[Contribution from the Chemical Corps Technical Command]

# REACTIONS OF DIALKYL PHOSPHITES. SYNTHESIS OF DIALKYL CHLOROPHOSPHATES, TETRAALKYL PYROPHOSPHATES, AND MIXED ORTHOPHOSPHATE ESTERS[1]

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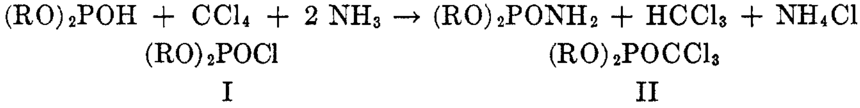
Consistent with the interest of the author in the reactions of organic phosphites, it was his purpose to determine the course of the new and interesting reaction discovered by Atherton, Openshaw, and Todd (1) that takes place with considerable vigor when a dialkyl or diaryl phosphite, carbon tetrachloride, and ammonia or a primary or secondary amine are mixed.

1.



$$(RO)_2POH + CCl_4 + 2\ NH_3 \rightarrow (RO)_2PONH_2 + HCCl_3 + NH_4Cl$$

$$\underset{\text{I}}{(RO)_2POCl} \qquad\qquad \underset{\text{II}}{(RO)_2POCCl_3}$$

In their paper, they suggested that the reaction probably goes through an intermediate stage involving the formation of either the corresponding dialkyl chlorophosphate (I) or dialkyl trichloromethylphosphonate (II).

It was found in this laboratory that the reaction between diethyl chlorophosphate and ammonia takes place at once with the evolution of much heat and the immediate formation of a copious white precipitate. The vigor of this reaction was of the same magnitude as that observed in the phosphite reaction. On the other hand, with diethyl trichloromethylphosphonate, prepared by the method described by Kosolapoff (2), ammonia gave no apparent reaction even after ten minutes. However, it has been reported (3) that reaction between dialkyl trichloromethyl phosphonates and amines can be made to take place with the resultant formation of dialkyl alkylamino phosphonates.

By replacing the ammonia with a tertiary base it was found possible to isolate the dialkyl chlorophosphate in yields of as high as 85%. The main reaction is accompanied by a side reaction which yields a high-boiling product and the base hydrochloride. These products are probably the result of reaction between the dialkyl phosphite and the dialkyl chlorophosphate in the presence of the base.

2. $(RO)_2POH + CCl_4 \xrightarrow{R'_3N} (RO)_2POCl + HCCl_3$

3. $(RO)_2POH + (RO)_2POCl + R'_3N \rightarrow (RO)_2POP(OR)_2(?) + R'_3N{\cdot}HCl$

When diethyl phosphite and diethyl chlorophosphate were reacted in the presence of triethylamine, there were formed triethylamine hydrochloride and a high-boiling liquid, which on the basis of chemical analysis and physical properties appeared to be a mixture of the expected tetraethyl hypophosphate (17%) and

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[1] Presented at the Atlantic City meeting of the American Chemical Society, September 1949.

tetraethyl pyrophosphate (83%). Nylen (4) obtained a similar mixture of products from the reaction of sodium diethyl phosphite and diethyl chlorophosphate. The mechanism of this reaction is obscure and warrants further study.

Dialkyl chlorophosphates have been prepared in a variety of ways (5), some of which include the reaction of trialkyl phosphates with phosphorus oxychloride, the reaction of two moles of an alcohol with one mole of phosphorus oxychloride, and the more practical chlorination of trialkyl and dialkyl phosphites (5, 6). In addition, several dialkyl phosphites have been converted successfully to dialkyl chorophosphates by treatment with sulfuryl chloride (7).

Because of the decreased stability of these compounds under acidic conditions, it had been necessary to free them of acidic reactants or products before distillation.

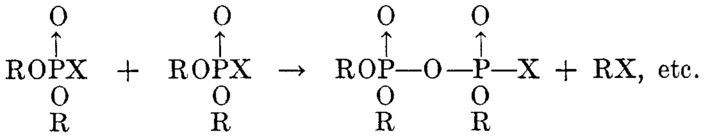
In this work the chlorophosphates were prepared under alkaline conditions, so that, except with especially unstable compounds, no precautions were necessary. It was found most convenient to run the reaction without an additional solvent, merely mixing the phosphite with an excess of carbon tetrachloride and 10–15 mole-percent of tertiary base. The reaction mixture was cooled at first, but after the initial vigorous phase had passed, it was stirred at room temperature until the reaction was completed.

The optimum quantity of base was found to be *ca.* 10–15 mole-percent. With less, the reaction was slowed; with more, there was obtained a colored, amine-odored product. In the latter case, distillation over potassium dihydrogen phosphate yielded a pure colorless product. The reaction could be speeded by raising the temperature, but this resulted in a reduction in yield.

It was found unnecessary to purify the phosphite before reaction. In fact, it is present practice to treat the crude phosphite directly with carbon tetrachloride and base, adding a sufficient excess of the latter to neutralize any hydrogen chloride present.

Dimethyl and diallyl chlorophosphates were found to be extremely sensitive to heat, so that modifications of the standard procedure had to be employed in the synthesis of each. Despite all precautions, considerable decomposition occurred during distillation, and there was left in each case a viscous polymer-like residue. In the case of the diallyl chlorophosphate the residue was analyzed and found to contain only 0.93% chlorine. Similar residues were found when the more stable chlorophosphates were redistilled after standing for several months. It seems reasonable to suppose that the residues are long chain compounds formed by the splitting out of RX between molecules.

4.



$$\mathrm{RO\underset{\substack{O\\R}}{\overset{\substack{O\\\uparrow}}{P}}X} + \mathrm{RO\underset{\substack{O\\R}}{\overset{\substack{O\\\uparrow}}{P}}X} \rightarrow \mathrm{RO\underset{\substack{O\\R}}{\overset{\substack{O\\\uparrow}}{P}}{—}O{—}\underset{\substack{O\\R}}{\overset{\substack{O\\\uparrow}}{P}}{—}X} + \mathrm{RX}, \text{ etc.}$$

On the basis of this hypothesis it is calculated that the diallyl chlorophosphate residue contained polymeric molecules having an average molecular weight of 3800 and containing an average of 36 repeating units per molecule.

Several attempts to prepare pure diethyl bromophosphate by an analogous reaction using carbon tetrabromide, bromoform or bromotrichloromethane in place of carbon tetrachloride were unsuccessful. In each case there was evidence of the formation of the desired product, for on distillation there was obtained the familiar sweet-smelling oil, and a viscous yellow-orange residue (polymer?). However, analysis indicated that halogen-containing impurities were always present. Apparently the by-products of the reaction were too high-boiling to be removed from this highly thermosensitive compound by the methods employed in this work.

In a recent paper, Toy (8) reviewed the methods that had previously been used for the preparation of tetraalkyl pyrophosphates and reported a new and far superior process for their preparation. He found that by the controlled hydrolysis of a dialkyl chlorophosphate in the presence of a base, he could prepare pure "pyro" compounds in high yield. Atherton and Todd (1b) prepared tetrabenzyl pyrophosphate by reaction of dibenzyl phosphite and carbon tetrachloride in the presence of an aqueous solution of potassium hydroxide.

Since the dialkyl chlorophosphates are here prepared under alkaline conditions, it seemed probable that if there was added to the "usual" mixture of dialkyl phosphite, carbon tetrachloride, and base, the correct quantity of water and sufficient base to neutralize the acid formed, the corresponding tetraalkyl pyrophosphate should be produced. This was indeed found to be the case.

A slight excess of water caused no difficulty under the conditions employed. When the organic base was replaced completely by sodium bicarbonate the reaction failed to take place. On partial replacement, there was obtained a product of somewhat lower purity.

Mixed orthophosphate esters have been prepared by several methods. Weger (9) reacted silver diethyl phosphate with methyl iodide to yield diethylmethyl phosphate. Dibutylethyl phosphate was prepared by Gerrard (10) by the reaction of dibutyl chlorophosphate with ethanol in the presence of pyridine. It was shown by Rueggeberg and Chernack (11) that when triethyl phosphate was warmed with sodium butoxide there was formed a mixture of dibutylethyl phosphate and butyldiethyl phosphate. Atherton and Todd (1b) found that dibenzyl phosphite could be reacted with ethanol at room temperature in the presence of bromotrichloromethane and a tertiary base to yield dibenzylethyl phosphate, but reported that the reaction did not take place in the presence of carbon tetrachloride.

In the light of previous experience, it seemed probable that the chlorophosphate formed would react with an alcohol to yield the mixed phosphoric acid esters. By running the reaction at an elevated temperature there was prepared, in good yield, butyldiethyl phosphate. Due to the greater reactivity induced by the allyl groups, diallylethyl phosphate could be prepared by reaction at room temperature. This compound could be polymerized by heating with benzoyl peroxide.

*Reaction mechanism.* A kinetic study was undertaken on the reaction between diethyl phosphite and carbon tetrachloride in the presence of triethylamine, equations 2 and 3, in order to ascertain the effect of varying the initial concentrations of the various reactants on the over-all rate of reaction, so that a reasonable mechanism might be proposed. In view of the complex nature of the reaction, an accuracy of ±5% was considered adequate.

It was planned to follow the course of the reaction by determinations of chloride in the solid (triethylamine hydrochloride) and of total hydrolyzable chlorine in the reaction mixture (triethylamine hydrochloride + diethyl chlorophosphate). This would give, by difference, the concentration of diethyl chlorophosphate in the liquid phase. In order to precipitate the triethylamine hydrochloride completely, ligroin was selected as the reaction solvent.

The effect of varying the concentrations of each of the reactants on the rate of formation of total hydrolyzable chlorine is shown in Fig. 1. In Fig. 2, there is plotted the rate of formation of triethylamine hydrochloride. The erratic nature of the results shown in Fig. 2 led to an investigation of possible faults in the analytical procedure. None could be found. The variations might be explained by a variable induction period for the side reaction, by a complex mechanism for the formation of triethylamine hydrochloride involving both formation and simultaneous reaction of that compound, or by the presence of variable quantities of an unknown catalyst from outside the system. The first supposition seems least reasonable for in each of 5 identical runs, it was determined that the white precipitate formed during the time interval between $3\frac{1}{4}$ and $4\frac{3}{4}$ minutes after the start of the reaction, hence, if it were only a matter of induction period, the percentage error would fall off quickly with time, so that after 100 or 200 minutes the curve would be uniform.

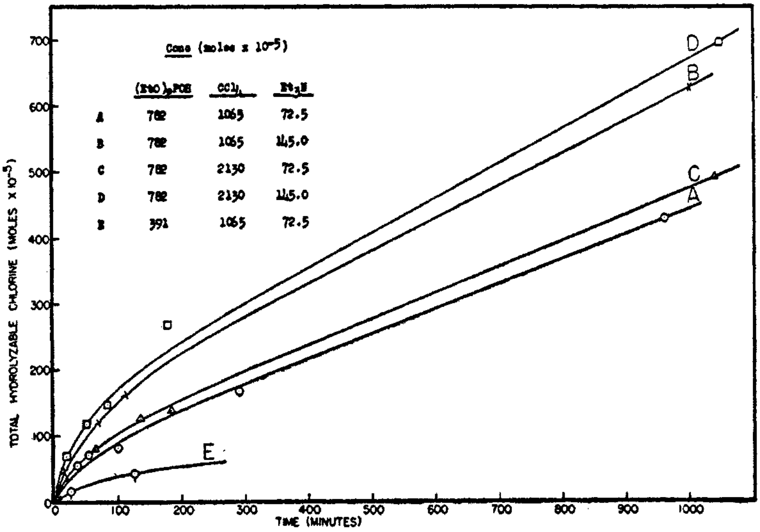


Fig. 1. Rate of Formation of Total Hydrolyzable Chlorine
[$(EtO)_2POCl + Et_3N{\cdot}HCl$]

An investigation of the literature led to the discovery of a reported reaction between bromoform or carbon tetrabromide, and amines, in the presence of air which yields aldehydes and base hydrobromide (12). Chloroform and carbon tetrachloride were reported to be unreactive. It was found in these laboratories that when carbon tetrachloride and triethylamine were mixed there was always obtained a small precipitate of triethylamine hydrochloride. The results of a light-absorption study, Fig. 3, indicate that association or reaction between triethylamine and carbon tetrachloride does occur. However, under the conditions of the kinetic study, in the absence of phosphite, no measurable amounts of triethylamine hydrochloride were formed in four hours. The possibility that triethylamine hydrochloride might act as a catalyst and so might affect the course of reaction when present in only trace amounts was shown to be invalid, for if the free base was replaced by the hydrochloride, the reaction did not take place.

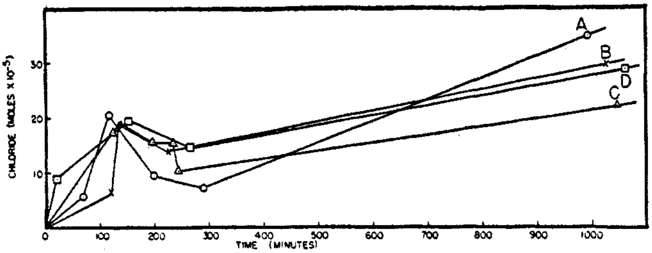


FIG. 2. RATE OF FORMATION OF CHLORIDE ($Et_3N \cdot HCl$)

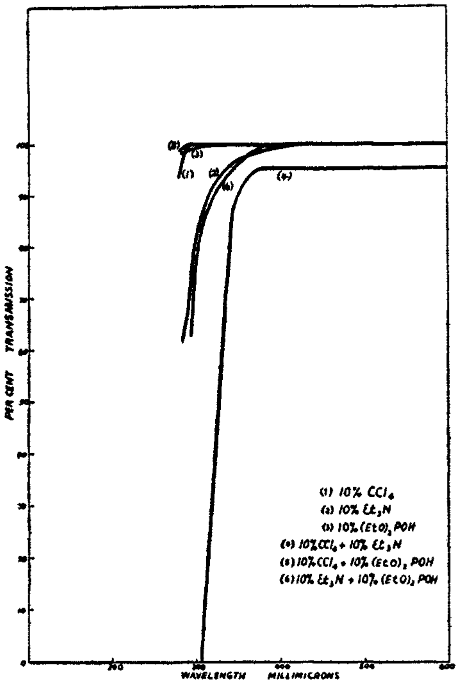


FIG. 3. LIGHT ABSORPTION OF REACTANTS

Variation of the concentration of the chlorophosphate with time could not be accurately calculated, and as was to be expected on the basis of simultaneous reactions, the over-all rate of reaction based on total hydrolyzable chlorine did not follow a constant order of reaction. It can be observed from Fig. 1 that the rate of formation of total hydrolyzable chlorine is affected differently by equivalent changes in the initial concentrations of each of the reactants. In each case, the rate of reaction appears to vary considerably with reactant concentration during its early stages, and to fall off to zero order later on. For the early part of the reaction, doubling the concentration of diethyl phosphite increased the rate of formation of the total hydrolyzable chlorine by a factor of 2.3, whereas doubling the concentration of triethylamine increased it only by 1.6 and of carbon tetrachloride by 1.15. Although the rate of the side reaction could not be determined, it will be seen by comparison of Figs. 1 and 2 that its magnitude is comparatively small. Hence, for the purpose of analysis it will be ignored.

The evidence obtained favors an ionic mechanism. In the absence of base, the reaction failed to occur. Catalysts for free radical reactions such as ultraviolet light and benzoyl peroxide were ineffective. The rate of reaction appears to be strongly dependent on the strength of the base. Triethylamine was only slightly more effective as a catalyst than tributylamine or triamylamine, but was more than 1000 times more effective than pyridine.

Since a zero order reaction in the liquid phase is so strongly indicative of a free radical mechanism, the possibility of a series of reactions involving the formation of an ion or unionized complex between phosphite and base followed by breakdown to free radicals was considered. But this mechanism was found to be highly improbable for in the presence of triethylamine, neither ultraviolet light nor benzoyl peroxide increased the rate of reaction. In fact, in the latter case, the reaction was slowed down, probably because of partial neutralization of the base.

Two possible mechanisms are proposed:

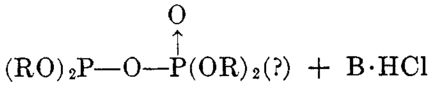
5. $$(RO)_2POH + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} [(RO)PO]^- + B{\cdot}H^+; \quad \frac{K_2}{K_1} = K_A \qquad \text{(a)}$$

$$CCl_4 + B \underset{K_4}{\overset{K_3}{\rightleftharpoons}} CCl_3^- + B{\cdot}Cl^+; \quad \frac{K_4}{K_3} = K_B \qquad \text{(b)}$$

$$B{\cdot}Cl^+ + [(RO)_2PO]^- \xrightarrow{K_5} (RO)_2POCl + B \qquad \text{(c)}$$

$$B{\cdot}H^+ + CCl_3^- \underset{K_7}{\overset{K_6}{\rightleftharpoons}} HCCl_3 + B; \quad \frac{K_6}{K_7} = K_D \qquad \text{(d)}$$

Side reaction: $(RO)_2POH + (RO)_2POCl + B \rightarrow$



$$(RO)_2P{-}O{-}\overset{\overset{\displaystyle O}{\uparrow}}{P}(OR)_2(?) + B{\cdot}HCl$$

6.

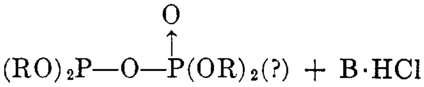
$$(RO)_2POH + B \rightleftharpoons [(RO)_2PO]^- + B\cdot H^+$$

$$[(RO)_2PO]^- + CCl_4 \rightleftharpoons (RO)_2POCl + CCl_3^-$$

$$CCl_3^- + (RO)_2POH \rightleftharpoons [(RO)_2PO]^- + HCCl_3$$

$$B\cdot H^+ + CCl_3^- \rightleftharpoons HCCl_3 + B$$

Side reaction: $(RO)_2POH + (RO)_2POCl + B \rightarrow$



$$(RO)_2P—O—\overset{\overset{\displaystyle O}{\uparrow}}{P}(OR)_2(?) + B\cdot HCl$$

On the basis of the available information the mechanism of this reaction cannot be stated. However, it is interesting that if several reasonably plausible assumptions are applied to the first of the proposed mechanisms, the relationship between rate of reaction and initial concentration of reactants that was found for the early part of the reaction can be explained.

If one simply assumes that step (a) is the "slow" or rate-determining step and that the equilibrium constants $K_A$, $K_B$, and $K_D$ are equal, then doubling the concentration of diethyl phosphite should increase the rate of reaction by a factor of nearly 2, triethylamine by 1.4, and carbon tetrachloride by 1.2.

Thus, the availability of $[(EtO)_2PO]^-$ for reaction in (c) will be a function of the relative concentrations of diethyl phosphite, triethylamine, and the triethylammonium ion. If the concentration of diethyl phosphite were doubled, the rate of formation of $[(EtO)_2PO)]^-$, and hence, the over-all rate of reaction should be nearly doubled; the concentration of triethylammonium ion being kept almost constant by (d) and (b). If the concentration of carbon tetrachloride were doubled, the concentration of $CCl_3^-$ would be increased by (b) and in turn, $Et_3N\cdot H^+$ would be decreased by (d) to about 50% of its former value. This in turn, should increase the availability of $[(EtO)_2PO]^-$ and hence the rate of reaction by a factor of 1.2. If the concentration of triethylamine were doubled, the concentration of $Et_3N\cdot H^+$ would be increased by a factor of 1.4 by (d) and (b) and hence by (a) the availability of $[(EtO)_2PO]^-$ should be increased by a factor of 1.4.

However, if the more reasonable assumption is made that $K_A > K_D > K_B$, and there is added the assumption that either reaction (b) or (c) is sufficiently slow to contribute 10–15% of its weight to the rate of the reaction, so that changes in the concentration of $Et_3N\cdot Cl^+$ become important, the rate of reaction should be affected by the more closely agreeing factors of 2.1–2.3 for diethyl phosphite, 1.4–1.6 for triethylamine, and 1.1–1.2 for carbon tetrachloride.

## EXPERIMENTAL

*Dialkyl chlorophosphates.* With the exception of the two specific cases listed below, the preparation of diethyl chlorophosphate may be considered typical and will serve to illustrate the procedure used for the preparation of the more stable chlorophosphates, which are listed in Table I. In the case of the diallyl and the dimethyl chlorophosphates, it is felt that the yields could be considerably improved with a more thorough study of the individual reactions.

*Diethyl chlorophosphate.* To a cooled (0°), stirred mixture of 27.6 g. (0.20 mole) of diethyl phosphite and 35 ml. (0.4 mole) of carbon tetrachloride, there was slowly added 3.2 ml. (0.023 mole) of triethylamine. The temperature was maintained at 0° for 15 minutes, then allowed to rise to room temperature and stirred for 3 hours. The reaction mixture was filtered, stripped completely of low-boiling components at room temperature (pressure *ca.* 20 mm.) and vacuum-distilled. Yield, 28 g. of a colorless, sweet-smelling oil.

It was found unnecessary to use a rectifying column for purification. In fact, the highest yields were obtained when distillation was done rapidly and at low temperature.

In one run, the by-products of reaction were examined. A distillation curve of the low-boiling fraction indicated the presence of considerable quantities of chloroform. The white precipitate was recrystallized from methyl ethyl ketone, m.p. 246–251° (uncorr.). Reported for *triethylamine hydrochloride*, 253–254°.

TABLE I

DIALKYL CHLOROPHOSPHATES

| ALKYL GROUP | REACTION TEMP. | TIME, HRS. | YIELD, % | B.P., °C. (MM.) | $n_D^{20}$ | ANALYSIS Cl | |
|---|---|---|---|---|---|---|---|
| | | | | | | Calc'd | Found |
| Ethyl......... | Room temp. | 3 | 81 | 64 (6–7) | 1.4167 | 20.58 | 20.39, 20.42 |
| Ethyl......... | Reflux[a] | ¼ | 70 | 64 (6–7) | 1.4169 | — | — |
| *n*-Propyl...... | Room temp. | 6 | 80 | 65 (3–4) | 1.4246 | 17.72 | 17.59, 17.61 |
| *n*-Butyl....... | Room temp. | 6 | 55[b] | 110–3 (6) | 1.4308 | 15.54 | 15.61, 15.73 |

[a] Triethylamine added dropwise to refluxing mixture.

[b] Decomposed in part due to high temperature of distillation.

*Anal.* Calc'd for $C_6H_{16}ClN$: N, 10.18; Cl, 25.8.
Found: N, 10.06, 9.72; Cl, 25.38, 25.21.

When an attempt was made to distill the dark high-boiling residue, there was obtained a small quantity, less than one gram, of a colorless oil distilling at 97–104°/0.01–0.04 mm. Some decomposition had probably occurred during this process. Yet, it is interesting that the analysis indicated the presence of a compound or compounds having a high percentage of phosphorus.

*Anal.* Calc'd for tetraethyl hypophosphate, $C_8H_{20}O_6P_2$: C, 35.05; H, 7.3; P, 22.6.
Found: C, 34.3; H, 7.3; P, 19.9, 20.0.

*Diallyl chlorophosphate.* To a cooled (0°), stirred mixture of 32.4 g. (0.20 mole) of diallyl phosphite and 35 ml. (0.4 mole) of carbon tetrachloride, there was slowly added 3.2 ml. (0.023 mole) of triethylamine. A very vigorous reaction ensued. The temperature was maintained at 0° for one hour and then slowly allowed to rise to room temperature. The mixture was stirred overnight. The solid was filtered off, 0.5 g. of hydroquinone was added to the filtrate and the low-boiling substances were carefully stripped off under a vacuum (10 mm.) at room temperature. The residue was vacuum-distilled on a high vacuum system, the pressure in which can ordinarily be reduced to 0.001 mm. As soon as distillation began, the pressure rose quickly and the McLeod gauge went "off scale". The sample distilled at 65°; pot 85°. By comparison with the data for di-*n*-propyl chlorophosphate, it is estimated that the pressure rose to 3–4 mm. There was obtained 8.5 g. of a sweet-smelling oil, $n_D^{20}$ 1.4504; yield 22%.

*Anal.* Calc'd for $C_6H_{10}ClO_3P$: Cl, 18.05. Found: Cl, 18.03, 18.09.

A large quantity of "chlorine-free" brownish-yellow material remained as residue.

*Dimethyl chlorophosphate.* To a cooled (0°) stirred mixture of 22.0 g. (0.20 mole) of dimethyl phosphite in 35 ml. (0.4 mole) of carbon tetrachloride, there was slowly added 2.8 ml. (0.020 mole) of triethylamine. The reaction mixture was stirred for one hour at 0° and then for one-half hour at room temperature. The solid was filtered off, the filtrate vacuum-stripped at room temperature (40 min.) and distilled under a vacuum. There was obtained 9 g. of sweet-smelling liquid, b.p. 70°/10 mm.; yield 28%, and a large residue of a viscous light colored oil. A determination of hydrolyzable chlorine indicated that the purity of the sample obtained was only 93%. By analogy with the results of earlier runs with similar products, it was assumed that the impurity was a low-boiling compound that had not been completely removed during the stripping operation.

## TETRAALKYL PYROPHOSPHATES

*Tetraethyl pyrophosphate.* (a) *Reaction in presence of triethylamine.* To a stirred mixture of 27.6 g. (0.20 mole) of diethyl phosphite and 35.6 ml. (0.40 mole) of carbon tetrachloride cooled to 5°, there was added 3.25 ml. (0.18 mole) of water and then dropwise 55.6 ml. (0.40 mole) of triethylamine. The temperature was allowed to rise slowly to 25° (½ hr.), and the mixture was maintained at that temperature for 3½ hours. The slurry was filtered and the filtrate vacuum-stripped and distilled. Yield, 21 g. (73%) of tetraethyl pyrophosphate, $n_D^{25}$ 1.4180, b.p. 105–109°/0.03 mm.

*Anal.* Calc'd for $(EtO)_4P_2O_3$: Ethoxyl, 62.11. Found: Ethoxyl, 61.92, 61.94.

Determination of $P^{III}$ (0.09%) indicated the presence of less than 1% of tetraethyl hypophosphate or similar impurity. When the order of addition of water and base was reversed, there resulted a less pure product.

(b) *Reaction in presence of triethylamine and sodium bicarbonate.* To a stirred mixture of 27.6 g. (0.20 mole) of diethyl phosphite, 35.6 ml. (0.40 mole) of carbon tetrachloride, ½ ml. of water, and 25.2 g. (0.30 mole) of sodium bicarbonate, there was added 3.2 ml. (0.023 mole) of triethylamine, keeping the temperature at 20–25.° The reaction mixture was stirred for 4 hours, filtered, and the filtrate vacuum-stripped and distilled. There was obtained 3 g. of recovered phosphite and 15 g. of tetraethyl pyrophosphate; yield 52%, conversion, 58% $n_D^{25}$ 1.4176.

The values for the index of refraction of tetraethyl pyrophosphate reported by Toy (8) varied between $n_D^{25}$ 1.4182 and 1.4172. Since his value for diethylphosphoric acid, the most probable impurity, is $n_D^{25}$ 1.4146–1.4152, it is assumed that the purer product has the higher index of refraction.

*Tetraisopropyl pyrophosphate.* This compound was prepared by the procedure described for tetraethyl pyrophosphate, method (a). Before stripping, however, it was found necessary to wash the mixture quickly with a cold dilute solution of sodium bicarbonate in order to prevent the distillation of solid impurities (probably $Et_3N \cdot HCl$) along with the reaction product. There was obtained 26.5 g. of tetraisopropyl pyrophosphate, b.p. 94–99°/0.01–0.02, $n_D^{25}$ 1.4165, yield 73.3%.

*Anal.* Calc'd for $(C_3H_7O)_4P_2O_3$: Isopropoxyl, 68.25; P, 17.89.
Found: Isopropoxyl, 67.97, 68.00; P, 17.82.

## MIXED ORTHOPHOSPHATE ESTERS

*n-Butyldiethyl phosphate.* To a mixture of 27.6 g. (0.20 mole) of diethyl phosphite, 35.6 ml. (0.40 mole) of carbon tetrachloride, and 16.3 g. (0.21 mole) of *n*-butanol, there was added 31.6 ml. (0.22 mole) of triethylamine. The reaction mixture was stirred and refluxed for 3 hours, then filtered, and the filtrate vacuum-stripped (25°/5) and distilled over potassium dihydrogen phosphate. There was obtained 22 g. of *n*-butyldiethyl phosphate, $n_D^{25}$ 1.4085, b.p. 100–101°/2–3, yield, 52%.

*Anal.* Calc'd for $C_8H_{19}O_4P$: P, 14.74. Found: P, 14.70, 14.73.

*Diallylethyl phosphate.* To a stirred mixture of 32.4 g. (0.20 mole) of diallyl phosphite, 20 ml. (0.22 mole) of carbon tetrachloride, and 12 ml. (0.21 mole) of ethanol cooled to 0°, there was added dropwise 41.7 ml. (0.3 mole) of triethylamine. The mixture was kept at 0°

for 30 minutes and then stirred overnight at room temperature. The reaction mixture was filtered, the filtrate vacuum-stripped, and distilled over hydroquinone and potassium dihydrogen phosphate. There was obtained 14 g. of diallylethyl phosphate, b.p. 72°/1-2, $n_D^{25}$ 1.4350, yield, 34%. A considerable quantity of a tan-colored viscous residue remained.

*Anal.* Calc'd for $C_8H_{15}O_4P$: Bromine no., 154.8; P, 15.02.

Found: Bromine no., 152.7, 152.7; P, 14.84, 14.86.

*Reaction between diethyl phosphite and diethyl chlorophosphate.* To a stirred mixture of 50 ml. of benzene, 34.5 g. (0.20 mole), of diethyl chlorophosphate, and 27.6 g. (0.20 mole) of diethyl phosphite, there was added 29 ml. (0.22 mole) of triethylamine. A considerable volume of white fumes was produced. The reaction mixture was stirred and refluxed for two hours. The white precipitate was filtered, the filtrate vacuum-stripped, and the residue distilled under a high vacuum. There was obtained a considerable quantity of a colorless liquid that distilled from 91–100°/0.06 (pot temperature 134–144°). On the same system, pure tetraethyl pyrophosphate distilled at a slightly higher temperature; 105–109°/0.03 (pot temperature 120–125°).

ANALYSIS

| | CALC'D FOR TETRAETHYL PYROPHOSPHATE | CALC'D FOR TETRAETHYL HYPOPHOSPHATE | FOUND |
|---|---|---|---|
| EtO | 62.11 | 65.69 | 62.72 |
| Total P | 21.41 | 22.62 | 21.15 |
| $P^{III}$ | 0.00 | 11.32 | 1.94 |

Based on the assumption that the most discriminatory determination was that for $P^{III}$, and that the product was a mixture of tetraethyl hypophosphate and tetraethyl pyrophosphate, it was calulated that there was present 17% of the former product.

## KINETIC STUDY

*Reagents.* The reagents were freshly distilled, a middle fraction of each being used for the study. These include: diethyl phosphite, b.p. 66–67°/6 prepared according to method (a) of McCombie, Saunders, and Stacey (5); triethylamine Eastman, C.P.; ligroin, Eastman Pract., 90–120°; carbon tetrachloride, Eimer and Amend C.P.

*Apparatus.* A large-scale run proved difficult to handle, for the solid settled and true aliquots could not be taken. The study was therefore made on individual 10-ml. runs that were maintained at 75 ± 1° F. in a thermostatically-controlled room. Each reaction was run in an Erlenmeyer flask of 20 ml. capacity fitted with a ground-glass-joint drying tube. The reaction mixture was stirred by a magnetic stirrer, and in order to keep the system from being heated by the stirrer motor, insulation or an air gap was provided. Stock solutions were prepared by diluting 100 ml. each of diethyl phosphite and carbon tetrachloride and 25 ml. of triethylamine to 250 ml. with ligroin. The three stock solutions and the solvent were dispensed from 5-ml. microburettes reading to 0.01 ml. The order of addition was ligroin, diethyl phosphite, carbon tetrachloride, and triethylamine; the time of reaction being calculated from the time at which the amine was added.

*Analysis.* To determine the quantity of solid formed, the samples were filtered on a Gooch crucible, washed with ligroin, then dissolved in water, and titrated for chloride by the Volhard method. Total hydrolyzable chlorine was determined by shaking the reaction mixture for 10 min. with 100 ml. of 2% aqueous sodium hydroxide, acidifying, and proceeding as above. Concentrated alkali was found to attack the carbon tetrachloride.

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## SUMMARY

1. Dialkyl chlorophosphates were prepared by the reaction of the corresponding dialkyl phosphites and carbon tetrachloride in the presence of a tertiary base. These include: the dimethyl, diethyl, di-*n*-propyl, di-*n*-butyl, and diallyl chlorophosphates.

2. The mechanism of this reaction was studied.

3. Tetraalkyl pyrophosphates were prepared by the reaction of a dialkyl phosphite, carbon tetrachloride, water, and a tertiary base. These include the ethyl and isopropyl pyrophosphates.

4. Mixed orthophosphate esters were prepared by the reaction of a dialkyl phosphite, carbon tetrachloride, an alcohol, and a tertiary base. These include the butyldiethyl and the diallylethyl phosphate. The latter compound can be polymerized.

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