TABLE III

INFRARED CARBONYL FREQUENCIES IN NICKEL DICARBONYL DERIVATIVES

Compound	ν_{C-O}, cm.$^{-1}$	Conditions	Ref.
$Ni(CO)_4$	2050, 2043	Gas	[a]
$Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2$	2000, 1935	Soln. in cyclohexane	[b]
$Ni(CO)_2[P(C_6H_5)_3]_2$	2010, 1955	Soln. in cyclohexane	[b]
$Ni(CO)_2[P(OC_6H_5)_3]_2$	2034, 1975	Soln. in cyclohexane	[b]
$Ni(CO)_2[(CH_3)_2N\cdot PF_2]_2$	2040, 1993	Pure liquid	This work
	2049, 1997	Soln. in chloroform	This work
$Ni(CO)_2(C_5H_{10}N\cdot PF_2)_2$	2041, 1993	Nujol mull	This work
	2049, 1996	Soln. in chloroform	This work
$Ni(CO)_2(PCl_3)_2$	2090, 2065	Soln. in cyclohexane	[b]

[a] B. L. Crawford and P. C. Cross, *J. Chem. Phys.*, **6**, 525 (1938). [b] L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

TABLE IV

INFRARED CARBONYL FREQUENCIES IN MOLYBDENUM TRICARBONYL DERIVATIVES

Compound	ν_{C-O}, cm.$^{-1}$	Conditions	Ref.
$Mo(CO)_6$	2000	Gas	[a]
$[(C_2H_5)_2N\cdot PF_2]_3Mo(CO)_3$	1995, 1919	Soln. in C_6H_6	This work
$(C_5H_{10}N\cdot PF_2)_3Mo(CO)_3$	1996, 1934	Solid in KBr	This work
$[(CH_3)_2N\cdot PF_2]_3Mo(CO)_3$	2000, 1923	Solid in KBr	This work
$C_7H_8Mo(CO)_3$	2000, 1935, 1911	Soln. in cyclohexane	[b]
$[(C_6H_5O)_3P]_3Mo(CO)_3$	2020, 1923	Soln. in CCl_4	[c]
$(ClCH_2PF_2)_3Mo(CO)_3$	2038, 1970	Soln. in C_6H_6	16
$(PCl_3)_3Mo(CO)_3$	2040, 1990	Solid in KBr	16
	2041, 1989, 1960(sh)	Soln. in CCl_4	9
$(PF_3)_3Mo(CO)_3$	2085, 2055, 1990	Solid in KBr	16

[a] N. J. Hawkins, H. C. Mattraw, W. W. Sabol, and D. R. Carpenter, *J. Chem. Phys.*, **23**, 2422 (1955). [b] R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960). [c] T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

The CO stretching absorptions for both nickel dicarbonyl and molybdenum tricarbonyl derivatives were found in the region typical for terminal CO groups. A pronounced increase in the CO frequencies of phosphine-substituted metal carbonyls, as compared with those of derivatives containing nitrogen donor molecules, has been attributed to the π-character of the metal–ligand bond in the phosphine complexes.[9] The multiple bond character of the metal–phosphorus bond is increased with increasing availability of donor atom d-orbitals due to the influence of the electronegative fluorine substituents. This effect is reflected in the steady rise of the carbonyl stretching frequencies in both series (Tables III and IV).

CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND COMPANY,
EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION, WILMINGTON, DELAWARE

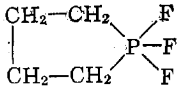
Phosphorus–Fluorine Chemistry. VI. A New Synthesis of Heterocyclic Phosphorus Compounds: Preparation of Di- and Trifluorophosphoranes *via* Phosphine Sulfide Intermediates[1a]

BY R. SCHMUTZLER[1b]

Received March 19, 1963

Reaction of α,ω-di-Grignard reagents with thiophosphoryl chloride led to the formation of novel heterocyclic biphosphine disulfides, bis(cyclotetramethylene)biphosphine disulfide and bis(cyclopentamethylene)biphosphine disulfide. Both were converted to the corresponding cyclic trifluorophosphoranes by means of antimony trifluoride. Further trifluorophosphoranes were prepared from tetraalkyl biphosphine disulfides and antimony trifluoride. Difluorophosphoranes could be obtained in a similar manner from tertiary phosphine sulfides by fluorination with antimony trifluoride.

In the course of a stereochemical study on fluorophosphoranes, R_nPF_{5-n} (R = organic hydrocarbon group; n = 1, 2, 3) by means of F^{19} n.m.r. spectroscopy, special interest arose in fluorophosphoranes containing a PF_3 group as part of a cyclic system, such as where a rapid intramolecular exchange of equatorial and apical fluorine atoms in the trigonal bipyramidal structure was found to occur.[2]



I

Cyclotetramethylenetrifluorophosphorane (I) was readily obtained as a volatile liquid, b.p. 62° (90 mm.), upon reaction of cyclotetramethylenemonochlorophosphine (II) with antimony trifluoride.[3] The chlorophosphine II, however, is available only by a rather complex, low-yield, three-step sequence,[4] and it appeared desirable to synthesize a heterocyclic phosphorus intermediate which might permit a more facile access to a fluorophosphorane such as I. The synthesis of I can be realized *via* a novel biphosphine disulfide intermediate III as shown in Scheme I.

The reaction of thiophosphoryl chloride with the double Grignard reagent from 1,5-dibromopentane gave the corresponding six-membered heterocycle IV, which

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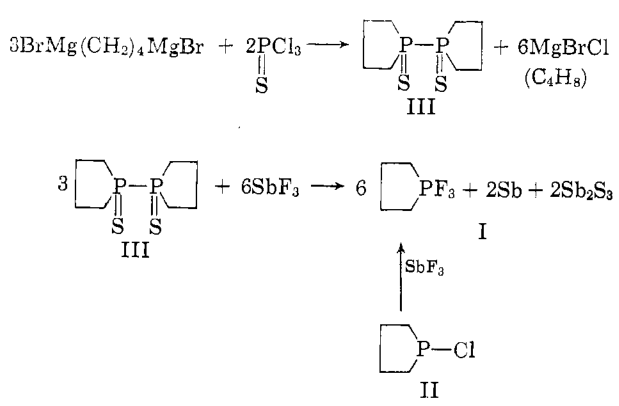
(1) (a) Preceding paper in this series: R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964); (b) University Chemical Laboratory, Cambridge, England.

(2) E. L. Muetterties, W. Mahler and R. Schmutzler, *ibid.*, **2**, 613 (1963).

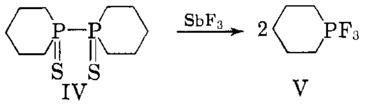
(3) R. Schmutzler, *ibid.*, **3**, 410 (1964).

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

SCHEME I



analogously was converted to the trifluorophosphorane V.

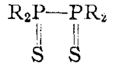


The reaction between thiophosphoryl chloride and the α,ω-di-Grignard reagents was carried out at various temperatures and under changing conditions. The best results were obtained when thiophosphoryl chloride and the double Grignard reagent were added simultaneously to ether stirred at $-78°$. Large amounts of viscous, polymeric by-products were invariably formed, but the separation of the readily crystallizing biphosphine disulfides III and IV was straightforward.

It is noteworthy that the five-membered heterocycle III shows a sharp melting point while compound IV, even after repeated recrystallizations, melts over a range of 40°, between *ca.* 185 and 225°. The presence of the six-membered heterocyclic ring system in IV, however, is well established from the analytical data as well as by the fact that oxidation of IV yields the previously described cyclopentamethylenephosphinic acid[5] as the sole product. Furthermore, only one fluorophosphorane V was obtained upon reaction of IV with antimony trifluoride. The presence of isomers in IV has to be assumed, therefore. In connection with the present study, the separation of the potential isomers was unnecessary and was not attempted.

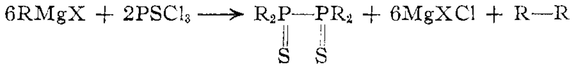
Evidence for the structure of III also stems from its conversion to the previously independently synthesized fluorophosphorane I[3] and from the mass spectrum of I, some of the most abundant fragments containing C_4 units. It is difficult to visualize a formula containing C_4 units with other than a cyclic structure for I, and, consequently, for III. Furthermore, oxidation of the biphosphine disulfide III with nitric acid led to cyclotetramethylenephosphinic acid. This acid has been described in the literature,[6] but the report could not be confirmed in more recent work.[7] The acid obtained by the oxidation of III had m.p. 53–54° and was identical with the independently synthesized compound of m.p. 53–54.5°.[7] It may be noted that the interaction of both heterocyclic biphosphine disulfides with mercuric oxide in benzene[8a,b] failed to yield any appreciable amounts of the phosphinic acid, although reaction was apparent and no unreacted starting material could be recovered.

The reaction of α,ω-di-Grignard reagents with thiophosphoryl chloride represents a novel route for the synthesis of heterocyclic phosphorus compounds. Although the reaction between thiophosphoryl chloride and an alkyl Grignard reagent was first studied as early as 1916,[9] it was correctly interpreted only in 1949[10] for the first time. Since then, in a great number of examples, the reaction was shown to be "anomalous." Under various conditions tetraalkylbiphosphine disulfides



$$\underset{\underset{S}{\|}}{R_2P}-\underset{\underset{S}{\|}}{PR_2}$$

rather than tertiary alkyl phosphine sulfides normally were formed. The course of reaction has usually been described by the equation[11,12]



$$6RMgX + 2PSCl_3 \longrightarrow \underset{\underset{S}{\|}}{R_2P}-\underset{\underset{S}{\|}}{PR_2} + 6MgXCl + R-R$$

The exact mechanism of the reaction is not known, however, and with respect to the formation of "R–R," the course of the reaction is probably more complicated than depicted in the above equation. Alkyl- or arylphosphonothioic dichlorides instead of thiophosphoryl chloride can also enter the reaction with Grignard reagents, mixed biphosphine disulfides, $R_1R_2P(S)P(S)R_1R_2$, being formed.[12–14]

Organophosphorus compounds bearing two organic hydrocarbon groups on the same phosphorus atom were previously accessible only with difficulty, and biphosphine disulfides, including the new heterocyclic compounds, were useful intermediates in the synthesis of compounds containing R_2P- and $R_2P<$ groups. Aside from the already mentioned utilization of bis(cyclotetramethylene)- and bis(cyclopentamethylene)-biphosphine disulfide in the synthesis of the cyclic trifluorophosphoranes, some scouting studies were undertaken on the former compound. Desulfurization of III with iron powder readily gave the novel biphosphine VI, a volatile liquid, spontaneously flammable in air. Ethylene, in the presence of catalytic amounts of iodine, was inserted between the two phosphorus atoms of III to give the bis-phosphine sulfide VII.

Further trifluorophosphoranes (*cf.* Table I) could readily be obtained upon interaction of biphosphine

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(5) (a) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **77**, 6658 (1955); (b) E. G. Howard and M. Braid, paper presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961.

(6) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 3739 (1957).

(7) B. Helferich and E. Aufderhaar, *Ann.*, **658**, 100 (1962).

(8) (a) W. Kuchen and H. Buchwald, *Angew. Chem.*, **71**, 162 (1959); (b) W. Kuchen, K. Strolenberg, and H. Buchwald, *Chem. Ber.*, **95**, 1703 (1962).

(9) W. Strecker and C. Grossmann, *Ber.*, **49**, 63 (1916).

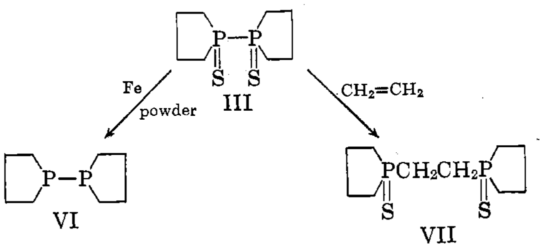
(10) M. I. Kabachnik and J. S. Shepeleva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 56 (1949).

(11) K. Issleib and A. Tzschach, *Chem. Ber.*, **92**, 704 (1959).

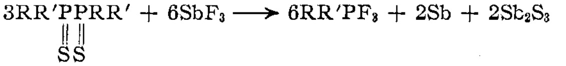
(12) L. Maier, *ibid.*, **94**, 3043 (1961).

(13) H. Schlör and G. Schrader (to Farbenfabriken Bayer A.G.), German Patent 1,067,021 (Oct. 15, 1959).

(14) L. Maier, *Angew. Chem.*, **71**, 575 (1959).



disulfides with arsenic trifluoride or, preferably, antimony trifluoride according to the equation



$$3RR'\overset{}{\underset{S}{\underset{\|}{P}}}\underset{S}{\underset{\|}{P}}RR' + 6SbF_3 \longrightarrow 6RR'PF_3 + 2Sb + 2Sb_2S_3$$

$$R = R' \text{ or } R \neq R'$$

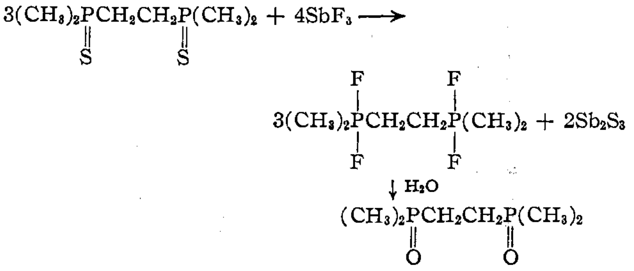
The reactions between the biphosphine disulfides and antimony trifluoride were carried out by gentle heating of mixtures of the solid reactants in a distillation apparatus in a dry atmosphere. The mixtures soon turned intensely red and gradually became black, thus indicating the progress of the reaction due to the formation of Sb–Sb_2S_3. Particularly in the case of higher boiling fluorophosphoranes, the reactions were carried out under a slight vacuum in order to reduce the influence of moisture. The fluorophosphoranes formed were recovered in good yield by distillation, at atmospheric pressure or *in vacuo*. The stoichiometry was established also by the isolation and characterization of the Sb–Sb_2S_3 mixture. Atomic ratios Sb:S of close to 1:1 support the formulation of the reaction according to the above equation.

It is believed that the reaction of biphosphine disulfides with antimony trifluoride is of a very general nature, making trifluorophosphoranes readily available compounds, since the starting materials are also easily obtained.

Not all types of P=S bonds are readily attacked by antimony trifluoride. Thus, reaction of $ClCH_2PSCl_2$ with antimony trifluoride clearly and in high yield gave the phosphonothioic difluoride, $ClCH_2PSF_2$,[15] and not the fluorophosphorane, $ClCH_2PF_4$,[3] which might be expected. On the other hand, only low yields of phosphonothioic difluorides have been observed in the reaction of arylphosphonothioic dichlorides with antimony trifluoride, and the formation of large amounts of sulfur-containing products due to side reactions was reported.[16]

A fluorophosphorane containing two phosphorus atoms in the same molecule could be synthesized starting from P,P,P′,P′-tetramethylethylenebiphosphine disulfide,[17] where the two phosphorus atoms are separated from each other by an ethylene bridge.

P,P,P′,P′-Tetramethylethylenebis-difluorophosphorane was formed readily upon heating a mixture of the phosphine sulfide with antimony trifluoride as a volatile, low melting, sublimable solid. Its hydrolysis led to the recently described P,P,P′,P′-tetramethylethylenebiphosphine dioxide,[18] providing a further proof of the structure.



$$3(CH_3)_2\underset{S}{\underset{\|}{P}}CH_2CH_2\underset{S}{\underset{\|}{P}}(CH_3)_2 + 4SbF_3 \longrightarrow 3(CH_3)_2\overset{F}{\underset{F}{P}}CH_2CH_2\overset{F}{\underset{F}{P}}(CH_3)_2 + 2Sb_2S_3$$

$$\downarrow H_2O$$

$$(CH_3)_2\underset{O}{\underset{\|}{P}}CH_2CH_2\underset{O}{\underset{\|}{P}}(CH_3)_2$$

The reaction of tertiary phosphine sulfides with antimony trifluoride is also of a more general nature and has been utilized for the synthesis of further difluorophosphoranes according to

$$3RR'R''P{=}S + 2SbF_3 \longrightarrow 3RR'R''PF_2 + Sb_2S_3$$

Similarly as above, phosphine sulfide–antimony trifluoride mixtures were heated for several hours, antimony trisulfide being precipitated and characterized by analysis and X-ray powder diagram in some cases. The volatile fluorophosphoranes were again recovered by distillation *in vacuo*.

No evidence was found for the reversibility of the reaction of phosphine sulfides with antimony trifluoride or for the formation of phosphinothioic monofluorides from trifluorophosphoranes and antimony trisulfide. Reactions such as

$$\begin{matrix} RPF_4 \\ R_2PF_3 \end{matrix} + \begin{matrix} \text{sulfur or} \\ \text{sulfides,} \\ \text{including } As_2S_3 \end{matrix} \longrightarrow \begin{matrix} RPSF_2 \\ R_2PSF \end{matrix}$$

have been described recently.[19] No mention was made of the possibly interesting by-products in the reaction of fluorophosphoranes with elemental sulfur. $RPSF_2$ and R_2PSF compounds are much more easily accessible by different routes.[15]

A single attempt was made to prepare a difluorophosphorane of the composition $(RO)_3PF_2$ by the interaction of trimethylphosphorothionate, $(CH_3O)_3P{=}S$, with antimony trifluoride. The only volatile product isolated after heating a mixture of the reactants for several hours was unchanged phosphorothionate, although a trace amount of elemental antimony was observed. Antimony trifluoride was dissolved rather readily in trimethylphosphorothionate, and it is possible that merely a formation of an adduct took place. Adducts of trimethylphosphorothionate with mercury(II) iodide, iron(III) chloride and bromide, and gold chloride have been described.[20]

Properties of Di- and Trifluorophosphoranes.—All the di- and trifluorophosphoranes reported in this paper are colorless, distillable liquids, except P,P,P′,P′-tetramethylethylenebis-difluorophosphorane, which is a crystalline, sublimable solid. Most of the tri-, and, especially, the difluorophosphoranes were virtually odorless when highly purified.

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[15] R. Schmutzler, *J. Inorg. Nucl. Chem.*, **25**, 335 (1963).

[16] L. M. Yagupol'skii and Zh. M. Ivanova, *Zh. Obshch. Khim.*, **30**, 1284 (1960).

[17] G. W. Parshall, *J. Inorg. Nucl. Chem.*, **14**, 291 (1960).

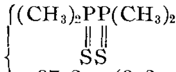
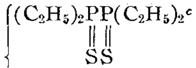
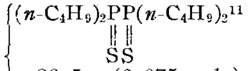
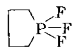
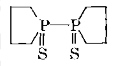
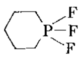
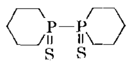
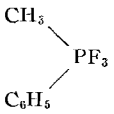
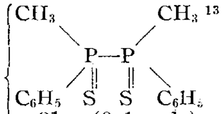
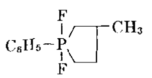
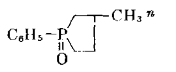
[18] G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 2423 (1961).

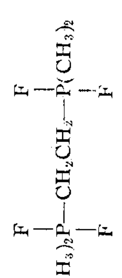
[19] I. P. Komkov, S. Z. Ivin, K. V. Karavanov, and L. E. Smirnov *Zh. Obshch. Khim.*, **32**, 301 (1962).

[20] P. S. Pishchimuka, *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912).

TABLE I

TRI- AND DIFLUOROPHOSPHORANES PREPARED FROM PHOSPHINE SULFIDE INTERMEDIATES

Compound	Reactants	Reaction conditions	Yield, %	B.p., °C. (mm.); refractive index	Analyses				
						C	H	F	P
$(CH_3)_2PF_3$	 $(CH_3)_2\underset{S}{\underset{\|}{P}}\underset{S}{\underset{\|}{P}}(CH_3)_2{}^a$ 37.2 g. (0.2 mole) SbF_3, 76 g. (0.4 mole)	25–220° (2 hr.) (atm. press.)	82	62°^{b}	Calcd.	20.4	5.1	...	...
					Found	20.0	4.8	...	...
$(C_2H_5)_2PF_3$	 $(C_2H_5)_2\underset{S}{\underset{\|}{P}}\underset{S}{\underset{\|}{P}}(C_2H_5)_2{}^c$ 36.3 g. (0.15 mole) SbF_3, 75.6 g. (0.4 mole)	25–140° (1.5 hr.) (atm. press.)	84.4	50° (100)^d	Calcd.	32.9	6.9	39.0	21.2
					Found	33.1	7.0	36.8[23]	21.8
$(n\text{-}C_4H_9)_2PF_3$	 $(n\text{-}C_4H_9)_2\underset{S}{\underset{\|}{P}}\underset{S}{\underset{\|}{P}}(n\text{-}C_4H_9)_2{}^{11}$ 26.5 g. (0.075 mole) SbF_3, 40 g. (0.22 mole)	25–130° (2 hr.)^e (vacuum; *ca.* 10 mm.)	43	71° (10)	Calcd.	47.5	9.0	...	...
					Found	47.6	8.9	...	...
	 11.9 g. (0.05 mole) SbF_3, 26.8 g. (0.15 mole)	25–150° (2 hr.) (vacuum; 130–150 mm.)	51.4	61–62° (90)	Calcd.	33.4	5.6	39.5	21.5
					Found	33.3	5.5	38.1[23]	21.8
	 5.75 g. (0.0215 mole) SbF_3, 8 g. (0.045 mole)	25–150° (2 hr.) (vacuum; 100 mm.)	67.3	64–65° (40)	Calcd.	38.0	6.4	36.0	19.6
					Found	38.4	7.1	35.5	19.8
	 ^{13} 31 g. (0.1 mole) SbF_3, 40 g. (0.22 mole)	25–150° (2.5 hr.) (vacuum; *ca.* 10 mm.)^f	79.2	64° (9) $n^{26.5}D$ 1.4646^g	Calcd.	46.7	4.5	31.6	...
					Found	46.7	4.5	31.5	...
$(C_2H_5)_3PF_2$	$(C_2H_5)_3P{=}S^h$ 6.0 g. (0.04 mole) SbF_3, 7.2 g. (0.04 mole)	25–120° (2.5 hr.) (vacuum; 100 mm.)^i	73.7	53° (20) $n^{25.5}D$ 1.4061^j	Calcd.	46.2	9.7	24.3	19.8
					Found	46.2	9.8	24.6	19.6
$(n\text{-}C_4H_9)_3PF_2$	$(n\text{-}C_4H_9)_3P{=}S$ 21 g. (0.09 mole) SbF_3, 13.4 g. (0.075 mole)	25–130° (2 hr.) (vacuum; 30 mm.); distillation at 75–125° (0.5–2 mm.)	61	71–72° (0.4) d^{25}_4 0.9398 $n^{25}D$ 1.4320^k	Calcd.	60.0	11.3	15.8	12.9
					Found	59.9	11.7	15.5	12.9
$C_6H_5(n\text{-}C_4H_9)_2PF_2$	$C_6H_5(n\text{-}C_4H_9)_2P{=}S^l$ 7.5 g. (0.03 mole) SbF_3, 5.4 g. (0.03 mole)	120° (2.5 hr.) (vacuum; 20 mm.); extracted with 80 ml. of boiling benzene	...	89° (0.3) 80° (0.08) $n^{24.4}D$ 1.5010^m	Calcd.	64.6	8.9	...	...
					Found	64.7	8.8	...	...
	 ^{n} 9.75 g. (0.05 mole) SF_4, 54 g. (0.5 mole)	Heated with shaking for 6 hr. at 50° under autogenous press.^{o}	32.2^p	89° (0.4) $n^{25}D$ 1.5139	Calcd.	60.8	7.4	17.5	14.3
					Found	61.4	7.3	17.5	14.4

	 $(CH_3)_2P(S)CH_2CH_2P(S)(CH_3)_2$[17,q] 16 g. (0.075 mole) SbF_3, 35 g. (0.195 mole)	Heated 2 hr. in a sublimation apparatus at 10 mm. (100°)	59.4	M.p. 47.1–48.4° (sealed capillary)[r]	Calcd. Found	31.8 31.6	7.1 7.4	33.6 33.65	27.4 26.0

[a] H. Reinhardt, D. Bianchi, and D. Mölle, *Chem. Ber.*, **90**, 1656 (1957). [b] The identity of the product with the independently synthesized $(CH_3)_2PF_3$[3] was further established by a comparison of the infrared spectra. [c] H. Niebergall and B. Langenfeld, *Chem. Ber.*, **95**, 64 (1962). [d] Previously found: b.p. 50° (100 mm.).[3] [e] Only a trace amount of the fluorophosphorane was formed when this reaction was conducted at atmospheric pressure, the bulk of the product consisting of $(n\text{-}C_4H_9)_2POF$.[15] The yield of $(n\text{-}C_4H_9)_2PF_3$ was greatly improved upon heating the reaction mixture *in vacuo* (2 hr. (*ca.* 10 mm.)). [f] Formation of the phosphinic fluoride, $CH_3(C_6H_5)POF$,[15] as a by-product was also observed in this experiment. [g] Hydrolysis of a small sample of phenylmethyltrifluorophosphorane with excess water (evaporation on a steam bath) gave phenylmethylphosphinic acid as white crystals (from ethanol–water 2:1), m.p. 134–136° (reported m.p. 134°: C. S. Gibson and J. D. Johnson, *J. Chem. Soc.*, 92 (1928). *Anal.* Calcd. for $C_7H_9O_2P$: C, 53.8; H, 5.8; P, 19.8. Found: C, 53.7; H, 6.0; P, 19.6. [h] A. Cahours and A. W. Hofmann, *Ann.*, **104**, 1 (1857). [i] Sb_2S_3 was recovered from the reaction residue in 93.8% yield and was identified by X-ray powder diffraction (comparison with ASTM 6-0474). [j] Purity check by v.p.c. analysis >99%. [k] Mol. wt.: calcd. for $(C_4H_9)_3PF_2$, 240.3; found (cryoscopic in benzene), 247. [l] $C_6H_5(n\text{-}C_4H_9)_2PS$ is a new compound. It was prepared by the addition of 1.3 g. (0.04 g.-atom) of sulfur to 8.9 g. (0.04 mole) of $C_6H_5(n\text{-}C_4H_9)_2P$ (W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 33 (1929)) in 25 ml. of benzene. After 0.5-hr. reflux the solvent was removed and the residue twice recrystallized from *n*-hexane to give white plates, m.p. 50.5–51.5°; yield 8.5 g. (83.5%). *Anal.* Calcd. for $C_{14}H_{23}PS$: C, 66.1; H, 9.1; P, 12.2; S, 12.6. Found: C, 65.9; H, 9.2; P, 12.2; S, 13.0. [m] The lowest infrared stretching frequencies ever recorded for a P–F compound were found in $(C_2H_5)_3PF_2$ (617 cm.$^{-1}$), $(n\text{-}C_4H_9)_3PF_2$ (620 cm.$^{-1}$), and $(n\text{-}C_4H_9)_2(C_6H_5)PF_2$ (638 cm.$^{-1}$). The slight increase in the latter compound may be due to the replacement of one alkyl group by the more electronegative phenyl group. [n] W. B. McCormack (to E. I. du Pont de Nemours and Co.): U. S. Patent 2,663,739 (Dec. 22, 1953); the author is grateful to Dr. W. B. McCormack for a sample of 1-phenyl-3-methyl-cyclotetramethylenephosphine oxide, b.p. 147–149° (0.45 mm.). [o] No distillable material could be obtained when the reaction mixture was heated with shaking for 4 hr. at 50°, 4 hr. at 100°, and 6 hr. at 150°, and only tarry products were recovered. [p] Part of the product accidentally lost during recovery from shaker tube. [q] A sample of this material was kindly supplied by Dr. W. Mahler of this laboratory. [r] The highly deliquescent fluorophosphorane was resublimed prior to analysis and was stored in Teflon vials. The compound could also be vacuum-distilled.

Particularly noteworthy is the hydrolytic stability of the fluorophosphoranes and, directly related, their behavior toward glass. All compounds were sufficiently stable to be handled in glass apparatus, but most of the fluorophosphoranes did attack glass upon prolonged contact. The hydrolytic stability may be qualitatively classified as $R_3PF_2 > R_2ArPF_2 = Ar_2PF_3 \gg R_2PF_3$. Thus, a trialkyldifluorophosphorane with a higher alkyl group such as butyl was found to be indefinitely stable on storage in glass without special protection from moisture, whereas triethyldifluorophosphorane was much more readily attacked by water. Triphenyldifluorophosphorane, the only previously known difluorophosphorane, on the other hand, has been reported to be extremely sensitive toward moisture.[21] During the preparation of trifluorophosphoranes from biphosphine disulfides, phosphinic fluorides, R_2POF, were frequently obtained as by-products in sizable quantities, if moisture was not rigorously excluded.[15]

$$R_2PF_3 + H_2O \longrightarrow R_2POF + 2HF$$

It proved advantageous, therefore, to run the fluorination reactions under vacuum, where the contact with atmospheric moisture was reduced or prevented.

Experimental

General.—Most of the phosphorus–fluorine compounds described in this paper were subject to rapid hydrolysis and anhydrous conditions had to be maintained throughout the experiments. Reaction systems usually were flushed with nitrogen or, more frequently, evacuated and filled with dry nitrogen. The fluorophosphoranes did not attack glass apparatus noticeably on brief exposure, but it was preferable to store most of the compounds, especially the trifluorophosphoranes, in Teflon containers or stainless steel cylinders. Tri-*n*-butyldifluorophosphorane could be stored indefinitely in glass.

Materials.—Thiophosphoryl chloride was obtained from Hooker Chemical Company. 1,4-Dibromobutane and 1,5-dibromopentane were of Eastman reagent grade. Antimony trifluoride was used as obtained from Ozark Mahoning Company. Phosphine sulfides were prepared according to published methods; new compounds will be described briefly.

Bis(cyclotetramethylene)biphosphine Disulfide (III).—This compound was prepared under a variety of conditions, *e.g.*, by addition of thiophosphoryl chloride to the di-Grignard reagent of 1,4-dibromobutane at 25° or at 0°. Both runs gave small amounts of the desired product, but the 0° temperature was definitely more favorable. An attempt to substitute the bromo Grignard reagent with the chloro derivative led to a yield of product of <1%. It was found that the reaction could best be accomplished by the simultaneous addition of thiophosphoryl chloride and the di-Grignard reagent of 1,4-dibromobutane to ether being stirred at −80°. A typical experiment was as given below.

A Grignard reagent was prepared from 216 g. (1 mole) of 1,4-dibromobutane and 48.6 g. (2 g.-atoms) of magnesium turnings in 700 ml. of ether. A 2-l. four-necked flask was fitted with a mechanical stirrer, a reflux condenser with a drying tube, and two dropping funnels (100-ml. and 1-l.). The system was evacuated and filled with nitrogen. Under a blanket of nitrogen, the Grignard solution was filtered through glass wool into the 1-l. dropping funnel, while 102 g. (0.6 mole) of distilled thiophosphoryl chloride was placed in the 100-ml. funnel. Ether (700 ml.) was placed in the flask and the simultaneous addition of the

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(21) W. C. Smith, *J. Am. Chem. Soc.*, **82**, 6176 (1960).

reactants was started after the ether was cooled to −80°. A white precipitate was formed immediately, sometimes accompanied by highly viscous materials so that stirring became difficult. The addition was completed in 3–4 hr., and after 1-hr. stirring at −80°, the mixture was allowed to warm up. Extreme care had to be taken that the mixture warmed up slowly enough, and the temperature was carefully observed. After 1-hr. refluxing the reaction mixture was decomposed with ice–10% sulfuric acid (*ca.* 1 l.). The water layer was extracted with four 250-ml. portions of chloroform, and the combined organic extracts were repeatedly washed with water, then dried over calcium chloride. Removal of the solvents by distillation left a yellow liquid, which solidified partially upon cooling to room temperature. The amount of solid precipitated was increased by cooling with ice. The product was readily separated from viscous by-products by filtration. An additional amount of biphosphine disulfide separated from the mother liquor upon prolonged cooling below 0°. The combined yield of product sufficiently pure for further reactions after one recrystallization from toluene–ethanol (3:1) ranged between 12 and 15 g. (15–19%). An analytical sample was recrystallized twice from the same solvent to give beautiful white prisms, some being up to 50 mm. long. In order to obtain good crystals it was found favorable to cool the solution in the boiling solvent very slowly and not below room temperature. Recovery of product was good due to its excellent solubility at higher temperatures, while it was only slightly soluble at room temperature; m.p. (purified product) 185°.

Anal. Calcd. for $C_8H_{16}P_2S_2$: C, 40.3; H, 6.8; P, 26.0; S, 26.9; mol. wt., 238.3. Found: C, 40.1; H, 6.9; P, 26.0; S, 27.3; mol. wt., 236, 231 (isopiestic in acetone). Infrared spectrum (in KBr): 2940, 2860 (m); 1439 (m); 1395 (m); 1298 (m); 1249 (w); 1103 (s); 1049 (m); 1019 (m); 958, 951 (w); 839 (s); 761 (m); 715 (vs); 697 (s); 590 (vs); 506, 415 (s). P^{31} n.m.r. chemical shift $\delta = -61.2$ p.p.m. from 85% H_3PO_4 (in chloroform solution).

Cyclotetramethylenephosphinic Acid.—Bis(cyclotetramethylene)biphosphine disulfide (0.72 g., 0.003 mole) was added in small portions to 7 ml. of 30% nitric acid with stirring at 70–80°. The mixture was heated on a steam bath and was partially evaporated. After two 10-ml. portions of water had been added and were partially evaporated, lead dioxide was added at 80° until the mixture was alkaline. The precipitate of lead sulfate was filtered and washed with water. Excess of lead was precipitated by hydrogen sulfide, filtered off, and the filtrate was evaporated on a steam bath. The oily residue was dried *in vacuo* over phosphorus pentoxide and was recrystallized from *n*-hexane to give white needles, m.p. 53–54°, in accordance with the literature report[7]; yield 0.41 g. (57%). The identity of the product as cyclotetramethylenephosphinic acid was further confirmed by analysis and by comparison of its infrared spectrum with that of an authentic sample.[22]

Anal. Calcd. for $C_4H_9O_2P$: C, 40.0; H, 7.6. Found: C, 40.7; H, 7.4.

Cyclotetramethylenetrifluorophosphorane (I).—A mixture of 11.9 g. (0.05 mole) of bis(cyclotetramethylene)biphosphine disulfide and 26.8 g. (0.15 mole) of antimony trifluoride was carefully ground in a drybox and placed under nitrogen protection into a 30-ml. round-bottom flask. The latter was immediately attached to a downward condenser, assembled for distillation *in vacuo*. The mixture was heated at 130–150 mm. Rapid darkening indicated that the reaction commenced. After heating for 1 hr. a liquid started to distil. Material boiling at 90–130° (130–150 mm.) (12.0 g.) was collected and redistilled *in vacuo* through a 4-in. micro-Vigreux column. The boiling point of the twice-distilled product was 61–62° (90 mm.), in accordance with the previous value[3]; 7.4 g. (51.4%) of the purified trifluorophosphorane was isolated, but the actual yield was probably considerably higher, since the glass apparatus was severely attacked. Three grams of a higher boiling material [b.p. 100–112° (35 mm.)] was also collected, but no attempts at its identification were made. By previous experience with fluorophosphoranes, the product is assumed to consist of the phosphinic fluoride, C_4H_8POF.

Cyclotetramethylenetrifluorophosphorane was extremely reactive with moisture. It was distilled directly into Teflon vials and was handled in a drybox only.

In a second preparation the yield of purified cyclotetramethylenetrifluorophosphorane was 61.8%. Distillation of the product over sodium fluoride proved advantageous.

From the residue of the reaction of the biphosphine disulfide with antimony trifluoride, a total of 12.9 g. (84%, based on the reaction equation) of antimony–antimony trisulfide was isolated. Analysis (Found: Sb, 77.87; S, 20.39; Sb + S, 98.26) of the product (carefully washed with methanol and dried *in vacuo*) gave an atomic ratio Sb:S = 1.01:1, in accordance with the stoichiometry of the reaction, which requires the formation of $2Sb + 2Sb_2S_3 \sim Sb_6S_6$.

The X-ray powder diagram confirmed the presence of antimony trisulfide, whereas elemental antimony could not be identified by X-ray diffraction with certainty in the presence of the sulfide.

Anal. Calcd. for $C_4H_8F_3P$: C, 33.4; H, 5.6; F, 39.5; P, 21.5. Found: C, 33.3; H, 5.5; F, 38.1[23]; P, 21.8. Infrared spectrum (liquid): 2960 (s); 2875 (m); 1450, 1429 (s), 1409 (sh); 1310 (w); 1267 (s); 1223, 1183 (m); 1110, 1086, 1012, 993 (s); 958 (w); 907, 880 (vs); 843 (m); 804 (m); 755, 717 (vs). The mass spectrum was obtained on a Consolidated Engineering Corp. Model 21–103C mass spectrometer. Some of the most indicative fragments are listed below.

m/e	Fragment	Relative intensity, %
115	$C_2H_3PF_3^+$	100
116	$C_2H_4PF_3^+$	51.6
125	$C_4H_8PF_2^+$	26.8
55	$C_4H_7^+$	10.8
102	$C_4H_4PF^+$	9.9
123	$C_4H_6PF_2^+$	6.2
144	Parent	0.08

Bis(cyclotetramethylene)biphosphine (VI).—A mixture of 11.9 g. (0.05 mole) of bis(cyclotetramethylene)biphosphine disulfide and 16.75 g. (0.3 g.-atom) of iron powder (electrolytically reduced) was placed in a 25-ml. flask which was attached to a vertical tube of 10 cm. length and *ca.* 15 mm. inner diameter. A distillation head was put on top of this tube, set up for distillation *in vacuo*.

Under a vacuum of *ca.* 150 mm., the reaction was started by gentle heating with a free Bunsen flame, until the gray mixture suddenly became intensely black after 5-min. heating. Cautious heating was continued until reflux of a volatile product was observed (10 min.). Material boiling at 100–160° (mostly 150–160°) (5 mm.) was collected by distillation *in vacuo;* 9.0 g. of a faintly red liquid was obtained, part of which solidified on standing.

This material was redistilled through a 5-in. Vigreux column under careful protection toward the atmosphere; 5.1 g. (58.5%) of the biphosphine, b.p. 50° (0.05 mm.), was obtained. From the distillation residue 3.3 g. (0.014 mole) of unreacted bis(cyclotetramethylene)biphosphine disulfide was recovered. The biphosphine was spontaneously inflammable in the atmosphere and was handled in a nitrogen atmosphere only.

Anal. Calcd. for $C_8H_{16}P_2$: C, 55.1; H, 9.3; P, 35.6. Found: C, 54.6; H, 9.1; P, 35.4. Infrared spectrum (liquid): 2933, 2858 (vs); 2252 (w, P–H?); 1441, 1415 (m); 1298 (w); 1267, 1248 (m); 1170 (m); 1105 (m); 1042, 1028 (w); 948 (m); 873, 852 (w); 821 (m); 731 (m).

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(22) The author is grateful to Prof. B. Helferich for a sample of authentic cyclotetramethylenephosphinic acid.[7]

(23) Fluorine analyses on moisture-sensitive fluorophosphoranes were frequently low, if the samples had to be stored over prolonged periods prior to analysis.

P,P,P′,P′-Bis(cyclotetramethylene)ethylenebiphosphine Disulfide.—A mixture of 21.5 g. (0.09 mole) of bis(cyclotetramethylene)biphosphine disulfide, 3.1 g. of ethylene (0.11 mole), and 0.6 g. of iodine was heated in a 300-ml. autoclave at 275–300° for 48 hr. A crystalline, but partially sticky, dark brown solid (23.0 g.) was recovered upon opening the autoclave at room temperature. The material was dissolved in boiling ethanol, decolorized with charcoal, and allowed to crystallize; 15.5 g. of brownish yellow product was thus obtained which was again recrystallized from ethanol. Analysis of this product indicated that some unreacted starting material was still present, and an analytically pure sample was finally obtained by three further recrystallizations from ethanol. Beautiful white needles of m.p. 174.5° were obtained. A mixture melting point with the starting material (m.p. 185°) showed a depression of 30° (154.5°).

Anal. Calcd. for $C_{10}H_{20}P_2S_2$: C, 45.1; H, 7.6; P, 23.2; S, 24.1; mol. wt., 266.35. Found: C, 45.1; H, 7.6; P, 23.4; S, 24.1; mol. wt., 268.5 (isopiestic in acetone). Infrared spectrum (KBr pellet): 2955 (m), 2872 (sh); 1455, 1407, 1300, 1252, 1182 (m); 1110 (s); 1088, 1051, 1021, 950, 871 (m); 857 (s); 770 (w); 757 (sh); 733 (vs); 715 (w); 686 (m); 598 (vs); 508 (w).

Bis(cyclopentamethylene)biphosphine Disulfide (IV).—The apparatus used was similar to that described for bis(cyclotetramethylene)biphosphine disulfide.

To a double Grignard reagent prepared from 230 g. (1 mole) of 1,5-dibromopentane and 48 g. (2 g.-atoms) of magnesium in 700 ml. of ether was added with stirring 113.2 g. (0.67 mole) of thiophosphoryl chloride in 80 ml. of ether at 0 ± 5°. During the strongly exothermic reaction a highly viscous oil was formed that made stirring difficult. Work-up after 1 hr. of reflux was as above, the aqueous phase being extracted with three 300-ml. portions of chloroform, which was combined with the ether phase. After washing with water and drying with calcium chloride, the solvents were distilled off on a steam bath. Upon standing overnight the yellow oil thus left partially crystallized, and the crystals were collected by filtration. Only 6 g. (~6.8%) of crystalline material was obtained, which was recrystallized from toluene–ethanol (3:1). An analytical sample was twice recrystallized from the same solvent. Even upon repeated recrystallizations the substance invariably softened first at 185° and was completely melted at 225°.

Anal. Calcd. for $C_{10}H_{20}P_2S_2$: C, 45.1; H, 7.6; P, 23.3; S, 24.1; mol. wt., 266.4. Found: C, 45.0; H, 7.7; P, 23.4; S, 24.0; mol. wt., 282, 284 (isopiestic in acetone). Infrared spectrum (in KBr): 2923, 2858 (m); 1630 (vw, bd); 1444, 1402 (m); 1340, 1329 (w); 1210, 1191, 1114 (m); 1028, 930 (vs); 875 (m); 825, 803, 778 (m); 711 (vs); 679 (m); 562 (vs); 518 (s). P^{31} n.m.r. chemical shift $\delta = -37.5$ p.p.m. from 85% H_3PO_4 (in chloroform solution).

No advantage was found in running this reaction at −80° as described for the cyclotetramethylene compound. The yield of the desired product was lower, and its isolation was more difficult due to the increased formation of gummy materials. Extraction of the latter with chloroform over 48 hr. did not yield any additional product.

Cyclopentamethylenephosphinic Acid.—In a similar fashion as described for the five-membered ring compound, 0.8 g. (0.003 mole) of bis(cyclopentamethylene)biphosphine disulfide was oxidized with nitric acid. The crude acid, dried *in vacuo* over phosphorus pentoxide, was recrystallized from benzene–hexane (1:6) to give white needles, m.p. 128–129°, in accordance with the reported data.[5a,b] The yield was 0.64 g. (79.5%). The infrared spectrum was identical with that of an authentic sample.[24]

Cyclopentamethylenetrifluorophosphorane (V).—A mixture of 5.75 g. (0.0215 mole) of bis(cyclopentamethylene)biphosphine disulfide and 8 g. (0.045 mole) of antimony trifluoride was carefully ground in a drybox and placed in a round-bottom flask attached to a Liebig condenser set up for vacuum distillation. *Ca.* 1 g. of sodium fluoride was placed in the receiving flask, together with a magnetic stirring bar.

The mixture was heated gently under a pressure of 100 mm. After 0.7 hr., distillation of a colorless liquid commenced and material boiling at 90–120° (100 mm.) was collected, 4.6 g. (67.3%) being obtained. Upon redistillation through a 5-in. Vigreux column the product had b.p. 64–65° (40 mm.). The highly moisture-sensitive fluorophosphorane was distilled directly into Teflon vials and stored at −80°. The compound was handled in a drybox only. Like cyclotetramethylenetrifluorophosphorane, the compound freezes slightly below room temperature, sometimes solidifying in the condenser upon distillation. From the reaction residue antimony and antimony trisulfide were isolated in nearly quantitative yield.

Anal. Calcd. for $C_5H_{10}F_3P$: C, 38.0; H, 6.4; F, 36.0; P, 19.6. Found: C, 38.4; H, 7.1; F, 35.5; P, 19.8. Infrared spectrum (liquid): 2940 (s), 2866 (w); 1447, 1419 (s); 1399 (sh); 1347 (w); 1310 (s); 1290 (vw); 1242, 1189, 1056 (s); 1038 (w); 1012 (m); 939 (vs); 924, 909 (vw); 876, 840 (vs); 798 (m); 716 (vs, bd). Mass spectrum: A small parent ion is found at *m/e* 158, while the parent less one fluorine (*m/e* 139) is of significant abundance. The *m/e* 140 ion is present in the correct abundance for C^{13} (5.7% of *m/e* 139) to support the presence of five carbon atoms in the fragment $C_5H_{10}PF_2^+$. Further fragments containing C_5 units were observed. A small *m/e* 70 could be due to $C_5H_{10}^+$. The abundant *m/e* 136 ion is believed to result from $C_5H_{10}POF$, formed upon contact of the fluorophosphorane with moisture in the mass spectrometer.

Preparation of Dialkyl- and Phenylalkyltrifluorophosphoranes.—The general procedure was similar to that described for the cyclic trifluorophosphoranes. Experimental conditions, yields, physical properties, and analyses are summarized in Table I.

Preparation of Difluorophosphoranes (*cf.* Table I).—The preparation of $(n\text{-}C_4H_9)_3PF_2$, described below, is typical.

Tri-*n*-butyldifluorophosphorane.—The starting compound, tri-*n*-butylphosphine sulfide, has now been reported in the literature,[25] but it was unknown at the time of this investigation and was prepared by the addition of elemental sulfur (0.25 g.-atom) to tri-*n*-butylphosphine (0.25 mole) with stirring and intensive ice cooling. The reaction was complete in less than 0.5 hr., and the mixture was distilled *in vacuo*. The phosphine sulfide was isolated in essentially quantitative yield as a colorless liquid, b.p. 129–130° (0.5 mm.); $n^{25}D$ 1.5011.

Anal. Calcd. for $C_{12}H_{27}PS$: C, 61.5; H, 11.6; P, 13.2; S, 13.7. Found: C, 61.1; H, 11.4; P, 13.7; S, 13.9.

It was found unnecessary to purify the phosphine sulfide for the subsequent fluorination, and the crude reaction mixture of tri-*n*-butylphosphine and sulfur could be employed directly.

An orange-yellow color was observed immediately when 13.4 g. (0.075 mole) of antimony trifluoride was added with stirring to 21 g. (0.09 mole) of tri-*n*-butyl phosphine sulfide. After 2 hr. heating with stirring at 30 mm. (maximum temperature 130°) the color became intensely red-black. Distillation *in vacuo* yielded 15.5 g. of a colorless liquid boiling at 75–125° (0.5–2 mm.) which was redistilled through a 5-in. Vigreux column to give 13.2 g. (61%) of the pure fluorophosphorane; b.p. 71–72° (0.4 mm.); $d^{25}{}_4$ 0.9398; $n^{25}D$ 1.4320.[26]

The black residue left after the distillation was completed was rinsed out with methanol, filtered, and dried; yield 9.35 g. (92.3%). The identity of the material was established by chemical and X-ray analysis.

Anal. Calcd. for Sb_2S_3: Sb, 71.7; S, 28.3. Found: Sb, 69.7; S, 28.5.

X-Ray comparison with authentic antimony trisulfide (ASTM 6–0474) showed complete identity.

Conversion of P,P,P′,P′-Tetramethylethylenebis-difluorophosphorane into P,P,P′,P′-Tetramethylethylenebis-phosphine Di-

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[24] A sample of cyclopentamethylene phosphinic acid[6b] was kindly furnished for comparison by Prof. E. G. Howard.

(25) R. A. Zingaro and R. E. McGlothlin, *J. Org. Chem.*, **26**, 5205 (1961).

(26) Tri-*n*-butyldifluorophosphorane has been obtained independently by the reaction of hexafluorothioacetone dimer with tri-*n*-butylphosphine; b.p. 76–77° (0.6 mm.); $n^{25.2}D$ 1.4335 (W. J. Middleton, personal communication).

oxide.—The solution of 2.26 g. (0.01 mole) of the bis-difluorophosphorane in 10 ml. of water was allowed to stand overnight and was then evaporated on a steam bath to leave a very deliquescent white solid, which was dried *in vacuo* over phosphorupentoxide at 80° (0.1 mm.) for 20 hr. The dried product was sublimed twice at 230-240° (oil bath temperature) (0.2 mm.); a melting point of *ca.* 230° being observed. A determination of the melting point on the sublimed material invariably led to values about 20° lower when the sample was sealed in the capillary at atmospheric pressure. A sample of the diphosphine dioxide was, therefore, placed in a capillary, heated at 130° (0.1 mm.) for 1 hr., and sealed under vacuum. A reproducible m.p. of 236.5-237.5° was thus observed, in excellent agreement with the literature[18] m.p. of 232°.

Anal. Calcd. for $C_6H_{16}O_2P_2$: C, 39.6; H, 8.9. Found: C, 39.3; H, 9.0.

Acknowledgment.—The author is indebted to Mr. R. J. Berndt, Central Research Department, E. I. du Pont de Nemours and Company, for the mass spectroscopic analyses.

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Preparation of Heterosubstituted Phosphonitriles by Ring Closure Reactions

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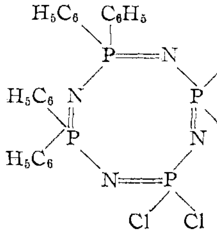
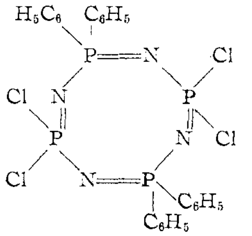
Iminobis(aminodiphenylphosphorane) chloride, $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$, reacts with pentavalent phosphorus halides to yield cyclic phosphonitrilic trimers and tetramers. Cyclization with phosphorus pentachloride gives 1,1,3,3-tetraphenyl-5,5-dichlorophosphonitrile trimer and 1,1,3,3-tetraphenyl-5,5,7,7-tetrachlorophosphonitrile tetramer. With phenyltetrachlorophosphorane, pentaphenyl monochlorophosphonitrile trimer and two hexaphenyldichlorophosphonitrile tetramers are formed. Reaction of the bis(aminophosphorane) with diphenyltrichlorophosphorane gives $[(C_6H_5)_2PN]_3$ and $[(C_6H_5)_2PN]_4$.

Introduction

The preparation of cyclic phosphonitriles of the type $R_{2x-y}Cl_yP_xN_x$ (where R = aryl or alkyl and X = 3 or 4) has been reported by several investigators. Bode and Thamer[1] treated dichlorophosphonitrile tetramer with phenylmagnesium bromide and isolated compounds I and II which were assigned the structures

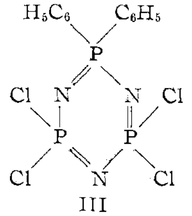


I, m.p. 205°

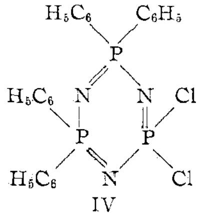


II, m.p. 176°

Using the Friedel-Crafts reaction, Bode and Bach[2] prepared III from dichlorophosphonitrile trimer and aluminum chloride; under more vigorous conditions, Shaw and Wells[3] obtained IV employing the same process.



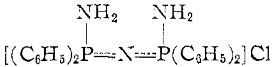
III



IV

In all these instances mixed substitution occurred geminally on the existing phosphonitrile ring systems. The procedures described above offer poor yields and a multiplicity of products. It seemed probable that higher yields of single component products could be obtained by the proper ring closure reaction.

This paper describes the results of ring closure reactions between pentavalent phosphorus halides and a bis(aminodiphenylphosphorane). The latter compound has been prepared by the reaction of diphenyltrichlorophosphorane with ammonia[4-6] and by the reaction of diphenylchlorophosphine with ammonia and chloramine.[7] The structure of the phosphorane has been postulated to be[7]



$$[(C_6H_5)_2\overset{NH_2}{\overset{|}{P}}=N=\overset{NH_2}{\overset{|}{P}}(C_6H_5)_2]Cl$$

V

Experimental

The phenyldichlorophosphine and diphenylchlorophosphine used in these experiments were obtained from Victor Chemical Works.

The reactions were conducted in all-glass assemblies either on a vacuum line or in an inert atmosphere chamber. All melting points are uncorrected.

Diphenyltrichlorophosphorane.—Dry chlorine gas (48.21 g., 0.68 mole) was condensed into a nickel-plated bomb containing 3000 ml. of carbon tetrachloride and 150.2 g. (0.68 mole) of diphenylchlorophosphine at −196°. After standing overnight at

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[1] H. Bode and R. Thamer, *Ber.*, **76B**, 121 (1943).

[2] H. Bode and H. Bach, *ibid.*, **75B**, 215 (1942).

[3] R. A. Shaw and F. B. G. Wells, *Chem. Ind.* (London), 1189 (1960).

[4] NavOrd Report 4600, July-Sept., 1956, U. S. Naval Ordnance Laboratory, Corona, Calif.

[5] V. V. Korshak, I. A. Gribova, T. V. Artamonova, and A. N. Bushmarina, *Vysokomolekul. Soedin.*, **2**, 377 (1960).

[6] I. I. Bezman and J. H. Smalley, *Chem. Ind.* (London), 839 (1960).

[7] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).