Acetoxyphosphines[1]

By Louis K. Peterson and Anton B. Burg

The stable acetoxyphosphine $(CF_3)_2POOCCH_3$ (m.p. $-58°$, b.p. estd. 98°, ultraviolet absorption at 2030 Å.) was made from $AgCO_2CH_3$ and $(CF_3)_2PBr$ or $(CF_3)_2PCl$, or by direct combination of $(CF_3)_2POP(CF_3)_2$ with $(CH_3CO)_2O$. It forms a moderately stable 1:1 $(CH_3)_3N$ adduct (m.p. $-31°$). The trifluoroacetoxyphosphine $(CF_3)_2POOCCF_3$ (55 mm. at 0°) was made by similar methods; it soon equilibrates with smaller amounts of $(CF_3)_2POP(CF_3)_2$ and $(CF_3CO)_2O$, with $K_D = 0.11$ at 40°. The diacetoxyphosphine $CF_3P(OOCCH_3)_2$ (0.4 mm. at 22°) was made by the silver salt method, or by the reaction of CF_3PCl_2 with $(CH_3CO)_2O$, apparently through an intermediate acetoxychlorophosphine. HCl converted it mostly to CF_3PCl_2 and $2CH_3COOH$. Also $CF_3P(OOCCF_3)_2$ (m.p. $-24°$, b.p. estd. 111°) was made from $AgCO_2CF_3$. Both diacetoxyphosphines were analyzed by basic hydrolysis to form HCF_3, HPO_2^{-2}, and either $2CH_3CO_2^-$ or $2CF_3CO_2^-$. They dissociate to the respective acetic anhydrides and polymeric material; there is evidence of an intermediate diacetoxydiphosphoxane stage, but no pure $(CF_3PO)_n$ polymer could be recognized. Trimethylamine seemed to promote both polymerizations. The infrared spectra of all four acetoxyphosphines are compared. In relation to the syntheses, pure $(CF_3)_2PI$, $(CF_3)_2PCl$, and CF_3PCl_2 were characterized in regard to volatility.

Acetoxyphosphines of the types $R_2POOCCH_3$ and $RP(OOCCH_3)_2$ might be expected to be unstable for at least two reasons. If R is a hydrocarbon group, effective base action by phosphorus should cause rearrangements analogous to the Arbuzov reaction, leading to acetylphosphine oxides and their further reaction products; or the first step could be the formation of acetic anhydride and P–O–P linkages, which would be susceptible to rapid rearrangement and disproportionation.[2] However, if R is a very electronegative group, tending to weaken the base action of phosphorus, such acetoxyphosphines could be fairly stable, or at least remain in equilibrium with the acid anhydrides.

These ideas are supported by the existence of the new compounds $(CF_3)_2POOCCH_3$ (A), $(CF_3)_2POOCCF_3$ (B), $CF_3P(OOCCH_3)_2$ (C), and $CF_3P(OOCCF_3)_2$ (D), all of which seem to be stable against rearrangement to acetylphosphine oxides, but differ among themselves in regard to splitting off acetic anhydrides. Compound A proved to be the stablest; in fact, it was argued beforehand that of the two disproportionations

$$2(CF_3)_2POOCCH_3 \rightleftharpoons (CF_3)_2POP(CF_3)_2 + (CH_3CO)_2O \quad (1)$$

$$2(CF_3)_2POOCCF_3 \rightleftharpoons (CF_3)_2POP(CF_3)_2 + (CF_3CO)_2O \quad (2)$$
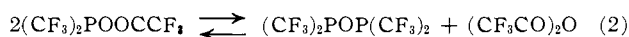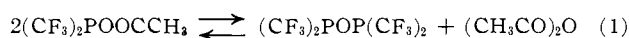
the latter would equilibrate more toward the right because the π-bonding interaction of the C–O–P oxygen with the P_{3d} orbitals would be weaker; and the difference would be the governing effect. Actually, reaction 1 went quantitatively to the left, whereas reaction 2 equilibrated easily at 25°, with the dissociation constant approximately equal to 0.11.

By a similar argument, one would expect compound C to be stabler than D, and it may well be so in the thermodynamic sense, but D seems to have a more enduring metastability. In either case, the loss of the pertinent acetic anhydride would lead to polymeric rings or chains of CF_3PO units; however, it seems that such polymerization is limited by the increasing stability of more widely separated $-O-P(CF_3)O-C(O)R$ end groups. A nonvolatile by-product of the synthesis

(2) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 3442 (1962).

of C seemed to be a diacetoxydiphosphoxane, but further reactions led to brown nonvolatiles suggestive of proton lability. Thus it never was possible to demonstrate a pure $(CF_3PO)_n$ polymer, although the P–O–P–O– polymer-bonding principle seems to have reality.

The experimental work here described was performed by means of high-vacuum manifolds, with U-tubes for separation of volatiles by fractional condensation methods; thus the syntheses could be studied quantitatively. Sometimes grease was avoided by the use of Stock-type mercury float valves; or for work with mercury-sensitive materials, halocarbon-greased stopcocks were used, and pressures were measured by means of a spoon gauge used as a null instrument. In some cases quantitative syntheses were found preferable to other types of analysis.

A. Bis(trifluoromethyl)acetoxyphosphine

Synthesis.—The initial syntheses of the new compound $(CF_3)_2POOCCH_3$ (A) were done by the action of $(CF_3)_2PBr$ or $(CF_3)_2PCl$ upon $AgCO_2CH_3$—well dried and mixed with broken glass in a flask attached to the high-vacuum system. The $(CF_3)_2PBr$ reaction gave a 95% yield of A during 3 min. at 24°, whereas the subsequent action of $(CF_3)_2PCl$ upon the remaining solids gave only a 61% yield after 10 min. The formation of some $(CH_3CO)_2O$ but no $(CF_3)_2POP(CF_3)_2$ suggested some loss of yield caused by the secondary process

$$(CF_3)_2POOCCH_3 + AgCO_2CH_3 \longrightarrow$$
$$AgOP(CF_3)_2 + (CH_3CO)_2O$$
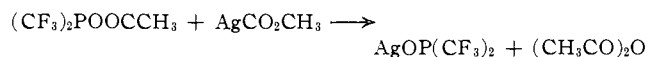
After A had proved to be stable in regard to reaction 1, its synthesis from 1.159 mmoles of $(CF_3)_2POP(CF_3)_2$ and 1.888 mmoles of $(CH_3CO)_2O$ was tried. After 6 days at 25° the mixture was quantitatively resolved into A and unused $(CH_3CO)_2O$ (trapped at $-23°$ and identified by its 40 mm. vapor tension at 62°), demonstrating the empirical equation

$$(CF_3)_2POP(CF_3)_2 + 1.128(CH_3CO)_2O \longrightarrow$$
$$1.919(CF_3)_2POOCCH_3$$
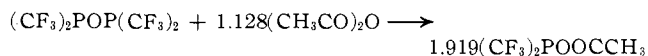
Thus the recovery of A represented 96% of the diphosphoxane (of which none at all could be recovered), and the deviations from a strictly quantitative stoichiometry could be ascribed to absorption in the stopcock grease.

Physical Properties.—Two separately purified samples of A both melted sharply at −57.8°. The vapor tensions of a pure middle fraction (trapped at −64°) were measured in an immersible tensimeter,[3] with no decomposition resulting from heating at 45°. The results, given with an equation in Table I, indicate the normal boiling point to be 97.5° and the Trouton constant 22.7 e.u.

TABLE I

VAPOR TENSIONS OF $(CF_3)_2POOCCH_3$

$\log P = 7.4481 + 1.75 \log T - 0.006525T - 2461/T$

Temp., °C.	0.00	9.5	17.2	21.35	28.3	39.5	44.85
P_{obsd}, mm.	8.32	15.3	24.5	31.0	45.2	80.0	103.7
P_{calcd}, mm.	8.32	15.4	24.4	31.0	45.3	80.0	103.2

Vapor density determinations gave molecular weight values varying from 224 to 236 (calcd. for A, 228), with inaccuracies due to unavoidable absorption in stopcock grease.

The ultraviolet absorption spectrum of A as a vapor at 1 mm. in a quartz cell of 10-mm. path length was recorded by the Cary Model 14PM instrument, showing a strong peak at 2030 Å. This is a shorter wave length than shown by $(CF_3)_2POP(CF_3)_2$ (2110 Å.)[2] or by a variety of acetyl compounds.[4]

A Trimethylamine Adduct.—A mixture of 0.249 mmole of A and 0.364 mmole of $(CH_3)_3N$ was allowed to stand for 2 hr. at −78°, and then the excess amine (0.119 mmole) was recovered by a 90-min. distillation into a trap at −196°. Thus the white solid residue contained $0.985(CH_3)_3N$ per $(CF_3)_2POOCCH_3$. Its dissociation pressures, correlated by the equation

$$\log P = 3.502 - 631/T$$

up to the melting point −31.4°, are presented with two deviant values above the melting point in Table II.

TABLE II

DISSOCIATION PRESSURES OF $(CF_3)_2POOCCH_3 \cdot (CH_3)_3N$

Temp., °C.	−78.5	−64.8	−46.0	−31.4	−23.4	0.00
P_{obsd}, mm.	1.75	3.0	5.5	7.8	11.8	22.5
P_{calcd}, mm.	1.82	3.0	5.3	7.9	9.5	15.6

These results are not directly interpretable in terms of free energies, since it is not known whether the adduct exists appreciably in the vapor phase. However, it is clear that this adduct is less stable than $(CF_3)_2POP$-$(CF_3)_2 \cdot (CH_3)_3N$,[2] and it can be understood that each phosphorus atom in the diphosphoxane undergoes less O_{2p} to P_{3d} π-bonding than occurs when one oxygen bonds in this manner to one P atom in the acetoxyphosphine A. Hence A would be expected to be a somewhat weaker electron acceptor than the diphosphoxane.

Attempts to demonstrate the attachment of a second $(CH_3)_3N$ to A did not succeed: there was only a continuous rise of pressure as the amine was introduced to the 1:1 adduct.

B. Bis(trifluoromethyl)trifluoroacetoxyphosphine

Synthesis.—Two samples of $(CF_3)_2PI$ (0.801 and 1.632 mmoles) were allowed to react (well below room temperature) with excess $AgCO_2CF_3$, rapidly develop-

ing the AgI color. The iodine-free volatile product would correspond to a 90% yield of the trifluoroacetoxyphosphine B; however, its variable volatility indicated a mixture. Vacuum distillation in a small wire spiral column (reflux at −60°) yielded a top fraction (102 mm. at 0°) strongly showing the infrared bands characteristic of $(CF_3CO)_2O$, and a bottom fraction (29 mm. at 0°), similarly proved to be mostly $(CF_3)_2POP(CF_3)_2$—both as demanded by eq. 2. However, a fairly large middle fraction (55 mm. at 0°) had the right molecular weight for the expected acetoxyphosphine B (obsd. and calcd., 282). Its infrared spectrum showed an intense band at 1104 cm.$^{-1}$ (C—OP stretching) and another at 1818 cm.$^{-1}$ (C=O stretching), both distinctly different from any bands in the spectra of $(CF_3)_2POP(CF_3)_2$ and $(CF_3CO)_2O$. The spectra of some fractions (all melting near −75°) showed the absence of either the diphosphoxane or the anhydride (but never both); hence, the spectrum of B could be inferred from results for the mixtures. This spectrum is presented with others in Table III.

Equilibria in Reaction 2.—The disproportionation of B was studied in an infrared cell of 10-cm. path, using known pressures of the volatile reaction product of the action of $(CF_3)_2PI$ upon $AgCO_2CF_3$; or the equilibrium was approached in the opposite direction, from mixtures of $(CF_3)_2POP(CF_3)_2$ and $(CF_3CO)_2O$ at known initial partial pressures. The rate of either equilibration could be observed best by means of the C=O stretching band of the anhydride, which was well isolated at 1883 cm.$^{-1}$. Constancy was attained within 80 min., and then the partial pressure of each of the three components could be determined by comparison of the intensity of the 1883 band with that for samples of $(CF_3CO)_2O$ at known pressures. The values of

$$K_D = \frac{[(CF_3)_2POP(CF_3)_2][(CF_3CO)_2O]}{[(CF_3)_2POOCCF_3]^2}$$

at the cell chamber temperature of the Beckman IR7 instrument varied over the range 0.09–0.13, independently of the direction of approach to equilibrium. The most reasonable average value for K_D was 0.11 at 40°.

C. Trifluoromethyldiacetoxyphosphine

Synthesis.—The instability of compound C prevented any quantitative synthesis; for example, the reaction

$$2AgCO_2CH_3 + CF_3PCl_2 \longrightarrow 2AgCl + CF_3P(OOCCH_3)_2$$
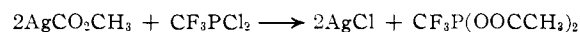
never gave more than a 35% yield of C. A major product was acetic anhydride, which passed a high-vacuum trap at −16° and condensed at −23°; it was identified by its melting point of −73°, its 40 mm. vapor tension at 62°, and its infrared spectrum.[5] Its presence suggests the disproportionation

$$CF_3P(OOCCH_3)_2 \longrightarrow (CH_3CO)_2O + CF_3PO$$
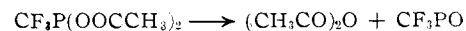
doubtless complicated by the variety of roles which the CF_3PO unit is expected to play in the waxy nonvolatile solid product.

The desired acetoxyphosphine C was trapped *in vacuo* at 0°, and on standing for 2 days at that temperature, it not only liberated acetic anhydride, but also developed a deep brown color. Its vapor tension at 22° was measured as 0.4 mm., and the 6.8 mm. value

(3) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 785 (1937).

(4) (a) H. Ley and B. Arends, *Z. physik. Chem.*, **B17**, 194 (1932); (b) C. Scheibe, P. Povenz, and C. F. Linström, *ibid.*, **B20**, 297 (1933).

(5) H. W. Thompson, *Analyst*, **70**, 447 (1945).

observed at 57.7° probably was too high on account of decomposition. The molecular weight of a fresh sample was determined in the immersible tensimeter[3] as 218 (calcd., 218). Further evidence of the formula $CF_3P(OOCCH_3)_2$ came from the basic hydrolysis and the HCl reaction. The saturated vapor showed no ultraviolet absorption (2000–3400 Å.).

Analysis of C by Hydrolysis.—A 31.6-mg. (0.145 mmole) sample of C was hydrolyzed in a closed tube by 15.10 ml. of 0.1025 N NaOH, liberating 0.138 mmole of HCF_3 (calcd., 0.145; identified by its infrared spectrum); then a back-titration by standard HCl showed that the consumption of NaOH had been 0.598 mmole, or 4.13 OH^- per unit of C. These results agree with the equation

$$CF_3P(OOCCH_3)_2 + 4OH^- \longrightarrow$$
$$HCF_3{}^- + HPO_3{}^{-2} + H_2O + 2CH_3CO_2{}^-$$
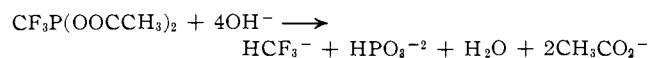
confirming the formula of C.

Synthesis from Acetic Anhydride.—An exchange of Cl for acetate, between CF_3PCl_2 and $(CH_3CO)_2O$, produced CH_3COCl and C, along with some other products. In the initial attempt, the equimolar mixture of CF_3PCl_2 and $(CH_3CO)_2O$ turned orange during 8 days at 25°; then the volatiles were resolved into various fractions: a mixture spectroscopically recognized as CH_3COCl and CF_3PCl_2, some acetic anhydride, an appreciable yield of C, and a middle fraction (14 mm. at 0°) which seemed to be the previously unknown $CF_3PCl(OOCCH_3)$. The red-brown nonvolatile oily residue dissolved partly in CCl_4 and the rest in acetone; the spectra of these nonvolatile solutes were somewhat diffuse, but showed vibration frequencies characteristic of methyl, trifluoromethyl, and C=O groups.

The reaction was repeated in one limb of a differential tensimeter, wherein the molecular weight of a nonvolatile solute could be determined by the vapor tension lowering of a solvent. With $3.556(CH_3CO)_2O$ per CF_3PCl_2 the process did not occur appreciably during 5 hr. at 0°, but progressed well and without coloration during 10 hr. at 25°. The yield of C (0.4 mm. at 22°) represented 28% of the original CF_3PCl_2, much of which was recovered in a top fraction including the similarly volatile CH_3COCl. There was no appreciable yield of the presumed $CF_3PCl(OOCCH_3)$, presumably because there was a large excess of $(CH_3CO)_2O$.

The weight of the nonvolatile white residue in the differential manometer tube was determined by the difference between the volatiles and the original reactants; thus it was possible to determine the molecular weight by the vapor tension lowering in ether solution. The result, 390, seems most reasonably interpretable in terms of the diacetoxydiphosphoxane $CH_3COO(CF_3)POP(CF_3)OOCCH_3$ (calcd. mol. wt., 334), probably containing some longer-chain material. On further standing in ether solution, it developed a red-brown color.

The Reaction of C with HCl.—The major result of the reaction of C with HCl can be expressed by the equation

$$2HCl + CF_3P(OOCCH_3)_2 \longrightarrow CF_3PCl_2 + 2CH_3COOH$$
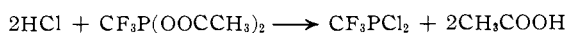
However some CH_3COCl and nonvolatile material also were formed. The 0.283-mmole sample of C consumed 0.450 mmole of HCl (from the initial 1.680-

mmole sample) during 3 days at 25°. The volatiles were removed and the residue absorbed a further 0.123 mmole of HCl during 3 hr. at 60°, producing more volatiles. The final nonvolatile residue reacted with aqueous KOH to yield 0.015 mmole of HCF_3, accounting for 5% of the CF_3P units. Of the volatiles, one fraction (29 mm. at −31°) passed through a high-vacuum trap at −78° and condensed at −96°; by its infrared spectrum, average molecular weight 156, and yield of HCF_3 by basic hydrolysis, this fraction was judged to be 0.232 mmole of CF_3PCl_2 with 0.071 mmole of CH_3COCl. The fraction trapped at −78° proved to be 0.491 mmole of acetic acid (10 mm. at 17.5°, infrared spectrum agreed).[6] Thus the recovery of acetyl units among the volatile products was 0.562 mmole or 99.3%, further demonstrating the formula of C. The accounting for Cl was only 94%, suggesting its presence in the nonvolatile product, which might be formulated as a P–O–P linked polymer having CF_3PCl or CF_3PHO end groups.

D. Bis(trifluoroacetoxy)trifluoromethylphosphine

Synthesis.—The action of CF_3PI_2 upon excess $AgCO_2CF_3$ during 10 hr. at 25° gave only $(CF_3CO)_2O$ (98%, based upon the decomposition of the expected D) and a nonvolatile wax. When the process was stopped after 10 min., the yield of $(CF_3CO)_2O$ was 72%, and other volatile fractions included $CF_3P(OOCCF_3)_2$ [D, 6 mm. at 0°; mol. wt., 332 (calcd., 326)]. A trace of less volatile material (2.5 mm. at 0°) showed an infrared band at 920 cm.$^{-1}$, strongly suggestive of P–O–P bonding,[2] as in the expected $CF_3COO(CF_3)POP(CF_3)OOCCF_3$. The two experiments taken together showed that the initially formed diacetoxyphosphine D slowly decomposes to P–O–P chain polymers, from which the last of the CF_3CO and CF_3COO units split off with some difficulty. An attempt to obtain a $(CF_3PO)_n$ ring by heating the nonvolatile material did not succeed.

For a more effective synthesis of D, a bed of $AgCO_2CF_3$ and broken glass at 25° was exposed repeatedly to a stream of CF_3PCl_2, mixed with $(CF_3CO)_2O$ to minimize dissociation of the product. Thus a mixture of 2.525 mmoles of CF_3PCl_2 and 6.335 mmoles of $(CF_3CO)_2O$ (previously shown to react only slightly together during 3 days at 25°) produced 1.465 mmoles of D, a 58% conversion from CF_3PCl_2. The product was isolated by slow passage through a high-vacuum trap at −45°, condensing as a white solid at −63°.

Physical Properties and Formula of D.—Two purified fractions of D melted sharply at −23.7°. The vapor tension values 6.4 mm. at 0° and 19.5 mm. at 18.5°, taken with the assumption of a normal Trouton constant (21.00 e.u. at the normal boiling point, estimated as 111°), determined the equation

$$\log P = 6.738 + 1.75 \log T - 0.005935T - 2342/T$$

It was not feasible to determine vapor tensions at higher temperatures, on account of dissociation. The molecular weight was redetermined as 323 (calcd., 326), with a slight absorption into stopcock grease accounting for the low result. The infrared spectrum (Table III) was the same as for the original sample.

(6) R. H. Pierson, A. N. Fletcher, and E. St. C. Gantz, *Anal. Chem.*, **28**, 1218 (1956).

A 0.3752-mmole sample of D was hydrolyzed in a standard base solution, liberating 0.3703 mmole of HCF_3 (98.7%); a back-titration showed the consumption of 1.55 mmoles (calcd., 1.50) of OH^-. Thus the equation for basic hydrolysis can be written as

$$CF_3P(OOCCF_3)_2 + 4OH^- \longrightarrow$$
$$HCF_3 + HPO_3^{-2} + 2CF_3CO_2^- + H_2O$$
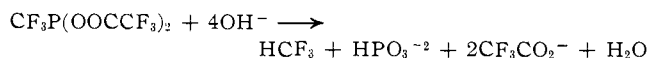
confirming the formula of D.

Thermal Instability.—A sample of D, stored for 66 hr. at 25°, gave an 8% yield of $(CF_3CO)_2O$ and nonvolatiles; however, after 12 hr. at 60°, this dissociation had progressed only 20%. It may be supposed that the initial dissociation rapidly forms $(CF_3CO)_2O$, which then exerts some inhibiting effect by suppressing a reversible first step of the mechanism.

The Reaction with Trimethylamine.—Compound D was converted to nonvolatile material by one-fifth as much $(CH_3)_3N$, with some liberation of $(CF_3CO)_2O$ to complicate interpretations. Thus a mixture of 0.818 mmole of D and 0.159 mmole of $(CH_3)_3N$ during 9 hr. at 25° formed 0.217 mmole of $(CF_3CO)_2O$, with recovery of 0.005 mmole of D and no amine. The main product was a slightly yellow, highly viscous liquid. It seemed that the amine might have attached to P (either in D or in a P–O–P dissociation product—as is known for the simplest of the diphosphoxanes),[2] inducing enough base action elsewhere to form a dative-bonded polymer chain.

Infrared Spectra

The vapor phase infrared spectra of the acetoxyphosphines A, B, C, and D, recorded by the Beckman IR7 instrument, are presented in Table III. The results cannot be regarded as complete in all respects, for the pressures were limited to the saturation values at the 40° cell chamber temperature of the instrument, and sometimes fast scans were necessary on account of instability. However, the observed bands can be assigned to expected vibrational modes without many or severe uncertainties. Quite expected for B and D were CC–F bendings and stretchings at frequencies higher than for PC–F bendings and stretchings; and the weakness of C–H stretching bands is normal for CF_3P compounds containing CH_3 groups. The $C=O$ bending bands for B and D should occur at slightly higher frequencies than for A and C, since the $C=O$ bond is tighter in CF_3CO_2 than in CH_3CO_2; hence there probably was some occlusion of these B and D bands by the especially intense C—F stretching bands. Thus the 1078-cm.$^{-1}$ band for D might be one of the two $C=O$ bending bands (in phase and out of phase) expected for two CF_3CO_2 groups.

Expected bands below 700 cm.$^{-1}$ were not sought, for the CsI optics were not available at the time (early 1962) when this work was performed.

As mentioned before, the spectrum of B had to be corrected for bands belonging to its dissociation products, $(CF_3CO)_2O$ and $(CF_3)_2POP(CF_3)_2$. Hence in order to validate the results here presented, it is useful to list the bands observed for these products under the same conditions. For the diphosphoxane these bands were 2280 w, 1280 w, 1234 vs, 1174 vs, 1142 vs, 943 m, 923 s, 886 m, 747 m, and 712 m cm.$^{-1}$; and for trifluoroacetic anhydride the bands were 2600 w, 2380 w, 1883 s, 1818 s, 1330 s, 1248 vs, 1200 vs, 1120 m,

TABLE III
INFRARED SPECTRA[a] OF FOUR ACETOXYPHOSPHINES[b]

Suggested assignment	A	B	C	D
2 × C=O stretch	3575 vvw	3565 w	(Too weak)	3600 w
C–H stretching	3030 vw		2963 w	
C–F stretching overtones etc.	2363 vw	2410 w	2375 vvw	
	2275 w			
894 + 1180	2075 vw			
Uncertain	1992 w		1994 w	1995 vw
	1967 vw			
	1914 vw			
C=O stretching	1800 s	1817 vs	1831 vw,sh	1828 s
	1775 m,sh		1781 ms	
CH₃, δ-a	1436 mw		1438 w	
C–O stretching	1378 ms	1337 s	1378 ms	1349 ms
CH₃, δ-e	1290 mw		1306 w	
	1275 mw		1284 w	
			1250 mw	
			1231 mw	
Uncertain		1290 w		
C–F stretching (may cover C=O bending)	1222 vvs	1245 vs	1202 s	1253 s
	1180 vvvs	1225 vs	1187 vs	1224 s
	1141 vvs	1200 vs	1155 vvs	1203 s
	1128 vvs	1177 vs		1167 s
		1139 vs		1126 s
		1103 vs		
C=O bending	1075 mw		1075 w	1078 s
			(1050 vw)	
CH₃ rocking	1006 ms		1005 ms	
CH₃ wagging	894 s		909 m	
Uncertain				907 mw
C–C stretching		853 m	881 ms	853 m
P–O stretching	781 ms	783 ms	788 mw	798 m
CC–F bending		765 m		778 ms
				762 ms
PC–F bending	750 w	750 m	769 m	730 m
Uncertain		729 m		710 w

[a] In cm.$^{-1}$. [b] w = weak, m = medium, s = strong, v = very, sh = shoulder, δ = deformation, a = asymmetric, e = symmetric.

1054 vs, 873 m, 757 m, and 730 w cm.$^{-1}$. Thus weak bands appearing in the spectrum of B at 922, 942, 1054, and 1883 cm.$^{-1}$ could be attributed to strong bands of the dissociation products, and in other cases of near coincidence the bands of B were strong enough not to be affected much by these minor components.

Characterization of Reactants

Most of our acetoxyphosphine syntheses required pure $(CF_3)_2PI$, $(CF_3)_2PCl$, or CF_3PCl_2 and evidence of their purity. As usually obtained, $(CF_3)_2PI$ contains oxyphosphine impurities and apparently some $P_2(CF_3)_4$, arising at least partly from a limited spontaneous liberation of iodine from $(CF_3)_2PI$. For a pure sample this iodophosphine was converted wholly to $P_2(CF_3)_4$, which was purified by a high-vacuum fractionating column and converted back to $(CF_3)_2PI$ by iodine in excess. A column-purified sample then showed the vapor tensions given in Table IV. These

TABLE IV
VAPOR TENSIONS OF $(CF_3)_2PI$

$$\log P = 6.0085 + 1.75 \log T - 0.005407T - 1964/T$$

Temp., °C.	0.00	15.6	25.4	32.7	41.5	47.4	32.3[a]
P_{obsd}, mm.	40.3	89.6	140.3	191.5	273.7	341.8	188.7
P_{calcd}, mm.	40.3	89.5	140.3	191.9	273.3	341.8	188.7

[a] Observation taken after cooling, showing that the sample was undamaged by heating.

pressures were measured by an immersed null-indicating spoon-gauge system, with the sample confined by a magnetically controlled inner-joint stopper caulked by Apiezon W wax. The values were corrected to 0°

mercury and also for a small deviation of the local g value (979.60 $vs.$ the standard 980.665). The equation gives the normal boiling point as 71.1° and the Trouton constant as 21.05 e.u. The consistency of the results indicates good purity, and the value at 0° can be used as a test of purity.

The chlorophosphines $(CF_3)_2PCl$ and CF_3PCl_2 were made from the highly purified iodophosphines by reaction with well-dried $HgCl_2$, present in excess. Both were purified by high-vacuum distillation methods, until each showed a uniform volatility for a series of fractions. The vapor tension data for middle fractions are shown with equations in Tables V and VI. For $(CF_3)_2PCl$ the normal boiling point is calculated as 23.2° and the Trouton constant as 22.05 e.u. For CF_3PCl_2, the boiling point is 39.4° and the Trouton

TABLE V
VAPOR TENSIONS OF $(CF_3)_2PCl$

$$\log P = 4.1432 + 1.75 \log T - 0.002582T - 1429/T$$

Temp., °C.	−80.8	−64.8	−46.0	−31.4	−22.7	0.00
P_{obsd}, mm.	1.64	6.34	24.8	59.8	97.5	295.3
P_{calcd}, mm.	1.64	6.38	24.5	60.1	97.5	295.3

TABLE VI
VAPOR TENSIONS OF CF_3PCl_2

$$\log P = 4.2229 + 1.75 \log T - 0.002743T - 1516/T$$

Temp., °C.	−64.8	−46.0	−19.5	0.00	10.15	17.3
P_{obsd}, mm.	2.72	11.3	57.2	154.0	243.4	329.1
P_{calcd}, mm.	2.72	11.2	57.3	154.0	243.4	329.1

constant is 21.75 e.u.; also, its melting point was observed as −129.6 ± 0.1° (ethylene vapor tension thermometer).

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID COMPANY, STAMFORD, CONNECTICUT]

Phosphonitrilic Compounds. II.[1] Reactions of Phosphonitrilic Chlorides with Catechol and Triethylamine

BY H. R. ALLCOCK

Phosphonitrilic chloride trimer undergoes dehydrochlorination reactions with catechol and triethylamine to form tris(o-phenylenedioxy)phosphonitrile trimer and polymers. An unusual side reaction, involving phosphorus–nitrogen ring cleavage, yields the triethylamine salt of 2-(o-hydroxyphenoxy)-2,2'-spirobi[1,3,2-benzodioxaphosphole], which appears to exist as the hexavalent phosphorus anion tautomer in the crystalline state. This product was also formed when phosphonitrilic chloride tetramer or polymer was treated with catechol and triethylamine. The results are interpreted in terms of possible reaction mechanisms.

Introduction

Several authors have reported the reactions of phosphonitrilic chlorides with alcohols or phenols, or with their alkali metal salts, to give alkyl or aryl phosphonitrilates according to the equations[2]

$$(NPCl_2)_n + 2nROH \xrightarrow{base} [NP(OR)_2]_n + 2nHCl$$

$$(NPCl_2)_n + 2nRONa \longrightarrow [NP(OR)_2]_n + 2nNaCl$$
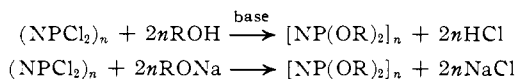
Such reactions have been investigated principally for the cyclic trimeric and tetrameric phosphonitrilic chlorides (where n is 3 or 4) under conditions which led to complete substitution of chlorine atoms by alkoxy or aryloxy groups.[3–9]
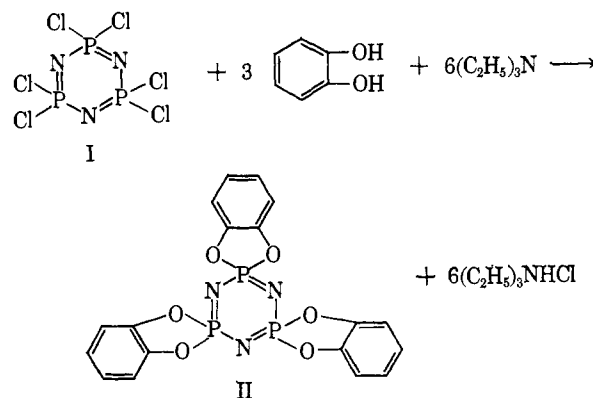
It was of interest, therefore, to ascertain if similar reactions could be employed to effect ring closure at each phosphorus atom using an aromatic $ortho$ diol such as catechol,[10] and to establish if a cyclization reaction of this type could be used to prepare partially substituted phosphonitrilic chlorides in which the exact location of the unreacted chlorine atoms would be known. Although no partially substituted products

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(10) For a preliminary account of parts of this work, see H. R. Allcock, $J. Am. Chem. Soc.$, **85**, 4050 (1963).

were isolated, the results suggested the mechanism of chlorine replacement in these reactions.

Results and Discussion

Treatment of phosphonitrilic chloride trimer (I) with catechol, in tetrahydrofuran or benzene, using triethylamine as a hydrogen chloride acceptor, resulted in three distinguishable reactions. These were: (a) cyclization reactions at the three phosphorus atoms, (b) polymer formation by cross-linking reactions between different phosphonitrilic chloride molecules, and (c) reaction of the cyclized phosphonitrilic ester formed in (a) with excess catechol and base to cleave the phosphorus–nitrogen ring system. These three processes are considered separately.

Cyclization Reactions at Phosphorus.—Ring closure at the three phosphorus atoms of I yielded tris(o-phenylenedioxy)phosphonitrile trimer (II) according to the reaction

I

II