from 1 ml. of $Fe(CO)_5$ and 3.3 ml. of piperidine. Initially, the reaction mixture showed a rise in temperature. White crystals appeared upon gradual cooling to room temperature; these were purified by vacuum sublimation.

Anal. Calcd. for $C_{11}H_{22}N_2O_2$: C, 61.6; H, 10.3; N, 13.1. Found: C, 60.4; H, 10.6; N, 12.0.

Pure piperidine carbamate was prepared by bubbling CO_2 through a solution of piperidine and water in ether according to the method of Faurholt, *et al.*[35] The crystals were filtered, dried, and stored in a desiccator containing concentrated H_2SO_4. The infrared spectra in a Nujol mull of crystals prepared in this manner was identical in every respect with that of the crystals isolated from the reaction mixtures. In addition, both compounds melted at 75–77°.

Determination of Moles of $HFe(CO)_4^-$ Formed/Mole of $Fe(CO)_5$ Added. Quantitative analysis for $HFe(CO)_4^-$ was performed gravimetrically by precipitating $Ni(o\text{-phen})_3(HFe(CO)_4)_2$[36] from the reaction mixtures. $Ni(o\text{-phen})_3Cl_2$ in aqueous solution was deaerated and added to the reaction mixtures until precipitation of the insoluble $HFe(CO)_4^-$ derivative appeared to cease. The precipitate was filtered, sucked dry, collected, and weighed. When the precipitation was carried out under N_2 with the subsequent operations in air, the result was 0.69 mole of $HFe(CO)_4^-$/mole of $Fe(CO)_5$. When *all* operations were carried out under N_2, the results were 0.971 and 0.990 mole of $HFe(CO)_4^-$/mole of $Fe(CO)_5$. It was found that $Ni(o\text{-phen})_3(HFe(CO)_4)_2$ occasionally burns in air, and some caution must therefore be executed in handling this compound and in disposing of samples.

Determination of Moles of Piperidine Carbamate/Mole of $Fe(CO)_5$ Added. The carbamate analysis was done by a Beer's law plot of a characteristic carbamate band at 1250 cm.$^{-1}$. Several standard solutions containing between 0.04 and 0.07 g./ml. of piperidine carbamate were prepared and their absorbances measured at 1250 cm.$^{-1}$ in a 0.015-mm. path length cell. A plot of log I_0/I *vs.* concentration in g./ml. gave a good straight line of slope 6.7. Typical analyses of reaction mixtures showed 0.99 and 1.0 mole of carbamate/mole of $Fe(CO)_5$.

Preparation and Spectra of N-Formylpiperidine. N-Formylpiperidine was prepared by the reaction of piperidine and ethyl formate.[37] N-Formylpiperidine, 0.88 mmole, was dissolved in 10 ml. of piperidine. Infrared spectra were taken using the usual cells used for the spectra of the reaction mixtures of $Fe(CO)_5$ and piperidine. In the 0.015-mm. cell, the transmittance of the band center at 1670 cm.$^{-1}$ was approximately 90% and in the 0.05-mm. cell, 67%.

The 6-μ Band of N-Formylpiperidine in the Presence of Fe^{2+} and Various Solvents. $FeCl_2 \cdot 4H_2O$, 0.1 mole, was mixed with 0.6 mole of formylpiperidine in the presence of 70 ml. of water. The resulting light green solution was evacuated under a high vacuum. After 3 days, a light brown sirup was obtained. The spectrum of this heavy liquid showed a band at 1640 cm.$^{-1}$ with shoulders at 1655 and 1668 cm.$^{-1}$ indicating that Hieber's assignment of the 1640-cm.$^{-1}$ band to the coordinated formylpiperidine might be correct. However, when 20 ml. of piperidine was added to the sirup, evolution of heat occurred and the spectrum of the resulting dark brown solution showed only a band at 1668 cm.$^{-1}$ which belongs to free formylpiperidine.

CO Evolution at Higher Temperatures. $Fe(CO)_5$ (1 ml.) was added to 6 ml. of piperidine in a reaction vessel connected to a vacuum system. After heating at 60°, for 50 hr., the reaction mixture was frozen in a liquid nitrogen bath. The noncondensable gas which remained was transferred to a 10-cm. infrared gas cell. Its spectrum was that of carbon monoxide.

(35) C. Faurholt and A. Jensen, *Acta Chem. Scand.*, **6**, 1073 (1952).
(36) W. Hieber and E. Fack, *Z. anorg. allgem. Chem.*, **236**, 83 (1938).
(37) M. Auerbach and R. Wolffenstein, *Ber.*, **32**, 2518 (1899).

Radiation-Induced Ammonolysis of Carbon Tetrachloride

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The major products formed in the γ-radiolysis of carbon tetrachloride and ammonia solutions are ammonium chloride, ammonium dicyanamide, and hexachloroethane. Minor products include cyanoguanidine, guanidine hydrochloride, and nitrogen. The G values of these products are as follows: ammonium chloride, 25.3; ammonium dicyanamide, 2.36; hexachloroethane, 2.13; cyanoguanidine, 0.48; guanidine hydrochloride, 0.53; and nitrogen, 0.80. A reaction scheme is given which explains the formation of these products on the basis of a common precursor, cyanogen chloride. Such a precursor seems to account for both the large yield of ammonium chloride and the great abundance of nitrile groups found in stable products. A comparison with the thermally induced reactions studied earlier by Watt and Hahn reveals that in both cases the same reaction scheme appears to be applicable.

Introduction

The results of the present studies show that from the γ-radiolysis of simple molecules like carbon tetrachloride and ammonia some unusual and rather complex organic nitrogen compounds can be synthesized. It has been reported[1] that, under normal laboratory

(1) H. H. Anderson, *J. Am. Chem. Soc.*, **74**, 1421 (1952).

conditions, such a system yields no detectable products. Stahler[2] has reported that at 140°, however (*i.e.*, above the critical temperature of ammonia), carbon tetrachloride does react with ammonia in the presence of copper and iodine to provide a 35–40% yield of guanidine together with lesser quantities of hydrocyanic acid or cyanogen. Watt and Hahn,[3] on the other hand, found that carbon tetrachloride and ammonia do not react at an appreciable rate at temperatures below 300°. In addition, they found that potassium and ammonium iodide were far more effective as catalysts for the ammonolysis reaction than copper and iodine; the former gave yields of guanidine as high as 80%. No additional products, other than ammonium chloride, were reported.

In the present investigation, 98% by weight of the product mixture formed in the γ-radiolysis of solutions of carbon tetrachloride and ammonia at 25° is accounted for by the compounds identified. A reaction scheme is postulated which attempts to explain the formation of these products, and some speculation is given as to its applicability to the thermal reactions studies by Stahler and by Watt and Hahn.

Experimental

Radiation Source. All irradiations were done in a "Wisconsin" Type Co-60 γ-irradiator which has been described previously.[4] Dose rates were measured relative to $G(Fe^{+3})$ of 15.6 for the Fricke dosimeter and corrected to dose absorbed in carbon tetrachloride using relative electron densities. For carbon tetrachloride and ammonia solutions, the dose rates for 4-, 25-, and 300-ml. samples were 0.734, 0.545, and 0.430×10^{18} e.v./ml. min., respectively. The total dose received by these solutions ranged from 1 to 12 Mrads. All irradiations were done at room temperature.

Reagents. "Baker Analyzed" reagent grade carbon tetrachloride and Matheson Co. ammonia were used without further purification.

Preparation of Sample. To a round-bottomed flask containing 4, 25, or 300 ml. of carbon tetrachloride, 1 g. of barium oxide was added for each 5 ml. of solvent. The flask was attached to the main manifold of a vacuum system by a ground-glass joint, and the mixture was degassed by four cycles of the freeze–evacuate–melt technique. Ammonia was dried by passage through a column of powdered barium oxide and stored in a 500-ml. bulb attached directly to the main manifold. It was then degassed in the same manner as carbon tetrachloride. After degassing, carbon tetrachloride was vacuum distilled into Pyrex irradiation vessels. Ammonia was added to these vessels as follows: the gas was admitted to the main manifold until a pressure of approximately 80 cm. was obtained; a calibrated volume of 45.5 ml. was trapped off from the manifold, and the excess ammonia was frozen down in the storage bulb; transfer from the calibrated volume to the irradiation vessel was then made directly. The number of aliquots of ammonia transferred depended upon the volume of carbon tetrachloride to be irradiated. In all cases a sufficient amount of ammonia was added to ensure that the solution had a concentration of about 0.2 *M*. After completion of the ammonia transfer, the vessel was sealed off under vacuum and brought up to room temperature.

Sample Analysis. Qualitative analyses of the solid-phase products were made using thin layer chromatography and infrared and ultraviolet spectrophotometry. All thin layer chromatography work was done using 10 × 20 cm. glass plates. These plates were coated with a layer of Brinkmann MN-300HR cellulose 1 mm. in thickness and dried at room temperature. For qualitative work the size of sample ranged from 3 to 100 mg. In a normal operation the sample was taken up in 0.5 ml. of methanol and transferred to the t.l.c. plate in the form of a band, as seen in Figure 2. Plates were presaturated in a vertical ascending developing chamber for 0.5 hr. using a solvent mixture of propanol, methanol, and water in the volume ratio of 40:40:20. Additional solvent was then added until the developing process was initiated. Developed plates were dried, and roughly one-fourth of the surface of each plate was sprayed with a $AgNO_3$ solution to make visible the separated compounds. By making simple extrapolations across the plate, it was possible to locate cellulose bands containing compounds. These bands were removed and the compounds within them were extracted with water. Measurements of ultraviolet and infrared spectra followed. R_f values were also determined for these bands and compared with those of pure organic nitrogen compounds.

To analyze quantitatively for guanidine hydrochloride, cyanoguanidine, and ammonium chloride, 100 mg. of radiolysis sample was taken up in 50 ml. of water and added to a Dowex 50W-X8 ion-exchange column 1.45 cm. in diameter and 37 cm. high. Approximately 400 ml. of water was passed through the column, removing cyanoguanidine, hydrochloric acid, and any other anionic species present in the sample. This volume was made up to 500 ml.; then 100 ml. of the solution was added to a Rexyn I-300(H-OH) strong cation–anion-exchange column 2.5 cm. in diameter and 6.0 cm. high. After 250 ml. of water had passed through this column, the optical density of the effluent was recorded at the λ_{max} for cyanoguanidine, 212.5 mμ., on a Beckman DU spectrophotometer (ϵ 1.37×10^4 M^{-1} cm.$^{-1}$).

Ammonium and guanidinium ions were removed sequentially from the Dowex 50W-X8 ion-exchange column with 300 ml. of 1 *N* and 200 ml. of 6 *N* HCl. Kjeldahl nitrogen determinations were subsequently run on each of these column fractions.

Analysis of ammonium dicyanamide involved a combination of thin layer chromatography and ultraviolet spectrophotometry. Normally 25 mg. of radiolysis mixture was transferred to a cellulose t.l.c. plate, and the plate was developed in the previously described solvent mixture of propanol, methanol, and water. After drying, the cellulose band containing ammonium dicyanamide was removed, and the ammonium dicyanamide was extracted with 50 ml. of water. Finally, the optical density of the solution was recorded at 215 mμ (a shoulder in the ammonium dicyanamide ultraviolet spectra, ϵ 1.25×10^3 M^{-1} cm.$^{-1}$) on a Beckman DU spectrophotometer.

For nitrogen and hydrogen measurements, irradiated

(2) A. Stahler, *Ber.*, 47, 909 (1914).
(3) G. Watt and H. T. Hahn, *J. Am. Chem. Soc.*, 77, 312 (1955).
(4) R. J. Hanrahan, *Intern. J. Appl. Radiation Isotopes*, 13, 254 (1962).

samples equipped with break seals were attached to a high vacuum line and opened at $-196°$. Small amounts of escaping condensable materials were caught in a cold trap. The noncondensable materials were collected *via* a Toepler pump. Each sample was degassed approximately seven times, and the pressure of the known volume of gas collected was measured on a McLeod gauge. The collected gas samples were analyzed on a Consolidated 20-130 mass spectrometer.

Irradiated solutions were analyzed for hydrazine by adding a known volume of a standardized solution of $KMnO_4$ and determining spectrophotometrically the amount of $KMnO_4$ reduced. In each case, before the addition of $KMnO_4$, unreacted ammonia was removed by vigorous stirring and slight heating.

Analysis of hexachloroethane was by vapor phase chromatography using a flame ionization detector. The column was silicone gum rubber on Chromosorb-W, approximately 0.25 in. diameter by 6 ft. long, operated at 135°.

Results

The major products formed in the γ-radiolysis of carbon tetrachloride and ammonia solutions are ammonium chloride, ammonium dicyanamide, and hexachloroethane. Minor products include cyanoguanidine, guanidine hydrochloride, and nitrogen with trace amounts of hydrazine, hydrogen, and probably cyanamide. The *G* values[5] of these products are as follows: ammonium chloride, 25.3; ammonium dicyanamide, 2.36; hexachloroethane, 2.13; cyanoguanidine, 0.48; guanidine hydrochloride, 0.53; nitrogen, 0.80; hydrazine, <0.1; and hydrogen, <0.1.

Table I gives the yields of four solid-phase products (ammonium chloride, ammonium dicyanamide, guanidine hydrochloride, and cyanoguanidine) as a function of the total dose of radiation absorbed by 25-ml. samples of the NH_3–CCl_4 system. If plots of these data are made, straight lines result for all four compounds, but these straight lines do not extrapolate to the origin for the three organic nitrogen compounds. The existence of this induction period for the formation of each of these three compounds is considered in the Discussion in terms of a mechanistic scheme.

Table I

Dose, e.v. × 10^{-21}	Moles of product × 10^6			
	NH_4Cl	$NH_4N(CN)_2$[a]	$CH_5N_3 \cdot HCl$[b]	CH_4N_3CN[c]
1.6	70	3.8	0.075	0.05
2.5	106	7.5	0.17	0.13
4.0	170	13.0	0.29	0.23
5.0	212	18.0	0.38	0.33

[a] Ammonium dicyanamide. [b] Guanidine hydrochloride. [c] Cyanoguanidine.

It can be seen in Figure 1 that the total yield of solid-phase products is directly proportional to the energy absorbed by the carbon tetrachloride up to a dose of 1.25×10^{20} e.v./g. In two additional experiments, 300 ml. of ammonia-saturated carbon tetrachloride was irradiated for a total of 31 hr. (the ammonia supply was replenished once in the course of this experiment), producing 4.5 g. of radiolysis products and showing that the direct proportionality relationship between product yield and energy absorbed can be extended up to approximately 3.33×10^{20} e.v./g.

Figure 2 depicts a cellulose t.l.c. plate after development with the propanol, methanol, and water solvent mixture followed by spraying with $AgNO_3$ solution. The purpose of this sketch is to show the t.l.c. band positions of the three identified organic nitrogen compounds, cyanoguanidine, guanidine hydrochloride, and ammonium dicyanamide, and to point out that trace amounts (<1%) of at least five other compounds are being formed from the γ-radiolysis of carbon tetrachloride and ammonia. Ultraviolet spectra and evidence of fluorescence indicate that at least four of these compounds probably have delocalized π-electron systems.

Discussion

The two most conspicuous features observed in the present radiolytic study are certainly the large yield of ammonium chloride and the great abundance of nitrile groups found in stable products. Both of these observations are consistent with the following series of reactions.

$$CCl_4 \rightsquigarrow CCl_3\cdot + Cl\cdot \quad (1)$$

$$Cl\cdot + NH_3 \longrightarrow HCl + NH_2 \quad (2)$$
$$\quad\quad\quad

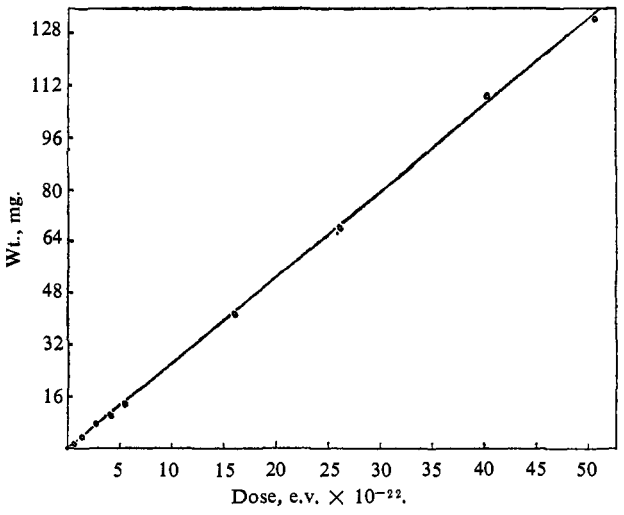

Figure 1. Weight of gross mixture of solid-phase products as a function of radiation dose. Samples were 25 ml., or approximately 40 g.

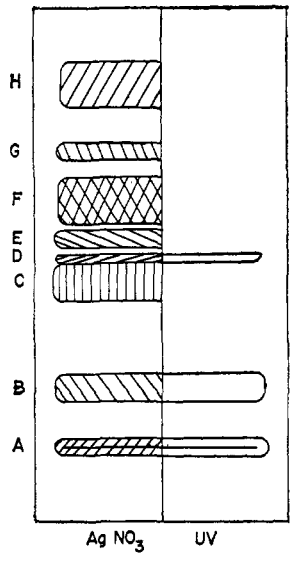

Figure 2. Sketch of a developed cellulose t.l.c. plate showing the separation of 15 mg. of solid-phase radiolysis products. Band areas are not directly proportional to the amount of compound present. The left-hand side of the plate has been sprayed with $AgNO_3$ solution to make visible the separated compounds, and the right-hand side shows those products which fluoresce under an ultraviolet mineral lamp. Band assignments: A–E, unknown; F, ammonium chloride plus guanidine hydrochloride; G, cyanoguanidine; H, ammonium dicyanamide and possibly trace amounts of cyanamide.

carried out by Ascher.[7] Ascher reported synthesizing trichloromethylamine, the reactive intermediate formed in reaction 3, and found that the compound is strongly acidic because of the inductive effect of the chlorine atoms. Reactions 4 and 5 are in keeping with these observations.

Additional studies were carried out in our laboratory in an attempt to show that cyanogen chloride is, in fact, the common precursor of the compounds cyanoguanidine, guanidine hydrochloride, and ammonium dicyanamide. When a stream of ammonia was bubbled into a solution of cyanogen bromide in carbon tetrachloride, the resulting solid products consisted of 57% ammonium bromide, 34.5% ammonium dicyanamide, 3.2% guanidine hydrochloride, and 1% cyanoguanidine. (Cyanogen bromide was used instead of cyanogen chloride because of its commercial availability.) In a subsequent experiment, a solution of cyanogen bromide in carbon tetrachloride was added dropwise to ammonia-saturated carbon tetrachloride. The latter experiment is more analogous to the radiolytic work and, as expected, gave similar product yields. The products from this reaction consisted of 67% ammonium bromide, 24% ammonium dicyanamide, 6.7% guanidine hydrochloride, and 1.8% cyanoguanidine. A question can be raised as to the relative reactivities of cyanogen bromide and cyanogen chloride toward ammonia. However, the fact that identical products are formed (with the exception of four very minor ones) in nearly the same ratios in both the thermal reaction with cyanogen bromide and the radiolysis experiment does lend additional support to the proposed scheme involving a common precursor, cyanogen chloride.

The formation of an intermediate such as cyanogen chloride is also consistent with the observations that all three of the identified organic nitrogen compounds show induction periods, with cyanoguanidine and ammonium dicyanamide exhibiting the most pronounced effects. The presence and relative extent of these induction periods follows from the fact that steady-state concentrations of cyanogen chloride and cyanamide must first be established before reactions 7a–c can give maximum yields of stable products. The ammonia concentration was nearly constant during the experiments for which quantitative yield data were taken; it decreased at most 30%. Presumably the constant yields of the products of reactions 7a–c reflect constant steady-state concentrations of cyanogen chloride and cyanamide. Since ammonium dicyanamide was the chief product, it must be concluded that reaction 7a is most rapid under the conditions of the present experiments.[8]

The four minor products formed in the radiolysis of ammonia and carbon tetrachloride but not in the cyanogen bromide–ammonia reaction are currently thought to be formed from reactions of hydrazine with cyanogen chloride; however, work is still in progress on this aspect of the present study. An additional fate of hydrazine is probably a reaction with $NH_2\cdot$ radicals finally giving 1 mole of nitrogen and 2 moles of ammonia.[9]

Although there are differences in the method of activation, temperature, phase, and relative concentrations of carbon tetrachloride and ammonia, a comparison of the present work with that of Watt and Hahn seems to indicate that the same basic reaction scheme, reactions 1 through 7c, can be applied to the two reaction systems. Watt and Hahn, for example, speculated that cyanogen chloride might also be an important intermediate in the thermally induced re-

(7) K. Ascher, *J. Chem. Soc.*, 2209 (1951).

(8) Although the proposed reaction scheme suggests that cyanogen chloride and cyanamide might be important products at low doses, this was not investigated because of the apparent analytical difficulties involved. The reaction scheme also suggests the possibility of post-irradiation reactions. We have some qualitative evidence that such reactions do occur.

(9) H. A. Dewhurst and M. Burton, *J. Am. Chem. Soc.*, 77, 5781 (1955).

action. This intermediate could be formed in the same manner as in the radiolytic experiment, from reactions 1 through 5. The reaction would presumably be initiated by the thermal bond rupture of carbon tetrachloride. Reaction 6 is also highly probable in the thermal case. The chief difference between the thermal and radiolytic reactions occurs in the competitive reactions 7a–c. Only one of these (7b) involves ammonia as a reactant. It would therefore be relatively more rapid in the experiments of Watt and Hahn, owing to the higher concentrations of ammonia, and thus give rise to the observed predominant formation of guanidine. Ammonium dicyanamide and cyanoguanidine which are formed from the other two reactions (7a and 7c) were identified as major and minor products under radiolysis but were not found in the thermal reaction. It is possible that the failure of the earlier workers to identify these compounds was due to lack of a sufficiently sensitive analytical procedure, such as t.l.c., rather than their total absence.

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The New Phosphinoamines $HN[P(CF_3)_2]_2$, $CH_3N[P(CF_3)_2]_2$, and $N[P(CF_3)_2]_3$[1]

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The new bis(phosphino)amines $HN[P(CF_3)_2]_2$ (m.p. −54°; b.p. 93° estd.) and $CH_3N[P(CF_3)_2]_2$ (m.p. −31°; b.p. 117° estd.) were made by using $(CH_3)_3N$ to force the action of $(CF_3)_2PCl$ upon $H_2NP(CF_3)_2$ or $CH_3NHP(CF_3)_2$. Both are stable up to 300° and resist acid cleavage at 100°. $CH_3N[P(CF_3)_2]_2$ forms no $(CH_3)_3N$ adduct but is cleaved by NH_3 or CH_3NH_2 (only in the liquid phase), whereas $HN[P(CF_3)_2]_2$ is not cleaved by NH_3 but exhibits acidity by forming vapor-dissociable NH_4^+ and $(CH_3)_3NH^+$ salts or by reaction with sodium to form H_2 and $NaN[P(CF_3)_2]_2$. Action by $(CF_3)_2PCl$ upon $HN[P(CF_3)_2]_2$ does not occur even with $(CH_3)_3N$, but the salt $NaN[P(CF_3)_2]_2$ reacts easily with $(CF_3)_2PCl$ to make the new volatile solid $N[P(CF_3)_2]_3$ (m.p. 37°; b.p. 152° estd.) stable to 150°. This is cleaved quantitatively by HCl to make $(CF_3)_2PCl$ and $HN[P(CF_3)_2]_2$, by NH_3 to make $H_2NP(CF_3)_2$ and $HN[P(CF_3)_2]_2$, by H_2O to make $HN[P(CF_3)_2]_2$ and $(CF_3)_2POH$, or by $H_2NP(CF_3)_2$ to make $2HN[P(CF_3)_2]_2$. The three new phosphinoamines are more resistant to cleavage than $(SiH_3)_3N$, and are presumed to have a similar π-enhanced planar bonding to N. Their infrared spectra have been recorded accurately and assigned.

Introduction, Results, and Discussion

The stable aminophosphine $H_2NP(CF_3)_2$ has shown no sign of direct and easy convertibility to poly(phosphino)amines,[2] whereas all attempts to make $H_2NP(CH_3)_2$ have led rather to the poly(phosphino)amines $HN[P(CH_3)_2]_2$ and $N[P(CH_3)_2]_3$.[3,4] It can be understood that the disproportionation of $H_2NP(CH_3)_2$ to $HN[P(CH_3)_2]_2$ and NH_3 might not be resisted by the loss of two $N_{2p}\rightarrow P_{3d}$ two-atom π-bonds, for such π-bonding here would be relatively weak and the gain of one $N_{2p}\rightarrow(P_{3d})_2$ three-atom π-bond would more than half compensate the loss. However, when such π-bonding is considerably stronger, as in the corresponding $P(CF_3)_2$ compounds, the net loss of bond energy in such a conversion might be considerably greater. But no such ideas would predict actual instability for $HN[P(CF_3)_2]_2$ or $N[P(CF_3)_2]_3$. Rather, as suggested by Harris,[2] the difficulty of conversion of $H_2NP(CF_3)_2$ to poly(phosphino)amines has been the lack of an effective mechanism: the $N_{2p}\rightarrow P_{3d}$ π-bonding is so strong as to deactivate N as a base and P as a site for nucleophilic attack. Also, $H_2NP(CF_3)_2$ cannot be expected to react with $(CF_3)_2PCl$ without some means of HCl removal; and for that purpose no protic base (*e.g.*, R_2NH) can serve because P–N–P cleavage products would be favored.

Accordingly, we have made the new compound $HN[P(CF_3)_2]_2$ quantitatively from $H_2NP(CF_3)_2$ and $(CF_3)_2PCl$, using $(CH_3)_3N$ to remove HCl. Similarly, the new compound $CH_3N[P(CF_3)_2]_2$ was made from CH_3NH_2 and $(CF_3)_2PCl$, again using $(CH_3)_3N$ in a nearly quantitative process. In both syntheses it is probable that the $(CF_3)_2PCl$ was activated toward loss of Cl^- by the effect of a weakly N→P bonded complex with $(CH_3)_3N$, as seems reasonable in view of analogous experience with $(CF_3)_2PI$.[5]

Both of these new bis(phosphino)amines decomposed only slowly at 300° and resisted cleavage by protic or Lewis acids; thus neither would react with HCl at 100°, and $HN[P(CF_3)_2]_2$ was tried also with BCl_3 and

(1) Supported by Grant No. GP-199 from the National Science Foundation, which contributed also through Grant No. G-14665 toward the purchase of the Beckman IR7 instrument.

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

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

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

(5) A. B. Burg and J. F. Nixon, *ibid.*, **86**, 356 (1964).