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Reactions of Chlorophosphines with Silyl Azides[1]

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In contrast to the formation of phosphineimines in the reaction of silyl azides with triorganophosphines, the analogous reaction with chlorophosphines produces (*via* an exclusive azide–halogen exchange) azidophosphine intermediates, which decompose to phosphonitrilic materials and nitrogen. These two processes cannot be separated. The rate of exchange of chlorine on phosphorus with an azido group increases with the extent of phenyl substitution on the trivalent phosphorus atom: $PCl_3 < C_6H_5PCl_2 < (C_6H_5)_2PCl$. The course of the reaction is dependent on solvent, reaction temperature, and to some extent concentration. In ether, diphenylchlorophosphine is quantitatively converted into cyclic diphenylphosphonitrilic trimer. In the corresponding reactions of phenyldichlorophosphine and trichlorophosphine, exchange of more than one chlorine substituent on a phosphorus atom occurs to an appreciable extent even when 1:1 molar ratios of the starting materials are employed; no trimeric species could be isolated.

Introduction

Triorganophosphines are readily converted to phosphineimines by azides such as phenyl azide,[3] diphenylphosphinyl azide,[4] and triphenylsilyl azide.[5,6] Nothing is known about the reactivity of tertiary phosphines with alkali metal azides.

Similar studies of chlorophosphines were limited almost entirely to alkali metal azides, which acted merely as azido-group donors in the chlorine–azide exchange. Using sufficiently low temperatures the intermediate azidophosphines could be isolated.[7,8] At elevated temperatures phosphonitriles were formed directly.[9] Diphenylphosphinyl azide, on the other hand, acted upon diphenylchlorophosphine both as an oxidant and an azide source for the exchange reaction.[10] The thermal decomposition of diphenylazidophosphine in the presence of excess diphenylchlorophosphine[8] cannot be easily classified in this respect, inasmuch as both processes, oxidation of $(C_6H_5)_2PCl$ by $(C_6H_5)_2PN_3$ and the subsequent P^V–Cl/P^{III}–N_3 exchange or oxidation of $(C_6H_5)_2PCl$ by P^V–azide are possible and indistinguishable.

It was therefore of interest to determine the behavior of silyl azides with chlorophosphines. The desired product was a N-triorganosilylchlorophosphineimine, which in analogy to diphenylphosphinyl azide was supposed to be investigated as a chain-terminating group in the preparation of linear phosphonitriles.[10]

Experimental

All reactions were conducted either in a nitrogen atmosphere or in a vacuum system with rigid exclusion of moisture and oxygen. Caution should be exercised during the initial stages of the reactions, since some of them tend to explode, especially in the absence of solvents.

Highest available purity chemicals were used after careful purifications. Diphenylchlorophosphine and phenyldichlorophosphine, obtained from Victor Chemical Works, were purified by fractional distillation, b.p. 112.5–116° (0.036 mm.) and 134–135° (56 mm.), respectively. Trichlorophosphine was purified immediately before reaction in a vacuum system by fractional condensation (vapor pressure 35.2 mm. at 0°). Triphenylsilyl azide, m.p. 82.5–84.0°, was prepared in 90.5% yield following the procedure of Wiberg, *et al.*[11]

For a preparation of trimethylsilyl azide, a variance of West and Thayer's procedure[5] was employed. To trimethylsilyl chloride (143.4 g., 1.320 moles) in diglyme (235 ml.) was added sodium azide (105.4 g., 1.616 moles). The resulting mixture was allowed to stand at room temperature, with occasional shaking, over a period of 8 days. Subsequently, the mixture was subjected to vacuum distillation at room temperature, the distillate being collected in a Dry Ice trap. The crude trimethylsilyl azide was fractionally distilled through an 80-cm. column, filled with glass helices; b.p. 97.2° (763 mm.), lit. 94°,[12] 96.0–96.2°,[13] 87° (extrapolated).[14] This fraction amounted to 104 g. (68%). The vapor pressure of 12.0 mm. at 0° and the gas-phase infrared spectrum were in agreement with the literature.[14] Fractional condensation of this material under vacuum in traps kept at −47, −63, −78, and −196° resulted in accumulation of about equal amounts in the traps maintained at −47 and −63°, minor amounts being collected in the −78° trap. Interestingly, only the −78° fraction exhibited an infrared spectrum identical with that reported; the other two fractions (−47°, −63°) did not show any absorption at 1090, 1145, and 1155 cm.$^{-1}$. Prolonged storage of the −47 and −63° fractions (in ampoules sealed under vacuum) at room temperature and exposed to normal laboratory light resulted in change of the infrared spectrum to that of the nonfractionated material; however, no measurable change in the 0° vapor pressure was detected. Accordingly, trimethylsilyl azide was fractionated as described above immediately prior to reaction, and the −47° fractions were used.

The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Reaction of $(C_6H_5)_2PCl$ with $(C_6H_5)_3SiN_3$ in Ether.—To a solution of $(C_6H_5)_3SiN_3$ (9.04 g., 0.03 mole) in ether (50 ml.) was added $(C_6H_5)_2PCl$ (6.60 g., 0.03 mole) in ether (50 ml.). The reaction flask, equipped with a reflux condenser, was then heated in an oil bath to *ca.* 50°. A sudden vigorous boiling, gas evolution, and yellow discoloration accompanied by precipitation were

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(3) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 61 (1921).
(4) R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961).
(5) R. West and J. S. Thayer, *ibid.*, **84**, 1763 (1962).
(6) N. Wiberg, F. Raschig, and R. Sustmann, *Angew. Chem. Intern. Ed. Engl.*, **1**, 551 (1962).
(7) G. Tesi, C. P. Haber, and C. M. Douglas, *Proc. Chem. Soc.*, 219 (1960).
(8) K. L. Paciorek and R. Kratzer, *Inorg. Chem.*, **3**, 594 (1964).
(9) D. L. Herring, *Chem. Ind.* (London), 717 (1960).
(10) K. L. Paciorek, *Inorg. Chem.*, **3**, 96 (1964).
(11) N. Wiberg, F. Raschig, and R. Sustmann, *Angew. Chem. Intern. Ed. Engl.*, **1**, 335 (1962).
(12) W. Sundermeyer, *Chem. Ber.*, **96**, 1293 (1963).
(13) W. T. Reichle, *Inorg. Chem.*, **3**, 402 (1964).
(14) J. W. Connolly and G. Urry, *ibid.*, **1**, 718 (1962).

observed. When the oil bath was removed, the gas evolution continued for about 1 hr. without external heating. The mixture was subsequently refluxed overnight. The yellow precipitate (4.90 g., 82% yield), that was filtered off, was shown by infrared spectral analysis to consist of impure $[(C_6H_5)_2PN]_3$. Crystallization from acetonitrile gave pure $[(C_6H_5)_2PN]_3$, m.p. 226–227°, in a 68% yield. Removal of the solvent from the ethereal filtrate afforded $(C_6H_5)_3SiCl$, identified by its melting point, 94–96°, and by comparison of its infrared spectrum with that of an authentic sample.

Reaction of $(C_6H_5)_2PCl$ with $(CH_3)_3SiN_3$ in Ether. (a) **Under Atmospheric Pressure.**—Diphenylchlorophosphine (6.60 g., 0.03 mole) in ether (50 ml.) was mixed with a solution of $(CH_3)_3SiN_3$ (3.46 g., 0.03 mole) in ether (50 ml.) at room temperature. The solution was shaken and an aliquot was withdrawn immediately for infrared examination. The strong absorption at 2130 cm.$^{-1}$ and the absence of a strong characteristically shaped band at 635 cm.$^{-1}$ (found in the infrared spectra of gaseous $(CH_3)_3SiCl$ and in those of its solution in ether and acetonitrile) were taken as indication that essentially only the starting materials were present. After standing at room temperature for about 5 min. the reaction mixture became cloudy; subsequently a yellow precipitate and gas evolution were observed. An aliquot withdrawn after 40 min. exhibited a strong absorption at 2105 cm.$^{-1}$. This was taken as evidence for the presence of $(C_6H_5)_2PN_3$,[8] while a strong band at 635 cm.$^{-1}$ showed the presence of $(CH_3)_3SiCl$. The mixture was allowed to stand without external heating for 3 hr., followed by refluxing overnight. After separation of the solid by filtration the infrared spectrum of the ethereal filtrate exhibited only a weak band at 2130 cm.$^{-1}$. The infrared spectrum of the solid (5.43 g., 91% yield) indicated pure $[(C_6H_5)_2PN]_3$; however, the melting point (200–220°) was depressed. Crystallization from acetonitrile afforded pure $[(C_6H_5)_2PN]_3$, m.p. 226–227°, in an over-all 61% yield.

(b) **In a Sealed Ampoule at −25 and −13°.**—On a high vacuum line ether (14.33 mmoles) was condensed onto $(C_6H_5)_2PCl$ (740.6 mg., 3.357 mmoles) at −196°. The mixture was warmed to 0° to effect solution, then trimethylsilyl azide (3.291 mmoles) was distilled onto the solution at −78°. The reaction mixture was warmed to −24° and maintained at this temperature for 4 hr. The volatiles were removed at −24° and fractionated through traps kept at −47, −63, −78, and −196°. No noncondensable gas had been formed. In the −47 and −63° traps $(CH_3)_3SiN_3$ was collected (vapor pressure at 0°, 16.5 mm.), while the −196° trap contained only ether (vapor pressure at 0°, 189 mm.). Accordingly the volatiles were distilled back onto the $(C_6H_5)_2PCl$ (at −78°); first ether, then $(CH_3)_3SiN_3$. The reaction ampoule was warmed to −13° and allowed to stand at this temperature for 70 min. Yellow discoloration was observed and some nitrogen (36% based on $(CH_3)_3SiN_3$ used) was evolved. The ampoule was cooled to −24° and the volatiles were distilled off again. These were fractionated through a Dry Ice cooled column[15] followed by fractionation of the less volatile materials through −24, −47, −63, −78, and −196° traps. By this procedure 13.39 mmoles of pure ether and 1.985 mmoles of pure $(CH_3)_3SiCl$ were separated together with a 2.097-mmole fraction which contained only ether and $(CH_3)_3SiCl$, as determined by infrared spectral analysis. In addition, 0.085 mmole of $(CH_3)_3SiN_3$ was recovered. Ether was returned to the ampoule, which was sealed and heated at 100° for 3 hr. On opening of the ampoule 1.834 mmoles of nitrogen was obtained. The ratio of $(CH_3)_3SiN_3$ consumed to $(CH_3)_3SiCl$ produced to total nitrogen evolved was 1.02:1.03:1.

The solid residue left in the ampoule was crystallized from acetonitrile (acetonitrile-insoluble material was discarded), followed by boiling with benzene. The benzene-soluble fraction consisted of pure $[(C_6H_5)_2PN]_3$, obtained in a 29% yield.

(c) **In a Sealed Ampoule at 0°.**—A parallel reaction to the one described in (b), but conducted at 0° for 30 min., afforded 35% of nitrogen and 99% of $(CH_3)_3SiCl$. The nonvolatile residue on warming to room temperature, followed by heating at 150°, gave an additional 63% of nitrogen. From the residue on purification a 39% yield of $[(C_6H_5)_2PN]_3$ was obtained. The over-all ratios were: $(C_6H_5)_2PCl:(CH_3)_3SiN_3:(CH_3)_3SiCl:N_2 = 1.02:1.04:1.02:1$.

Reaction of $(C_6H_5)_2PCl$ with $(CH_3)_3SiN_3$ in Acetonitrile.—On a high vacuum line, acetonitrile (7.8422 g.) was condensed onto $(C_6H_5)_2PCl$ (877.0 mg., 3.975 mmoles) at −78°. The mixture was warmed to 0° to effect solution, then 4.029 mmoles of $(CH_3)_3SiN_3$ was distilled onto the solution at −78°. After sealing the ampoule was allowed to stand at room temperature for 3 hr.; during this period the solution discolored yellow and precipitation was observed. Subsequently the mixture was heated in an oil bath at 50–55° for 12 hr. A considerable quantity of yellow material was formed. Opening to the vacuum system gave 3.775 mmoles (95%) of nitrogen. The volatiles were removed initially at room temperature, then at 50°. The total amount of volatiles obtained was 8.2239 g.; the calculated amount was 8.2793 g. (based on CH_3CN employed, $(CH_3)_3SiCl$ produced, and $(CH_3)_3SiN_3$ recovered, assuming that no silicon moiety was incorporated in the residue). The residue did not contain any cyclic trimer. The bulk of the product was soluble in boiling benzene; on cooling an amorphous precipitate was formed which failed to melt up to 480°, although some darkening was evident at this temperature. *Anal.* Calcd. for $(C_6H_5)_2PN$: C, 72.36; H, 5.06; P, 15.55; N, 7.03. Found: C, 71.87; H, 5.15; P, 14.85; N, 7.40. The high nitrogen value, in conjunction with the lowered phosphorus and carbon values, tends to indicate the presence of azido-terminated chains.

For infrared spectral examinations to a solution of $(C_6H_5)_2PCl$ (660 mg.) in CH_3CN (5 ml.) was added a solution of $(CH_3)_3SiN_3$ (346 mg.) in CH_3CN (5 ml.). The infrared spectrum recorded immediately after mixing exhibited a strong band at 2105 cm.$^{-1}$ and an absorption at 635 cm.$^{-1}$ due to $(CH_3)_3SiCl$; whereas a solution of equal concentration of $(CH_3)_3SiN_3$ in CH_3CN had a strong band at 2130 cm.$^{-1}$ and no absorption between 645 and 625 cm.$^{-1}$.

Reaction of $C_6H_5PCl_2$ with $(C_6H_5)_3SiN_3$ in Ether.—To $(C_6H_5)_3SiN_3$ (9.03 g., 0.03 mole) in ether (50 ml.) was added $C_6H_5PCl_2$ (5.37 g., 0.03 mole) in ether (50 ml.). The solution was refluxed for 48 hr.; some oil was deposited and the ethereal layer exhibited in its infrared spectrum a strong band at 2128 cm.$^{-1}$. The refluxing was continued for a total of 7 days; at this stage the ethereal layer showed only a weak absorption at 2128 cm.$^{-1}$ in its infrared spectrum. Ether was subsequently decanted from the oil, which was washed several times with *ca.* 20-ml. aliquots of ether. The ethereal washings were combined and, on evaporation of ether, mainly triphenylsilyl chloride was obtained (on the basis of the infrared spectral analysis), admixed with ether-soluble $[(C_6H_5)XPN]_n$ material. The ether-insoluble oil was subjected to vacuum, whereupon a puffy solid (2.34 g.), soluble in benzene, but insoluble in boiling heptane, was obtained. Its infrared spectrum (weak band at 2128 cm.$^{-1}$; bands at 1290, 1212, and 712 cm.$^{-1}$) indicated a $[C_6H_5XPN]$ material, where X can be either Cl or N_3, with N_3 present only in trace quantities. Heating at 130° under vacuum failed to give any sublimate except a trace of $(C_6H_5)_3SiCl$, pointing to an absence of $[(C_6H_5)ClPN]_3$. Exposure of $[(C_6H_5)XPN]_n$ to the atmosphere resulted in hydrolysis as emphasized by insolubility in benzene and markedly altered infrared spectrum.

Reaction of $C_6H_5PCl_2$ with $(CH_3)_3SiN_3$. (a) **Under Atmospheric Pressure.**—This experiment was conducted in a manner analogous to that described for $(C_6H_5)_3SiN_3$, the only difference being that $(CH_3)_3SiCl$ was distilled off together with the ether. The ether-insoluble portion exhibited in the infrared a much stronger azido band than the material obtained from the $(C_6H_5)_3SiN_3$ reaction. The ether-soluble oil had a strong absorption at 2132 cm.$^{-1}$, showing the presence of azido groups, while a shoulder at 1095 cm.$^{-1}$ was indicative of a trivalent phosphorus species.

An infrared spectrum recorded immediately after mixing the ethereal solutions of $C_6H_5PCl_2$ and $(CH_3)_3SiN_3$ exhibited only

(15) J. R. Spielman and A. B. Burg, *Inorg. Chem.*, **2**, 1139 (1963).

bands associated with $(CH_3)_3SiN_3$, $C_6H_5PCl_2$, and $(C_2H_5)_2O$. Another aliquot withdrawn after 3 hr. standing at room temperature had an identical infrared spectrum. After refluxing for 20 min., the solution became cloudy, and an aliquot withdrawn at this time showed in its infrared spectrum a definite shift of the azido band from 2128 to 2105 cm.$^{-1}$, an absorption at 635 cm.$^{-1}$ (attributed to $(CH_3)_3SiCl$), and new bands at 714 and 678 cm.$^{-1}$.

(b) *In Vacuo.*—On a high vacuum line ether (*ca.* 3 ml.) and $(CH_3)_3SiN_3$ (3.964 mmoles) were condensed onto $C_6H_5PCl_2$ (709.2 mg., 3.962 mmoles) at −196°. The ampoule was sealed, heated at 45° for 45 min., and then cooled to −196° and opened; 3.075 mmoles of nitrogen was obtained. The volatiles were removed at −24°. They did not exhibit any absorption in the 2220 to 2040 cm.$^{-1}$ region, showing the absence of azido groups. The contents of the ampoule were warmed up slowly to room temperature, followed by heating at 105° for 24 hr. The total nitrogen evolved was 3.866 mmoles (98% based on $C_6H_5PCl_2$ employed).

The residue was benzene-soluble, m.p. 61–66°; mol. wt. 1015. It exhibited in the infrared absorptions at 1430, 1290, 1205, 1170, 1120, 741, 714, and 690 cm.$^{-1}$, together with a weak band at 2130 cm.$^{-1}$. *Anal.* Calcd. for $[(C_6H_5)ClPN]_x$: C, 45.74; H, 3.20; N, 8.90; P, 19.60. Found: C, 45.98; H, 3.60; N, 8.99; P, 19.85.

Reaction of PCl_3 with $(CH_3)_3SiN_3$. (a) **In Ether.**—On a high vacuum line PCl_3 (2.559 mmoles), ether (3 ml.), and $(CH_3)_3SiN_3$ (2.566 mmoles) were condensed in an ampoule. The ampoule was sealed, warmed to room temperature, and heated at 57° for 16 hr. On opening to the high vacuum system only a trace of noncondensable gas was present. The contents were fractionated from a warming trap through −47, −63, −78, and −196° traps. Repeated fractionations failed to afford pure components. On the basis of infrared spectra the higher vapor pressure fractions consisted mainly of ether admixed with an azido-group-containing moiety and $(CH_3)_3SiCl$. The lower vapor pressure fractions appeared to contain more of the azido moiety and much less ether. A fraction (vapor pressure at 0°, 16 mm.; mol. wt. 117) was free of ether and appeared to consist only of $(CH_3)_3SiCl$ and an azido-group-containing material. The characteristic band of $(CH_3)_3SiN_3$ at 1315 cm.$^{-1}$ was absent, whereas the characteristic band of $(CH_3)_3SiCl$ at 635 cm.$^{-1}$ was present. Furthermore, the material was very sensitive to pressure changes (rapid cooling from room temperature to liquid nitrogen temperature resulted in explosions), which points to the presence of a PCl_2N_3-type molecule. A 283.8-mg. portion of this mixture was heated at 76° for 72 hr.; on opening to the vacuum system 0.5601 mmole of nitrogen was obtained, and the residue consisted of azido-substituted chlorophosphonitriles.

(b) **In the Absence of Solvent.**—A mixture of PCl_3 (2.545 mmoles) and $(CH_3)_3SiN_3$ (3.121 mmoles) deposited a waxy precipitate after standing in a sealed ampoule for 30 days at room temperature. The ampoule was subsequently heated at 79–81° for 64 hr. On opening to a high vacuum system 2.036 mmoles (80% based on PCl_3 used) of nitrogen was evolved. The volatiles (3.476 mmoles; vapor pressure at 0°, 70.0 mm.) could not be separated by vacuum fractionation; however, no azido-group-containing material was present. On the basis of infrared spectral analysis and vapor pressure, the material appeared to consist of $(CH_3)_3SiCl$ admixed with PCl_3. Since 3.121 mmoles of $(CH_3)_3SiN_3$ was originally employed, 3.121 mmoles of $(CH_3)_3SiCl$ would be expected (providing none of the silyl moieties was incorporated in the phosphonitrilic system), accordingly the 0.355-mmole excess must be PCl_3. Elemental analysis of the volatiles gave 3.36% of phosphorus, corresponding to 0.432 mmole of PCl_3. Thus, PCl_3 consumed to N_2 = 1.08:1; while PCl_3 consumed to azido groups in the residue = 2.02:1.

The involatile residue, which was semisolid, exhibited in the infrared a strong band at 2150 cm.$^{-1}$ (azido group), a broad absorption in the 1350 to 1220 cm.$^{-1}$ region (phosphonitrile linkages), a broad band centered at 990 cm.$^{-1}$, and a band at 770 cm.$^{-1}$. No absorption was observed in the 3125 to 2700 cm.$^{-1}$ region, indicating the absence of CH groups.

Treatment of PCl_3 with $(C_6H_5)_3SiN_3$ in Ether. (a) **At 62°.**—On a high vacuum line, ether (26.22 mmoles) and PCl_3 (2.776 mmoles) were condensed onto $(C_6H_5)_3SiN_3$ (641 mg., 2.127 mmoles) at liquid nitrogen temperature. The ampoule was sealed, warmed to room temperature, and heated at 62° for 8 hr. On opening to a high vacuum system, no noncondensable gas was present. Distillation at room temperature resulted in a quantitative recovery of PCl_3 and $(C_2H_5)_2O$.

(b) **At 78–80°.**—Following the same procedure as described in (a), $(C_6H_5)_3SiN_3$ (792.1 mg., 2.628 mmoles) was sealed in an ampoule with 3.711 mmoles of PCl_3 and 26.14 mmoles of ether. The ampoule was heated at 78–80° for 64 hr.; on opening to a high vacuum system, 2.214 mmoles (84% based on $(C_6H_5)_3SiN_3$) of nitrogen was obtained. The room temperature volatiles (27.98 mmoles) were composed of ether admixed with PCl_3; no azido-group-containing compounds were present. No separation could be attained by high vacuum fractionation. The materials were volatile at −63°, indicating the absence of $(PNCl_2)_3$.

The resealed ampoule containing a white solid residue was opened in an inert atmosphere enclosure. The residue was washed several times with ether; an oil remained. Its infrared spectrum showed a strong band at 2150 cm.$^{-1}$ due to azido linkages (in agreement with the recovery of an excess of PCl_3 and the formation of only 84% of nitrogen). The broad absorption in the 1350 to 1220 cm.$^{-1}$ region pointed to P=N groupings. The ethereal washings on evaporation yielded pure $(C_6H_5)_3SiCl$ identified by mixture melting point and by comparison of the infrared spectra.

Discussion

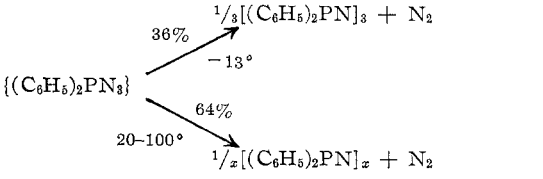
The evaluation of the experimental results and the postulation of reaction mechanisms can be attempted by recognizing: (1) No compounds are formed which contain both silicon and phosphorus, thus eliminating the reaction

$$R_3SiN_3 + R_{3-x}PCl_x \longrightarrow R_3SiN{=}PR_{3-x}Cl_x + N_2$$

(2) The exchange of the halogen and azido moiety is complete, even in the case of the polyhalophosphines, where multiple exchange can and did occur. However, in all the reactions studied, the isolation of the intermediate azidophosphine was not possible, inasmuch as the exchange reaction was always accompanied by nitrogen evolution, even at temperatures as low as −13°. (3) It should be noted that the nitrogen formation can be brought to completion

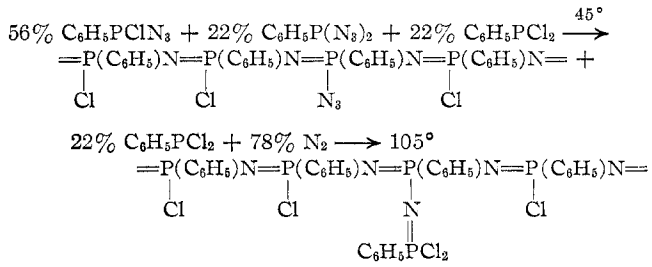
$$(C_6H_5)_2PCl + (CH_3)_3SiN_3 \longrightarrow [{=}(C_6H_5)_2PN{=}] + (CH_3)_3SiCl + N_2$$

This does not imply that all the nitrogen is evolved in one distinct step and that it leads to the formation of only one product under varying conditions (solvent, concentration, temperature). Obviously, the reaction mechanisms are complex and very sensitive to changes of these conditions. An explanation of the −13° reaction of diphenylchlorophosphine with trimethylsilyl azide is shown in the following scheme.

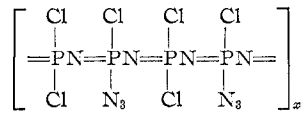


The sequences depicted below appear plausible for the

reaction of phenyldichlorophosphine with an equimolar amount of trimethylsilyl azide



The product from the reaction of trichlorophosphine with trimethylsilyl azide can be similarly assumed to have the statistical composition



The incorporated azido groups do not oxidize trichlorophosphine at 81°. This is in contrast to the oxidation of excess phenyldichlorophosphine by azido groups incorporated in the initial product.

In view of the results obtained, it can be said that the rate of replacement of chlorine by the azido group increases with the degree of phenyl substitution on phosphorus. Yet, this conclusion has to be limited to the case where only one chlorine per mole of chlorophosphine is exchanged. The trichlorophosphine experiment proves that a second chlorine atom can be exchanged easier than the first, as demonstrated by the recovery of trichlorophosphine. Since nitrogen formation occurred simultaneously with the exchange retion, the possibility that the second chlorine was exchanged on an already oxidized, pentavalent phosphorus atom cannot be excluded. The same reasoning can be applied to the phenyldichlorophosphine case, if one assumes again a double exchange.

Regarding the stability of the intermediate azidophosphines, it could be deduced that it decreases with the extent of phenyl substitution. The lowered oxidative activity (toward trivalent phosphorus) of an azido group bonded to a pentavalent phosphorus atom and its relatively high thermal stability are evident from the trichlorophosphine experiment. In this experiment roughly 30% of all azido groups available survived heat treatment at 81° in the presence of trichlorophosphine. However, no pure phenylchloroazidophosphine or dichloroazidophosphine was ever isolated, and it thus is likely that the decomposition temperatures of these materials lie below the temperature at which exchange with trimethylsilyl azide and the chloro precursor occurs. For comparisons, diphenylazidophosphine decomposes at 13.6° yielding 90% of the theoretical amount of nitrogen, the rest being evolved upon heating to 180°.[8]

A mechanism for the predominant formation of diphenylphosphonitrilic trimer can be postulated based on experimental observations and infrared spectral data. The shift of the asymmetric azide band from 2130 cm.$^{-1}$ in trimethylsilyl azide to lower wave

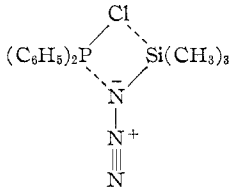


Figure 1.—Transition state of the exchange reaction.

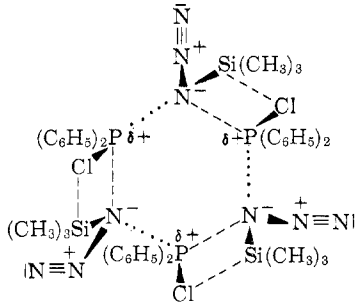


Figure 2.—Possible mechanism for the formation of diphenylphosphonitrilic trimer.

numbers in the course of the reaction can be due to the formation of azidophosphine (diphenylazidophosphine absorbs[8] at 2090 cm.$^{-1}$). It can be attributed equally well to complex formation, which was found by Thayer and West[16] to give rise to a shift of comparable magnitude. Thus a four-center transition state (Figure 1) similar to the triphenylphosphine–triphenylsilyl azide complex formulated by Thayer and West[16] appears plausible for the exchange process.

However, in view of the high yield of cyclic diphenylphosphonitrilic trimer and the fact that complete exchange was never reached without simultaneous nitrogen evolution, the above transition state may not be responsible merely for the exchange reaction. Under certain conditions of solvent, temperature, and concentration, it may be instrumental in the production of the trimer. One reason for its formation is the inherent polarization of the P–Cl bond in diphenylchlorophosphine, which is very likely increased in the transition state. Each phosphorus atom, thus bearing a larger $\delta+$ charge in the four-center transition state, conceivably coordinates with a second identical complex. This trimerization of the above four-center transition state provides a mechanistic route for the preferential formation of diphenylphosphonitrilic trimer (Figure 2). In this complex a weakening of the N–N bonds in the azido group will take place, resulting finally in the evolution of molecular nitrogen. The close correlation between nitrogen formation at −13° and final yield of trimer in the $(C_6H_5)_2PCl$–$(CH_3)_3SiN_3$ experiment supports this speculation. Furthermore, this dipole mechanism would also explain the sensitivity of the reaction in regard to solvent (dielectric constant) and concentration.

It may be possible to clarify these processes by ^{31}P or even by ^{1}H n.m.r. spectroscopy. Yet, even if n.m.r.

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studies would support the proposed mechanism, the absence of cyclic tetramer will still remain unexplained.

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The Molybdenum Carbonyl–Phosphorus Trifluoride System

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The carbon monoxide groups in molybdenum hexacarbonyl are readily replaced by phosphorus trifluoride using either high temperature–high pressure or atmospheric pressure–ultraviolet irradiation conditions. By various means, all possible compositions for monodentate substitution, including three pairs of *cis* and *trans* isomers, were identified. Most of these isomers could be clearly isolated by preparative gas–liquid chromatography. Substitution studies of the various compounds clearly indicate that PF_3 is a slightly stronger *trans* labilizer than CO. The compounds are colorless liquids or solids, with good thermal and hydrolytic stabilities and frequently having volatilities greater than that of the parent hexacarbonyl.

Introduction

The substitution of phosphorus trifluoride for carbon monoxide of metal carbonyls has been studied for a number of the metals, with the nickel tetracarbonyl[1] and iron pentacarbonyl[2] systems being studied with the greatest thoroughness. In these studies, all possible compositions were prepared, isolated, and characterized. Other studies of PF_3 complexes have been made, especially by Kruck,[3–5] in which a limited number of the possible complexes were prepared.

This paper reports work done on one of the hexacarbonyls—molybdenum hexacarbonyl. While the work was in progress, Kruck[4] and Schmutzler[6] reported the preparation of chromium and molybdenum compounds of the type $M(PF_3)_6$ and $M(CO)_3(PF_3)_3$ by indirect means. Their work also showed clear evidence for other compounds.

The identification of all possible compounds in the $Mo(CO)_x(PF_3)_{6-x}$ system including three pairs of *cis* and *trans* isomers is presented in this report. The preparation and actual isolation of most of the complexes will be described and information will be reported concerning the mode of the substitution reactions.

Experimental

The phosphorus trifluoride used during the latter portion of the work was obtained from K and K Laboratories. It was purified before use by bubbling it through a 12-in. tower of water packed with glass beads. This material was then dried by vacuum distilling it from a trap cooled to −95°. The remainder of the PF_3 used was prepared as described previously.[2]

Two methods were used for the preparation of substituted products. One was a high pressure–high temperature synthesis and the other was an atmospheric pressure–ultraviolet light-induced reaction. In the former technique, the sample handling and recovery procedures were essentially as described earlier,[2] but somewhat simplified by the use of $Mo(CO)_6$, which is a stable solid of low volatility. The reactions were allowed to proceed for 8–18 hr. at temperatures ranging from 175 to 325°. The higher reaction temperatures produced products predominating in the higher substitution compounds, and the lower reaction temperatures yielded products with a lower degree of substitution. To obtain the totally substituted compound by this technique, it was necessary to heat the vessel to the higher temperature, then cool it frequently to −195° and remove the carbon monoxide by vacuum. Attempts to use higher reaction temperatures resulted in extensive decomposition.

The ultraviolet method is particularly well suited for the preparation of products with a low degree of substitution. In a typical reaction, about 0.7 g. of $Mo(CO)_6$ and 20 ml. of spectral grade pentane were placed in a 1-l. flask equipped with a standard taper joint at the top and a 35-mm. long by 30-mm. diameter extension at the bottom. The main function of the bottom extension was to allow a better exposure angle, but it also contained a magnetic stirring bar to mix the contents. The flask was closed with an adaptor containing a vacuum stopcock and a joint for connection to a vacuum system. The flask was evacuated at room temperature until about half of the solvent had vaporized. This resulted in the complete removal of the air and the degassing of the solvent. Phosphorus trifluoride was admitted until its partial pressure was about 500 torr.

The lower portion of the flask was irradiated at nearly the full intensity of an AH-6 ultraviolet lamp while the contents were being stirred. (The lamp contained a Pyrex velocity tube, and the irradiation vessel was made of Pyrex; so it appears that the far-ultraviolet is not important.) For the production of predominantly mono- and disubstituted materials, an irradiation time of 1.5–2 hr. was used, and for di- and trisubstituted materials, 3–4 hr. Higher substitution was readily produced, although at a progressively slower rate, by extensive irradiation with the evolved carbon monoxide being removed frequently at −195°. So long as the flask was adequately degassed and the PF_3 was pure, no noticeable decomposition appears to take place. The product from the irradiation was recovered by cooling the

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