			
2,6-Diethylaniline	2,6-Dimethylaniline	2,4-Dimethylaniline	Isopropylamine
3400 m	3350 m	3400 m	3420 m
3360 m		3350 m	
1270 m	1265 m	1265 m	1178 s
1205 m	1218 ms	1225 m	1160 ms
1115 m	1101 s	1130 m	1136 m
1052 s	1042 s	1043 vs	1108 s
1032 ms	1028 s		
941 s	948 s	941 vs	940 vs
857 vs	863 vs	860 vs	845 vs
820 ms	810 s	845 s	
801 m	780 s	782 m	794 m
760 m			
749 m			

[a] Absorptions are given in cm^{-1}; carbon-hydrogen bands at 2800 and 1420 cm^{-1} have been omitted.

single maximum between 840 and 828 cm^{-1}. Although the other products reported here also had absorptions in this region, these were less intense and were composed of several bands. Also present was a weaker, but still strong band at 741-747 cm^{-1}. Each of these bands has been reported[20] to be characteristic of the PF_6^- anion. The primary amine salts had absorptions at 1600 cm^{-1} characteristic of NH_3 groups and a strong absorption in the nonbonded N-H stretching region at 3200 cm^{-1}, which could not be resolved by sample dilution. The salts had none of the bonded N-H absorptions from 2500 to 2800 cm^{-1} usually present in amine salts, since the large hexafluorophosphate anion is capable of only weak coordination to the amine.

The primary amine phosphorus pentafluoride adducts were readily distinguished from the hexafluorophosphate salts at two points in the spectra. The N-H absorption at 3200 cm^{-1} could be resolved into a doublet for the adduct, but not for the salt. Again although the adducts had strong absorptions in the 830-900-cm^{-1} region, as did the salt, these absorptions gave several peaks when the sample was diluted. The spectra of the amine salts and adducts are listed in Tables VII and VIII.

Experimental Section

Reagents.—Phosphorus pentafluoride was obtained during the early stage of this research by the decomposition at 160-180° of Phosfluorogen (*p*-chlorophenyldiazonium hexafluorophosphate) from Ozark-Mahoning Co. More recently it was obtained in cylinders from Ozark-Mahoning Co. or the Matheson Co. Diisopropylethylamine was obtained from Aldrich Chemical Co. Depending upon volatility amines were distilled from potassium hydroxide pellets onto calcium hydride either in an atmosphere of N_2 or at reduced pressures. Solvents such as benzene or heptane were *in situ* by azeotroping them in the reaction flask, then cooling under N_2.

Procedure.—Standard laboratory three-necked flasks and Trubore stirrers were used. The reaction vessel was thoroughly flushed with dry N_2 and vented only to dry N_2. During phosphorus pentafluoride addition the flask was vented to a N_2 stream through a mineral oil bubbler which served to indicate phosphorus pentafluoride absorption by the reaction mixture. All filtrations were done in sintered-glass pressure funnels under N_2.

TABLE VII

MAJOR INFRARED BANDS[a] OF PHOSPHORUS PENTAFLUORIDE-AMINE ADDUCTS

Aniline	2,6-Dimethylaniline	*n*-Propylamine
3250 d, m	3270 d, m	3290 s
3110 w		2525 s
1600 w	1505 m	
1575 m	1560 m	1640 s
		1600 s
1475 mw		1510 m
1495 mw		
1320 s		
	1295 s	
1080 m	1173 m	1190 m
920 s	1098 m	1050 m
892 vs	1037 m	1018 m
848 s	939 s	862 s, sh
835 s	892 vs	840 vs
812 s	872 vs	748 s
798 vs	820 vs	
766 m	770 m	
	715 m	
692 s		

[a] Absorptions are given in cm^{-1}; carbon-hydrogen bands at 2800 and 1420 cm^{-1} have been omitted.

In a typical experiment 50 ml of benzene was distilled from 300 ml of benzene contained in a 500-ml flask. After the flask and contents had cooled the amine was transferred to the flask by pipetting under the benzene in the N_2-flushed flask. The flask contents were then stirred rapidly while phosphorus pentafluoride was admitted at a rate that gave slow or no gas evolution at the exit bubbler. It was necessary to cool the flask at this time since the reaction is quite rapid and exothermic. After phosphorus pentafluoride addition was completed the flask was warmed to reaction temperature (except in a few instances where the mixture was filtered cold). After reaction was completed the system was flushed with N_2 to remove excess phosphorus pentafluoride and the reaction mixture was filtered. Generally, the solvent-insoluble solids contained salt or adduct while the filtrate contained dehydrofluorination products and/or excess amine.

Reaction of Aniline and Phosphorus Pentafluoride. A. In Absence of Tertiary Amine.—Aniline was treated with phosphorus pentafluoride under different conditions as listed in Table IX. It is apparent from Table IX that the initial adduct is reactive toward either aniline or phosphorus pentafluoride.

A sample of the cyclic dimer 2,2,2,4,4,4-hexafluoro-2,2,4,4-tetrahydro-1,3-diphenyl-1,3,2-4-diazadiphosphetidine was analyzed.

Anal. Calcd. for $C_{12}H_{10}N_2P_2F_6$: C, 40.25; H, 2.78; N, 7.82; P, 17.30; F, 31.83. Found: C, 40.04; H, 2.89; N, 7.73; P, 17.46; F, 31.66.

The adduct was also analyzed.

Anal. Calcd. for $C_6H_7NPF_5$: N, 6.57; P, 13.9; F, 43.4. Found: N, 6.39; P, 14.1; F, 43.4.

Analyses[21] of the anilinium hexafluorophosphate for the hexafluorophosphate anion indicated 60.77% PF_6^- (theory, 60.63%).

The stability of the adduct depended upon its method of preparation and purity. Adduct contaminated with salt was recovered from refluxing benzene. However, adduct prepared with a deficiency or equal quantity of phosphorus pentafluoride decomposed according to eq 4 in the text when refluxed in benzene or heated at reduced pressure. (This conclusion is tentative since $PhNHPF_4$ was inferred from the spectra and volatility but not analyzed; salt $PhNH_3^+PF_6^-$ was isolated and analyzed.) Adduct prepared in excess phosphorus pentafluoride decomposed to salt and cyclic dimer when refluxed in benzene, heated in N_2 at 165°, or heated at reduced pressure to 120°. Apparently small quantities of residual aniline (or phosphorus pentafluoride to which the analytical methods and spectra are not sensitive) changes the stability and mode of decomposition of the adduct.

Refluxing 0.35 g (0.001 mol) of $(PhNPF_3)_2$ with 0.1 g (0.00107 mol) of aniline in 25 ml of benzene for 2 hr left 0.45 g of benzene-soluble solids containing none of the starting cyclic dimer.

B. In Presence of Triethylamine.—Aniline (8.4 g, 0.07 mol) and triethylamine (18.2 g, 0.181 mol) in 250 ml of benzene were

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(20) R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1959).

(21) H. E. Affsprung and V. S. Archer, *Anal. Chem.*, **35**, 976 (1963).

TABLE VIII

MAJOR INFRARED BANDS[a] OF AMINE HEXAFLUOROPHOSPHATE SALTS

n-Propylamine	Isopropylamine	*t*-Butylamine	Triethylamine	Aniline	2,4-Dimethylaniline	2,6-Dimethylaniline	2,6-Diethylaniline
3270 ms	3270 ms	3250 m	3200 s	3210 s	3200 s	3210 s	3200 s
1600 ms	1605 s	1610 m		1580 s	1590 m	1640 m	1620 ms
				1515 m		1590 m	1590 ms
				1492 m	1493 s	1490 s	1497 s
		1300 s					
	1210 s	1215 ms	1190 mw				
	1160 m	1140 ms	1168 m				
	1135 m		1062 ms	1088 m	1040 m	1100 m	1100 m
1009 m			1030 s				990 m
985 m	985 m					862 s	862 s
822 vs	835 vs	832 vs	840 vs	828 vs	833 vs	830 s	830 vs
753 m	740 m	740 m	740 m	740 m	740 m	770 m	742 m
				685 m		740 m	

[a] Absorptions are given in cm^{-1}; carbon–hydrogen bands at 2800 and 1420 cm^{-1} have been omitted.

TABLE IX

REACTION OF ANILINE WITH PHOSPHORUS PENTAFLUORIDE

Aniline, g	PF_5	Time, min (temperature, °C)	Subsequent reaction time, min (temperature, °C)	Products
25.6	Deficient	15 (0)	None	Adduct 45.6 g, 100%; recovered aniline 6.0 g
10.2	Equal	10 (0–5)	10 (5)	Adduct 20.4 g, 90%; 1 g of others
33.6	Equal	30 (0)	8 hr (25)	Adduct 64.7 g, 82%; 6.3 g of oils, aniline + others
1.02	Equal	60 (5)	None	Adduct 2.3 g, 100%
10.2	Deficient	2.5 hr (25)	8 hr (25)	5.8 g of $PhNH_3^+PF_6^-$, 11.2 g of soluble products, possibly $PhNH_3^+PF_5PhNH$ and $(PhNH)_2PF_3$
1.02	Equal	3 (25)	None	Adduct 2.2 g, 92%
5.1	Excess	10 (0)	10 (0)	Adduct 85%; decomposed in 2 days to dimer and salt
10.2	Excess	30 (25)	8 hr (25)	$PhNH_3^+PF_6$ 15.2 g, 86%; cyclic dimer 5.6 g, 86%

treated with phosphorus pentafluoride at 25° giving 42.2 g (0.172 mol, 95% yield) of insoluble white solids, mp 80°, triethylammonium hexafluorophosphate, and 14.4 g of $(PhNPF_3)_n$ dehydrofluorination product. The latter was sublimed to give 7.8 g (0.0218 mol, 48.5% yield) of cyclic dimer. The remaining product (6.6 g) could not be distilled at 0.5 mm to 225°. Ebullioscopic molecular weight of the residue was 703. The infrared spectrum of the residue indicated weak NH and PF_4 bands, perhaps as end groups.

Analysis of triethylammonium hexafluorophosphate for the hexafluorophosphate anion indicated 58.50% PF_6^- (theory, 58.87%).

Reaction of the Adduct of Aniline and Phosphorus Pentafluoride with Diisopropylethylamine Boron Trifluoride.—A stirred solution of 38.6 g (0.196 mol) of diisopropylethylamine boron trifluoride in 250 ml of benzene was allowed to react at 25–35° with 20.0 g (0.0197 mol) of aniline phosphorus pentafluoride from a solids addition funnel. Recovered were 43.4 g of insoluble solids, mainly diisopropylethylammonium tetrafluoroborate[22] (0.200 mol, 100+% yield) and 11.9 g of crude dehydrofluorination product $(PhNPF_3)_n$. Purification gave 4.5 g (0.0126 mol, 25% yield) of cyclic dimer. The remaining product was higher molecular weight oils.

Reaction of 2,4-Dimethylaniline and Phosphorus Pentafluoride. A. In Absence of Tertiary Amine.—Reaction of 9.78 g (0.0806 mol) of 2,4-dimethylaniline with excess phosphorus pentafluoride in 250 ml of benzene followed by 4 hr of refluxing gave 10.4 g (0.0389 mol, 96.7% yield) of benzene-insoluble 2,4-dimethylanilinium hexafluorophosphate and 8.7 g (0.0384 mol, 95.5% yield) of crude 2,4-dimethylanilinophosphorus tetrafluoride. Distillation of the crude material at 60° (5 mm) gave 5.0 g (0.022 mol, 55% yield) of 2,4-dimethylanilinophosphorus tetrafluoride.

Anal. Calcd for $C_8H_{10}NPF_4$: N, 6.17; P, 13.64; F, 33.46. Found: N, 6.24; P, 13.74; F, 32.75.

The distillation residue contained 2,4-dimethylanilinium hexafluorophosphate, cyclic dimer described below, and an oil, bp 140° (0.1 mm). The oil was not characterized but had an infrared spectrum consistent with the structure $(ArNH)_2PF_3$.

Analysis of 2,4-dimethylanilinium hexafluorophosphate for the hexafluorophosphate group indicated 54.74% PF_6^- (theory, 54.26%).

B. In Presence of Triethylamine.—Reaction of 10.9 g (0.09 mol) of 2,4-dimethylaniline and 18.2 g (0.181 mol) of triethylamine in 125 ml of benzene with phosphorus pentafluoride at 25° gave 42.4 g (0.172 mol, 95% yield) of triethylammonium hexafluorophosphate and 20.0 g of benzene-soluble liquid–solids. Heating the latter at 0.5 mm caused distillation of a small quantity of 2,4-dimethylanilinophosphorus tetrafluoride (see above) at 42–44°. At 140–150° there was sublimed 15.8 g (0.0382 mol, 85% yield) of 2,2,2,4,4,4-hexafluoro-2,2,4,4-tetrahydro-1,3-bis(2,4-dimethylphenyl)-1,3,2,4-diazadiphosphetidine.

Anal. Calcd for $C_{16}H_{18}N_2P_2F_6$: C, 46.39; H, 4.38; N, 6.76; P, 14.96; F, 27.52; mol wt, 414.3. Found: C, 46.38; H, 4.56; N, 6.99; P, 14.94; F, 27.48; mol wt, 413 (ebullioscopic).

Reaction of 2,6-Dimethylaniline with Phosphorus Pentafluoride. A. In Absence of Tertiary Amine.—A solution of 9.8 g (0.081 mol) of 2,6-dimethylaniline in 150 ml of benzene was allowed to react at 25° with phosphorus pentafluoride, then refluxed for 5 hr. Recovered were 10.8 g (0.0405 mol, 100% yield) of benzene-insoluble 2,6-dimethylanilinium hexafluorophosphate, subliming unchanged at 160–180° (0.5 mm), and 8.9 g (0.0392 mol, 97% yield) of 2,6-dimethylanilinophosphorus tetrafluoride. There was no evidence for formation of the completely dehyrofluorinated cyclic dimer.

Anal. Calcd for $C_8H_{10}NPF_4$: C, 42.30; H, 4.44; N, 6.17; P, 16.64; F, 33.46. Found: C, 42.75; H, 4.61; N, 6.15; P, 16.35; F, 33.47.

Analysis of 2,6-dimethylanilinium hexafluorophosphate for the hexafluorophosphate anion indicated 54.42% PF_6^- (theory, 54.26%).

Stopping the reaction of 9.8 g (0.081 mol) of 2,6-dimethylaniline in 125 ml of benzene with phosphorus pentafluoride while absorption was rapid and filtering immediately gave 5.7 g (0.0207 mol, 26.6% yield) of solid 2,6-dimethylaniline phosphorus pentafluoride adduct. The filtrate in which solids had formed soon after filtration gave, after standing 6 hr, 6.1 g (0.0228 mol, 28% yield) of 2,6-dimethylanilinium hexafluorophosphate and 5.8 g (0.0255 mol, 31.5% yield) of crude 2,6-dimethylanilinophosphorus tetrafluoride. Apparently the adduct is somewhat

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[22] J. J. Harris, *Inorg. Chem.*, 5, 1627 (1966).

soluble in benzene and disproportionates upon standing. Repeating the above reaction in heptane at 15° gave 7.0 g (0.0254 mol, 31%) of heptane-insoluble adduct. The filtrate contained only 6.73 g (0.0556 mol) of unreacted 2,6-dimethylaniline. The adduct, being heptane insoluble, precipitates immediately and further reaction was stopped.

2. **In Presence of Triethylamine.**—Addition of phosphorus pentafluoride to 14.1 g (0.121 mol) of 2,6-dimethylaniline and 26.4 g (0.26 mol) of triethylamine in 250 ml of benzene until its absorption was complete at room temperature, followed by refluxing for 3 hr, gave a tan oil and a clear supernatant liquid. The reaction mixture, cooled without stirring, formed a solid cake from the bottom oil and 15.2 g of long white needles in the top layer. Refluxing the oil with fresh benzene gave recovery of 6.5 g of additional product for a total recovery of 21.7 g (0.0525 mol, 86.5% yield) of 2,2,2,4,4,4-hexafluoro-2,2,4,4-tetrahydro-1,3-bis(2,6-dimethylphenyl)-1,3,2,4-diazadiphosphetidine.

Anal. Calcd for $C_{16}H_{18}N_2P_2F_6$: C, 46.39; H, 4.38; N, 6.76; P, 14.95; F, 27.52; mol wt, 414.3. Found: C, 46.97; H, 4.61; N, 6.47; P, 15.07; F, 27.03; mol wt, 398 (ebullioscopic).

The dimer sublimed leaving no appreciable residue; hence significant quantities of higher molecular weight products were absent. The solid formed when the bottom layer oil from the reaction was cooled to room temperature gave 62.3 g (0.253 mol, 100% yield based on 2,6-dimethylaniline) of triethylammonium hexafluorophosphate.

Reaction of 2,6-Diethylaniline with Phosphorus Pentafluoride. A. In Absence of Tertiary Amine.—Phosphorus pentafluoride was added at 25° to 9.5 g (0.0637 mol) of 2,6-diethylaniline in 250 ml of benzene until it s absorption was complete, then the mixture was refluxed 4 hr. Recovered from the filtrate was 7.9 g (0.031 mol, 97% yield) of 2,6-diethylanilinophosphorus tetrafluoride.

Anal. Calcd for $C_{12}H_{14}NPF_4$: C, 47.06; H, 5.53; N, 5.49; P, 12.14; F, 29.78. Found: C, 47.06; H, 5.83; N, 5.81; P, 11.86; F, 30.09.

Also formed was 9.4 g (0.0318 mol, 100% yield) of white benzene-insoluble solids (2,6-diethylanilinium hexafluorophosphate). Analysis of the salt for the hexafluorophosphate anion indicated 49.45% PF_6^- (theory, 49.11%).

Reacting 2,6-diethylaniline at 10° with a deficiency of phosphorus pentafluoride in either benzene or heptane for 10 min followed by immediate filtration gave the same products as above. The rapid formation of solid 2,6-diethylanilinium hexafluorophosphate in the filtrate from the reaction indicated that a soluble adduct may have formed but rapidly disproportionated.

B. In Presence of Triethylamine.—Treating 17.0 g (0.114 mol) of 2,6-diethylaniline and 25.3 g (0.25 mol) of triethylamine in 250 ml of benzene with phosphorus pentafluoride at room temperature followed by 6 hr of reflux gave a two-layer system. Removal of volatiles from the top layer left 25.4 g (0.054 mol, 94% yield) of yellow crystals, crude 2,2,2,4,4,4-hexafluoro-2,2,4,4-tetrahydro-1,3-bis(2,6-diethylphenyl)-1,3,2,4-diazadiphosphetidine. These formed white crystals when sublimed at 120–140° (0.025 mm) or recrystallized from benzene.

Anal. Calcd for $C_{20}H_{26}N_2P_2F_6$: C, 51.07; H, 5.57; N, 5.96; P, 13.17; F, 24.24; mol wt, 470.9. Found: C, 51.55; H, 5.60; N, 6.00; P, 13.29; F, 24.42; mol wt, 466 (ebullioscopic).

The bottom layer cake was mainly triethylammonium hexafluorophosphate containing cyclic dimer and a small amount of unreacted 2,6-diethylaniline.

No reaction occurred when 1.65 g (0.0035 mol) of the cyclic dimer $(2,6\text{-}Et_2C_6H_6NPF_3)_2$ was refluxed with 0.45 g (0.003 mol) of 2,6-diethylaniline for 4 hr in benzene.

Reaction of Phosphorus Pentafluoride with *o*-Phenylenediamine. A. In Absence of Triethylamine.—Phosphorus pentafluoride, when added to 25 g (0.232 mol) of *o*-phenylenediamine in 125 ml of chlorobenzene formed 53.6 g (0.23 mol) of *o*-phenyl enediamine phosphorus pentafluoride. A 1:1 adduct was indicated by reaction stoichiometry and analysis.

Anal. Calcd for $C_6H_8N_2PF_5$: C, 30.90; H, 3.46; N, 12.01; P, 12.90; F, 40.73. Found: C, 29.58; H, 3.73; N, 11.30; P, 12.76; F, 38.73.

These figures, although somewhat unsatisfactory in regard to product purity, definitely indicate the product to be a 1:1 adduct.

B. In Presence of Triethylamine.—Reagents were used in the proper stoichiometry to give 1,3-dihydro-2,2,2-trifluoro-1,3,2-benzodiazaphosphate.

A mixture of 50 g (0.463 mol) of *o*-phenylenediamine and 96.3 g (0.926 mol) of triethylamine in 250 ml of chlorobenzene was treated with 185 g (1.47 mol) of phosphorus pentafluoride. As the reaction progressed solids formed and redissolved, immiscible layers formed, then solids reappeared. The solids finally formed contained all but traces of the reaction products. By infrared spectra they contained triethylammonium hexafluorophosphate and aromatic species. Separation of the aromatic product was not achieved in chloroform, benzene, dioxane, diethyl ether, triethylamine, or tetrahydrofuran used separately or in combinations. Only a fraction sublimed to 210° (0.5 mm) and the sublimate did not show separation into definite products. Repeating the experiment using sufficient triethylamine to form a benzodiazaphosphate as the repeating unit of polymer IV gave similar results.

Reaction of Phosphorus Pentafluoride with *n*-Propylamine. A. In Absence of Tertiary Amine.—A mixture of 7.3 g (0.122 mol) of *n*-propylamine in 125 ml of benzene was treated with phosphorus pentafluoride at 25°, then refluxed 6 hr. Filtering the mixture gave 13.4 g (0.065 mol) of *n*-propylammonium hexafluorophosphate. Removing benzene from the filtrate left a liquid product distilling at 40–100° (20 mm) to give a two-layer distillate and 0.7 g of still residue. The top layer contained 1.0 g (0.0035 mol, 17% yield) of 2,2,2,4,4,4-hexafluoro-2,2,4,4-tetrahydro-1,3-di-*n*-propyl-1,3,2,4-diazadiphosphetidine.

Anal. Calcd for $C_6H_{14}N_2P_2F_6$: C, 24.84; H, 4.86; N, 9.66; P, 21.35; F, 39.29. Found: C, 25.00; H, 5.21; N, 9.75; P, 21.29; F, 39.19.

The bottom layer was an oil containing NH and PF_4 or PF_5 infrared bands, perhaps from linear species containing PrNH or PF_4 end groups.

A similar reaction of 3.6 g (0.061 mol) of *n*-propylamine in 100 ml of heptane at 10° with a deficiency of phosphorus pentafluoride gave 5.0 g of very hygroscopic heptane-insoluble solids. The filtrate yielded 2.0 g of liquid product. These solids, when heated at 1 mm of pressure, were molten at 80°, gave 0.5 g of liquid distillate at 90–115°, and resolidified at 110°. The solid product was *n*-propylammonium hexafluorophosphate. The distillate, not identified, was similar, by infrared analysis, to the liquid product from the filtrate, and distilled at 25–75° (1 mm). Cyclic dimer was not present in the liquid product from the reaction nor in the liquid distillate from pyrolysis of the solids. The original insoluble solids presumably contained adduct which decomposed when heated to salt and other products.

B. In Presence of Triethylamine.—A mixture of 7.18 g g (0.121 mol) of *n*-propylamine and 25.5 g (0.25 mol) of triethylamine in 125 ml of benzene was treated at 0° with phosphorus pentafluoride, then allowed to warm to room temperature. Filtering the mixture followed by removal of benzene from each fraction gave 60.0 g (0.243 mol, 97% yield) of triethylammonium hexafluorophosphate and 12.0 g of benzene-soluble liquid. The benzene-soluble liquids formed a two-layer system. Distillation gave 6.3 g (0.0217 mol, 36% yield) of cyclic dimer. Further distillation gave 2.0 g of liquid, bp 90–105° (0.8 mm), free from infrared bands in the N–H regions but showing absorption at 1620 cm^{-1} indicating a C=C or C=N group. Dehydrofluorination may have occurred at the aliphatic carbon atom. Analysis indicated a ratio of $(PrN)_3P_2F_4$.

Reaction of Phosphorus Pentafluoride with Isopropylamine.—A solution of 17.3 g (0.293 mol) of isopropylamine in 125 ml of benzene was treated at 25° with phosphorus pentafluoride until its absorption was complete. Filtering the mixture gave 23.7 g of wet filter cake indicated by infrared analysis to contain isopropylammonium hexafluorophosphate and other products. The solids were heated to 190° (0.5 mm), then slurried in benzene, filtered, and dried to obtain an analytical sample of the salt. Analysis for the hexafluorophosphate anion indicated 70.74% PF_6^- (theory, 70.69). Removal of solvent from the two-layer filtrate left 16 g of viscous oil which consisted of a mixture of products (not identified). Similar results were obtained when addition of phosphorus pentafluoride was stopped before its absorption was completed. In neither instance were there indications of formation of the adduct or cyclic dimer. The infrared spectrum of the oil was consistent with a formula of the type $RNH_3^+PF_5NHR^-$ since it contained absorptions of the $-NH_3^+$ group, NH group, and absorptions intermediate between PF_6^- and $RNH_2 \cdot PF_5$.

Reaction of 0.7 g of isopropylamine in heptane at −20° until absorption was complete gave 1.4 g of heptane insolubles indicated by infrared to be impure adduct. When heated to 100° the adduct formed $i\text{-}PrNH_3^+PF_6^-$ and other products.

Reaction of Phosphorus Pentafluoride with *t*-Butylamine in Presence of Triethylamine.—A mixture of 6.98 g (0.0955 mol) of *t*-butylamine and 19.4 g (0.181 mol) of triethylamine in 250 ml of benzene was treated with phosphorus pentafluoride at 10° until absorption was complete, then refluxed 5 hr. Filtering the mixture gave 45.9 g (0.186 mol, 97% yield) of insoluble triethylammonium hexafluorophosphate, whereas removal of volatiles from the filtrate at 10 mm left 8.8 g of solids. These were sublimed to give 6.0 g (0.0188 mol, 40% yield) of 2,2,2,4,4,4-hexafluoro-2,2,4,4-tetrahydro-1,3-di-*t*-butyl-1,3,2,4-diazadiphosphetidine.

Anal. Calcd for $C_8H_{18}N_2P_2F_6$: N, 8.81; P, 19.47; F, 35.83. Found: N, 8.33; P, 19.56; F, 35.58.

Dehydrofluorination of the Adduct of Ammonia and Phosphorus Pentafluoride.—The adduct of ammonia and phosphorus pentafluoride[23] was prepared by several procedures: (1) the addition of phosphorus pentafluoride to ammonia dissolved in ethyl ether at −78° or at 25°, (2) addition of phosphorus pentafluoride to liquid ammonia at −78° until its absorption was complete, and (3) alternate addition at room temperature of ammonia and phosphorus pentafluoride to an evacuated flask until a desired quantity had formed. Finally the flask was kept in an atmosphere of phosphorus pentafluoride for several hours to ensure that no $(NH_3)_2PF_5$ formed.[23] Procedure 3 gave material with the "cleanest" spectrum. *Warning:* The powdery adduct, even when handled in the hood, at times caused a choking feeling and tightness around the throat. This feeling lasted from 1-8 hr in two workers in the vicinity. Due caution in handling is advised.

The adduct formed above was treated with quantities of triethylamine or diisopropylethylamine–phosphorus pentafluoride stoichiometrically or in slight excess of that required for dehydrofluorination to phosphonitrilic fluorides using benzene, diethyl ether, tetrahydrofuran, pyridine, or mixtures as solvent at room to reflux temperatures. Insolubility of the adduct was a problem when benzene was used for the solvent but small yields of phosphonitrilic fluorides (trimer, tetramer, and pentamer) were found. No phosphonitrilic fluorides were formed when pyridine, diethyl ether, or tetrahydrofuran was the solvent. The principal product with each solvent was an oil not readily separated from the by-product tertiary amine hexafluorophosphate salt. Although some concentration of the oil was obtained by centrifugation, analysis was not meaningful. The oil had very strong infrared bands at 1280–1250 and 910–930 and weaker bands at 3350 cm^{-1}. Possibly polymeric products of the type $(\text{–NH–PF}_4\text{–})_n$ were formed The dehydrofluorination of ammonia phosphorus pentafluoride is evidently quite complex. There were indications of other types of products. For example, distillation of the solvent in one instance gave a fraction with a strong phosphine odor and a strong infrared band at 2400 cm^{-1}, characteristic of phosphines.

Analyses were from these laboratories, Galbraith Laboratories, and Schwarzkopf Microanalytical Laboratories. Nmr analyses were made by Varian Associates.

Registry No.—**A1**, 15199-01-6; **A2**, 15893-20-6; **A3**, 15893-21-7; **A4**, 15893-23-9; **A5**, 15893-24-0; **A6**, 15893-22-8; **B1**, 15893-25-1; **B2**, 15893-26-2; **B3**, 15893-27-3; **B4**, 15893-28-4; **C1** (adduct), 15261-57-1; **C3** (adduct), 15893-30-8; **C5** (adduct), 15893-31-9; **C6** (adduct, 15893-32-0; **C1** (salt), 12077-62-2; **C2** (salt), 12239-94-0; **C3** (salt), 12239-95-1; **C4** (salt), 12239-97-3; **C6** (salt), 12239-90-6; **C7** (salt), 12239-93-9; **C8** (salt), 12239-96-2; **C9** (salt), 12239-91-7; *t*-butylamine hexafluorophosphate, 12239-92-8; phosphorus pentafluoride, 7647-19-0; aniline, 62-53-3.

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[23] S. Johnson, Ph.D. Dissertation, Purdue University, Lafayette, Ind., 1952.

Reactions of Hexafluoroacetone or *sym*-Dichlorotetrafluoroacetone with Allylic Olefins

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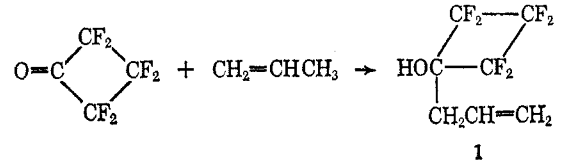
The noncatalyzed addition of highly fluorinated perhalo ketones to substituted olefins containing allylic hydrogen atoms leads to 3,4-unsaturated alcohols. The ketones act as strong electrophiles, with significant steric effects. The reaction mechanism offered involves a four-membered, cyclic dipolar intermediate, rather than a concerted mechanism previously postulated. This is based on data such as (a) interception of the intermediate by a very sensitive (difunctional) trapping agent, allyl glycidyl ether, which leads to a homopolymer of the latter, (b) formation of the adduct of β-pinene without rearrangement, and (c) an appreciable solvent effect. Implications of these findings in 1,5 hydrogen shifts, olefin additions, and concerted reactions are discussed.

The uncatalyzed addition reactions of highly fluorinated perhalo ketones to substituted olefins containing allylic hydrogen atoms generally lead to the formation of 3,4-unsaturated alcohols (2-alkenylcarbinols).

This was first demonstrated by D. C. England[1] in reaction of perfluorocyclobutanone with propylene 1.



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Davis[2] and Knunyants and Dyatkin[3,4] showed that hexafluoroacetone (HFA) or *sym*-dichlorotetrafluoroacetone (DCTFA) reacted similarly. Middleton[5] and Gambaryin, *et al.*,[6] extended the reaction to allylic compounds containing more polar groups (α-methyl styrene, methyl methacrylate, allyl methyl ether).

In this paper are reported results of uncatalyzed reactions of HFA and DCTFA with various allylic olefins which were carried out under comparable conditions. Qualitative comparisons are made of the effects of structure and solvent on reactivity and product character. Reaction mechanism is considered, as well as implications for other systems.

General Procedure

The reactions were carried out under the mildest conditions which led to appreciable conversion into

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[1] D. C. England, *J. Amer. Chem. Soc.*, **83**, 2205 (1961).

[2] H. R. Davis, Abstracts, the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 25M.

[3] I. L. Knunyants and B. L. Dyatkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (Eng. Transl.), 329 (1962).

[4] Belgian Patent 625,425 (1962).

[5] W. J. Middleton, Central Research Department, Du Pont, unpublished work.

[6] N. P. Gambaryin, El. M. Rokhlina, and Yu. V. Zeifman, *Bull. Akad. Sci., USSR, Div. Chem. Sci.* (Eng. Trrnsl.), **8**, 1425 (1965).