styrene or indene. A cetane solution (300 ml.) containing 2-naphthalenethiol and indene or styrene both in 0.01 mole/l. concentration was stored in a 500 ml. open Pyrex (borosilicate glass) Erlenmeyer flask at room temperature. A rapid peroxidation followed by a decrease in peroxide content as measured by the ferrous sulfate method[8] occurred. Under the same conditions, cetane solutions of any of the components alone did not show any peroxidation. From the indene-thiol solution after 70 hr., some 2-(2-naphthylsulfinyl)-1-indanol, m.p. 138.5–139.5° with decomposition, from the styrene-thiol solution after 23 hr., some 2-(2-naphthylsulfinyl)-1-phenylethanol, m.p. 145–147° precipitated.

Similar peroxidation was observed with indene-thiol solutions at 43°.

Formation of 2-sulfinylethanol sediments during storage at 43°. For the study of the role of mercaptan-olefin co-oxidation in sediment formation accelerated storage tests at 43° were carried out with cetane solutions (300 ml.) containing mercaptans and styrene or indene, each in 0.3 mole/l. concentration. In 2 weeks precipitation (0.2–4.0g.) occurred. The precipitates, which were only in part crystalline in the case of the thiophenol-indene and *p*-toluenethiol-indene combinations, were all recrystallized from benzene-*n*-heptane and gave the corresponding 2-arylsulfinyl-1-indanols shown in Table II. The mother liquors were distilled *in vacuo* and yielded about 200 mg. of 2-indanyl phenyl sulfide and 180 mg. of 2-indanyl 4-tolyl sulfide, respectively.

Acknowledgment. The author wishes to thank J. L. Tiedje and C. B. Rupar for many helpful discussions, F. Noël for technical help, A. J. Stephenson for the infrared, J. F. Eagen and the late C. H. Stein for the elemental analyses.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

The Thermal Decomposition of Tributyl Phosphate[1]

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The thermal stability of tributyl phosphate (TBP) was measured by determining the rate of formation of dibutyl phosphoric acid (DBP) as a function of temperature. Tributyl phosphate decomposed to form 1.2% acid in seventy hours at 178° and 8.4% acid in two hours at 240°. Stability increased if the alkoxy bonds were replaced with carbon-to-phosphorus bonds; the rate of scission of the remaining C—O bonds was retarded to a much greater degree than might have been expected simply from the statistical reduction in number of C—O bonds per molecule. The reaction TBP $\xrightarrow{\Delta}$ DBP + C_4H_8 was first order only in the dilute acid range (up to 3% dibutyl phosphoric acid). The specific reaction rates in this range were: 0.389, 3.33, 20.1, 27.1, and 132 × 10^{-7} sec.$^{-1}$ at 178°, 198°, 221°, 223°, and 240°, respectively. From these was calculated an "apparent" activation energy of 40 kcal. per mole for the formation of dibutyl phosphoric acid by thermal decomposition of tributyl phosphate. Butene-1 comprised at least 99% of the gases formed in eight hours at 221°. Minor yields of butanol, dibutyl ether, and tetrabutyl pyrophosphate were obtained, indicating a dealkoxylation mechanism to be occurring in addition to the main dealkylation reaction to simultaneously form dialkyl phosphoric acid plus alkene.

Trialkyl-, alkyl aryl-, and triaryl phosphates are remarkably thermally stable compounds at temperatures up to 100°.[2] Only at elevated temperatures do they decompose to form unsaturated hydrocarbons and phosphorus acids. With prolonged heat at 150° Gamrath, Hatton, and Weesner[2] converted 2-ethylhexyl diphenyl phosphate into 2-ethyl-1-hexene and diphenyl phosphoric acid. Baumgarten and Setterquist[3] pyrolyzed tributyl phosphate and many other alkyl phosphates at optimum temperatures of 300–350° to obtain essentially quantitative yields of olefins. Cherbuliez, Cordahi, and Rabinowitz[4] also observed nearly quantitative formation of octene from the pyrolysis of trioctyl phosphate. However, no study of the effect of temperature on the rate of decomposition has been made.

It was the purpose of this investigation to determine, if possible, the rate constants for dibutyl phosphoric acid formation as a result of heat on tributyl phosphate at several temperatures. The experiments were performed under conditions whereby the acid formed normally constituted less than 10 mole percent because the decomposition of trialkyl phosphates was found to be acid catalyzed.[2,4,5] Mixtures of the alkyl phosphoric acids are known to react vigorously[5,6]; Hochwalt, Lum, Malowan, and Dyer[6] reported the vacuum distillation of a mixture of mono- and diethyl phosphates at 200° to yield alcohol, ethylene, triethyl phosphate, and a condensed phosphate residue. Only by performing the study in the low acidity range where the acid formed was the dialkyl phosphoric acid would the desired constants be obtainable.

It was also of interest to demonstrate the effect

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[1] This paper is based upon work performed for the United States Atomic Energy Commission at the Oak Ridge National Laboratory operated by Union Carbide Corporation.

[2] H. R. Gamrath, R. E. Hatton, and W. E. Weesner, *Ind. Eng. Chem.*, 46, 208 (1954).

[3] H. E. Baumgarten and R. A. Setterquist, *J. Am. Chem. Soc.*, 79, 2605 (1957).

[4] E. Cherbuliez, G. Cordahi, and J. Rabinowitz, *Helv. Chim. Acta*, 42, 590 (1959).

[5] E. Cherbuliez and J. P. Leber, *Helv. Chim. Acta* **35**, 644 (1952).

[6] C. A. Hochwalt, J. H. Lum, J. E. Malowan, and C. P. Dyer, *Ind. Eng. Chem.* **34**, 20 (1942).

TABLE I

ACID FORMATION FROM HEATING ORGANOPHOSPHORUS COMPOUNDS[a]

Temp. ± 2°	Time, hr.	Mole Acid per Mole Starting Compound: Tributyl phosphate	Dibutyl butylphosphonate	Butyl dibutylphosphinate
178	3.25	0.00096		
	8.00	.0016		
	70.0	.0121		
198	5.00	0.0056		
	10.00	.0122		
223	0.33	0.0028		
	1.00	.0098	0.0073	0.0062
	3.00	.0284	.0181	.0082
	3.00[b]	.0671[b]		.0158[b]
	5.00	.0518	.0216	.0168
	5.00[c]	.0371[c]	.0079[c]	.0029[c]
	7.00	.0870		
	7.50		.0284	.0201
	10.00	.1335	.0300	.0277
240	1.00	0.0384		
	2.00	.0839		

[a] Sealed in Pyrex tubes after degassing by freezing-and-thawing method at 1 mm. [b] Not degassed. Pumped down to 20 mm., cooled, and sealed. [c] Degassed 2.5 hr. at 1 mm. using small glass magnetic stirring bar for agitation.

of carbon-to-phosphorus bonds on the thermal stability of trialkyl phosphorus compounds. For this purpose dibutyl butylphosphonate (DBBP′) and butyl dibutylphosphinate (BDBP″), containing 1 and 2 C—P bonds, respectively, were compared with tributyl phosphate at 223°.

The amounts of acid formed by heat on tributyl phosphate at various temperatures, and on dibutyl butylphosphonate and butyl dibutylphosphinate at 223°, can be seen in Table I. Tributyl phosphate decomposed to form 1.2% acid in seventy hours at 178° and 8.4% in two hours at 240°.

The extent to which acid formed in a given heating period for each compound was governed by the thoroughness with which the sample was degassed. Samples which were dry but not degassed by the freezing-and-thawing-*in-vacuo* technique contained twice as much acid as did those degassed by this method (Table I, 223°, three hours). Neither phosphonate nor phosphinate in pyrex tubes could be frozen more than once without breaking the tube, whereas tributyl phosphate could be safely frozen many times. This undoubtedly accounts for their results being less consistent than those obtained using tributyl phosphate. The most thorough degassing was found to be accomplished by vibrating a small glass encased magnetic stirring bar (made by sealing a small nail in a capillary tube) vigorously in the sample for two and a half hours at 1 mm. of mercury before cooling and sealing. Samples thus treated gave acid yields of 3.7%, 0.8%, and 0.3% in five hours at 223° for tributyl phosphate, dibutyl butylphosphonate, and butyl dibutylphosphinate, respectively, compared with 5.2%, 2.2%, and 1.7% after the freezing and thawing technique.

Stability increased if the alkoxy bonds were replaced with carbon-to-phosphorus bonds. Difficulty in degassing the dibutyl butylphosphonate and butyl dibutylphosphinate caused inconsistent acid values to be obtained (Table I), but there was an indication that the rate of acid formation was reduced to a value smaller than might be expected statistically, *i.e.*, two-thirds and one-third the rate of tributyl phosphate for phosphonate and phosphinate, respectively. Indeed, when the samples were thoroughly and equally degassed the ratio of acid yields was 1 to 0.21 to 0.078 for tributyl phosphate, dibutyl butylphosphonate, and butyl dibutylphosphinate, respectively (Table I, 223°, five hours, degassed by Method c). Therefore the rate for tributyl phosphate was about five times faster than that for dibutyl butyl phosphonate and over ten times faster than that of butyl dibutylphosphinate. Replacement of C—O—P by C—P bonds considerably retarded the scission of the remaining C—O bonds.

The effect of gases such as water vapor and oxygen on the decomposition rate of tributyl phosphate at 221° is demonstrated in Table II. Tributyl phosphate which was swept with dry nitrogen gave acid yields comparable to those obtained in the Pyrex bomb tests. The presence of water vapor in the nitrogen increased the rate of acid formation slightly, coincidentally resulting in a lesser amount of tetrabutyl pyrophosphate formation. When dry oxygen was passed through the tributyl phosphate at the same temperature, twenty times as much acid was formed in one hour as that formed in the same time with the nitrogen sweep.

From Fig. 1 it can be seen that the reaction TBP $\xrightarrow{\Delta}$ DBP + C_4H_8 appears to be first order only when the acid concentration is low (up to 3%). The rate then begins to increase steadily, apparently due to acid catalysis. Acid fragments from the dibutyl phosphoric acid may be contrib-

TABLE II

EFFECT OF GAS SWEEP ON PYROLYSIS OF TRIBUTYL PHOSPHATE[a]

	Mole Acid per Mole of Starting Tributyl Phosphate				
Time, hr.[b]	Dry nitrogen	Nitrogen satd. with H_2O	Dry oxygen	Dry argon[c]	Dry helium[c]
0.00	0.0012	0.0009	0.028		
0.25		.0034			
0.50	.0058	.0060	.107		
1.00	.0094	.0108	.184		
1.50	.0128	.0155	.262		
2.00	.0162	.0201			
2.50	.0198	.0258			
3.00	.0232	.0320			
3.50	.0273	.0390			
4.00	.0319	.0468			
4.50	.0372	.0540			
5.00	.0431	.0636			
5.50	.0501	.0728			
6.00		.0848			
6.50	.0662	.0960			
7.00		.111			
7.25		.118			
7.75	.0966				
9.00	.1404				
Final concn.	.1430	.120		0.0351 (in 3.5 hrs.)	0.103 (in 8 hrs.)
Grams polymer per mole starting TBP	9.13	2.13	4.79[d]	0.80	2.02
Mole tetrabutyl pyrophosphate per mole starting TBP	0.0226	0.0053	0.0036	0.0020	0.0050
Moles acid per mole tetrabutyl pyrophosphate	6.3	25	80	18	21

[a] Tributyl phosphate, 100–300 g., heated at 221° ± 2°. [b] Zero sample taken when sample temperature got up to 220°. [c] No sweep during heating period. [d] Only 30% of this weight represents tetrabutyl pyrophosphate–remainder unknown.

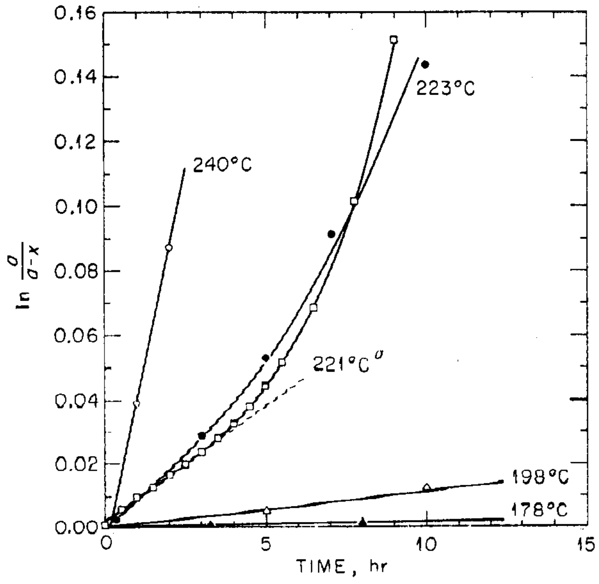

Fig. 1. Plot of integrated first order rate equation for the thermal decomposition of tributyl phosphate to acid
[a] Large scale run, Table II; zero time when t = 220°C.

uting here, as dibutyl phosphoric acid is less thermally stable than tributyl phosphate, and the monobutyl ester is even less stable than the dibutyl phosphoric acid.[7] The partial esters are quite reactive; Cherbuliez and Leber[6] found a mixture of mono- and diethyl phosphates to undergo an autocatalytic reaction at 200° to form orthophosphoric acid and ethylene. Similarly the authors[7] observed a 2 to 1 mixture of orthophosphoric acid and tributyl phosphate to decompose rapidly at 176°. All the reactions occurring after the initial one, in which dibutyl phosphoric acid and butene-1 are formed, thus accelerate the decomposition of the tributyl phosphate.

An Arrhenius plot of the acid formation rates (Table III) obtained from Fig. 1, using the straight line portion of the curves, gives the straight line shown in Fig. 2. From this is obtained an apparent activation energy of 40 kcal. per mole for the formation of dibutyl phosphoric acid from tributyl phosphate by heat. The discussion in the previous paragraph emphasizes that this can be considered only the energy for the overall early stage reaction and not strictly that for the thermal bond breakage, as other reactions are evidently going on simultaneously.

At least two types of reactions are occurring. The main one involves the formation of olefin and

TABLE III

SPECIFIC REACTION RATES FOR THERMALLY INDUCED FORMATION OF DBP FROM TBP

Temp.	178	198	221	223	240
(k, sec.$^{-1}$) × 10^7	0.389	3.33	20.1	27.1	132

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(7) C. E. Higgins and W. H. Baldwin, *J. Org. Chem.* 21, 1156 (1956).

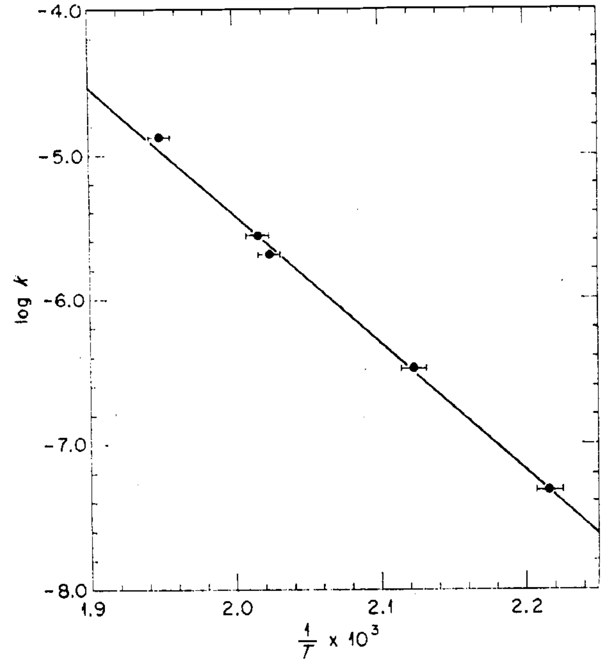

Fig. 2. Arrhenius plot of the specific reaction rates for the formation of dibutyl phosphoric acid by the thermal decomposition of tributyl phosphate.

resulting phosphoric acid ester by C—O bond scission, presumably by an ionic mechanism (3, 8). The formation of the lesser yields of butyl alcohol, dibutyl ether, and tetrabutyl pyrophosphate found requires a dealkoxylation reaction, or P—O bond rupture, and in the last two cases at least also requires a dealkylation reaction. The ratio of C—O to P—O bond scission as indicated from Table II was 6+ (nitrogen sweep) to 20+ (no sweep during pyrolysis), ignoring the run where dealkylation was aided by oxygen.

Butene-1 was the only gaseous product evolved in the early stages of pyrolysis and comprised at least 99% of the total gas collected by the eight-hour run at 221°. The composition of the gas emitted as a function of heating time over a nine-hour period at the same temperature was >99% butene-1 for the first five hours. The isomerization of the olefins reported by Baumgarten and Setterquist (3) then began to manifest itself, and the composition of the gas being emitted at the end of the 9-hour period was 97% butene-1, 2% trans-butene-2, and 1% cis-butene-2. Further studies are being made on the composition of the gases produced over the range 0 to 100% degradation of the tributyl phosphate and will be submitted separately.

EXPERIMENTAL

Rate measurements. (1). *Glass bomb.* Weighed samples (~2 g., dry, acid-free) of tributyl phosphate, dibutyl butylphosphonate, and butyl dibutylphosphinate in separate Pyrex tubes were degassed at 1 mm. of mercury by the freezing and thawing technique and finally sealed *in vacuo.* The tubes were heated in an aluminum block, insulated with a large Pyrex pipe and asbestos cloth, in which the temperature was controlled to ±2°. At the end of the heating period the tubes were quenched in water and then opened. The samples were washed into a beaker with ethanol, diluted with water, and titrated electrometrically with 0.1*N* sodium hydroxide (carbonate-free). The temperature range of this study was 178° to 240°. Temperatures listed are corrected.

(2). *Large scale runs.* The effect of type of atmosphere on the pyrolysis of tributyl phosphate was investigated using 100+ grams of ester at a temperature of 221° ± 2°, sweeping with a gas (nitrogen and oxygen) throughout the runs. The tributyl phosphate was first degassed at room temperature on the vacuum pump, then treated overnight by bubbling purified nitrogen (through copper turnings at 230–250°, sulfuric acid drying tower, and empty drying tower) into the reaction flask at 50–100 ml./min. *via* capillary tube. The reaction flask was fitted with the gas inlet, capillary sampling arm, a condenser, and a thermometer suspended in the tributyl phosphate through the condenser. Heating was provided by a glas-col mantle. The temperature of the test was attained in 20 min., at which time a "zero time" sample was taken. Samples were removed at 30-min. intervals using gentle suction, first flushing the capillary with a small amount of the reaction mixture each time. Weighed samples were titrated in 50% ethyl alcohol.

Similar tests were made with nitrogen saturated with water vapor, and with dry oxygen. The nitrogen was saturated with water vapor by passing it in fine bubbles through water at 0° into the dried, degassed tributyl phosphate just before starting the pyrolysis. When oxygen was used it was passed only through the sulfuric drying tower and empty drying tower spray trap, then into the tributyl phosphate for an hour prior to and during pyrolysis.

Identification of reaction products. The method used will be illustrated by the thermal decomposition of tributyl phosphate labeled with P-32. The pyrolysis was conducted as in (2) above with the following exceptions. Tributyl phosphate (242 g. containing 3.6 g. of tributyl phosphate-P^{32}, 0.5 mc./g.) was degassed at room temperature on the vacuum pump, then swept for 4 hr. with tank helium (oxygen-free, dry) at 150–200 ml./min. The gas flow was stopped and the gas inlet was replaced with a stopper. The reaction flask, fitted with a thermometer well instead of the capillary gas sampler, had a gas outlet tube connected in series to a trap cooled in ice, a Dry Ice trap, and a leveling bulb in which the product gases were collected over water. The tributyl phosphate was heated at 220° ± 3° for 8 hr. during which time no noncondensable gases were obtained.

(1). *Condensable gases.* After the reaction mixture had cooled, the Dry Ice trap was allowed to warm to room temperature and samples of the condensed gases were analyzed by gas chromatography on a 12-foot column of dimethylformamide at 0°.[9] The butene isomers were the only products detected and butene-1 constituted at least 99% of the condensable gases.

(2). *Volatile liquids.* These were collected in the ice trap by cooling it with Dry Ice while evacuating the system to 1 mm. of mercury. Difficulty was experienced in removing the products completely. Three portions were collected and analyzed separately by gas chromatography at 115° on a column packed with 1 meter of dinonyl phthalate supported on Celite. The compounds *n*-butyl alcohol and di-*n*-butyl ether were detected in the ratio 17%–81% in the first fraction and 9%–91% in the third fraction.

(3). *Acids.* The amounts of acids formed were determined by titration of the residue from the reaction flask with 1*N* sodium hydroxide, and represented 0.103 mole per mole of

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(8) G. Berti, *J. Am. Chem. Soc.* **76,** 1213 (1954).

(9) G. W. Taylor and A. S. Dunlop in *Gas Chromatography,* edited by V. J. Coates, H. J. Noebels, and I. S. Fagerson, Academic Press, Inc., New York, 1958, pp. 73–85.

starting tributyl phosphate. A small amount of monobutyl phosphoric acid (3% of total acid) was evidenced by a second inflection in the titration curve. The aqueous layer was separated and the organic layer was washed twice with water.

Dibutyl phosphoric acid was recovered by cooling and acidifying (sulfuric acid) the aqueous solution of salts and extracting with carbon tetrachloride (two equal volume extractions). Any co-extracted monobutyl phosphoric acid was removed with a one-fourth volume water wash.[10] The dibutyl phosphoric acid, dried *in vacuo*, was identified by titration, density, and melting point of the copper salt; d_4^{25} 1.054, reported 1.057,[11] 1.054.[7]

Anal. Neut. equiv. Calcd.: 210. Found: 212. The copper salt of dibutyl phosphoric acid, Cu(DBP)$_2$, melted at 118–119° alone and when mixed with an authentic[12] specimen.

(4). *"Polymer."* The residue remaining after removal of tributyl phosphate by distillation at 1 mm. of mercury was identified as tetrabutyl pyrophosphate (TBPP). The alkali- and water-washed, dried residue (1.8 g.) contained 15.6% P (radioactive assay), had a molecular weight in benzene of 392[13] and an equivalent weight of 208 (16 hr. hydrolysis with 1*N* sodium hydroxide at room temperature, alkaline solution passed through cation resin in H$^+$ form, regenerated acid titrated with sodium hydroxide). Required for $(C_4H_9O)_2P(O)OP(O)(OC_4H_9)_2$: 15.4% P; m.w., 402; equivalent weight, 201. A small amount of inert (to sodium hydroxide) material was recovered and found to contain 18–20% phosphorus by radioactivity assay.

A derivative of the tetrabutyl pyrophosphate was prepared in 66% yield by heating 2 mmoles of dibenzylamine with 1 mmole of tetrabutyl pyrophosphate for 5 hr. at 100° and recrystallizing the amine salt of dibutyl phosphoric acid (precipitated by addition of petroleum ether) twice from hot *n*-hexane. Similarly, from an authentic sample of tetrabutyl pyrophosphate (prepared by the method of Toy[14] but not distilled), was derived the same amine salt. The melting point of each salt alone and mixed with an authentic specimen of $(C_6H_5CH_2)_2NH \cdot DBP$ was 109°.

OAK RIDGE, TENN.

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(10) D. C. Stewart and H. W. Crandall, *J. Am. Chem. Soc.* **73**, 1377 (1951).

(11) H. Adler and W. W. Woodstock, *Chem. Ind.* **51**, 516 (1942).

(12) W. H. Baldwin and C. E. Higgins, submitted to *J. Inorg. and Nuclear Chem.*

(13) F. Daniels, J. H. Mathews, and J. W. Williams, *Experimental Physical Chemistry*, 2nd ed., McGraw-Hill Book Co., Inc., New York-London, 1934, pp. 58–64.

(14) A. D. F. Toy, *J. Am. Chem. Soc.* **70**, 3882 (1948).

[CONTRIBUTION FROM THE CAROTHERS RESEARCH LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Reaction of Arylphosphinic Acids with Phosphorus Trichloride: Conversion of a Tetracovalent to a Trivalent System

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A facile method has been discovered for converting primary phosphinic acids to phosphonous dichlorides by reaction with phosphorus trichloride. The reaction provides a simple and convenient method for preparing phosphonous dichlorides of high degree of purity, and proves that the primary phosphinic acids, which are normally monobasic, are capable of reacting in their tautomeric dibasic form as phosphonous acids. An attempt to extend this reaction to the synthesis of a phosphinous chloride from a secondary phosphine oxide was not successful.

Compared to the preparation of acid chlorides from phosphonic acids (RPO_3H_2) and secondary phosphinic acids (R_2PO_2H), the conversion of primary phosphinic acids (RPO_2H_2) to the corresponding acid chlorides ($RPCl_2$) has received scant attention.[2] The probable reasons for this are twofold: The acids are usually prepared by hydrolysis of the chlorides in the first place, and this hydrolysis is accompanied by an apparently irreversible transformation in which the trivalent phosphorus atom becomes tetracovalent:

$$\begin{array}{ccccc} RPCl_2 & \longrightarrow & RP(OH)_2 & \rightleftarrows & RPH(O)OH \\ \text{I} & & \text{II} & & \text{III} \end{array}$$

The product is a monobasic phosphinic acid (III) and not the expected dibasic phosphonous acid (II).

The reversal of this hydrolysis would, as pointed out by Kosolapoff,[3] be of great interest for both theoretical and practical reasons. It would prove that the phosphinic acids are capable of reacting in their tautomeric trivalent form, and would provide a simple and convenient method for the synthesis of phosphonous dichlorides of high degree of purity. The phosphinic acids, especially those of the aromatic series, are almost all well defined crystalline solids, whereas the dichlorides are usually fuming liquids. Also, several syntheses of phosphinic acids have appeared recently which do not proceed through the dichlorides as intermediates.[4]

A facile method for carrying out this reversal has now been discovered. The reaction of phenyl-

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[2] The synthesis of phosphonous dichlorides from phosphonous diesters by an exchange reaction with phosphorus trichloride according to the equation $RP(OC_2H_5)_2 + PCl_3 \rightarrow RPCl_2 + (C_2H_5O)_2PCl$ was recently described by M. Sander, *Chem. Ber.*, **93**, 1220 (1960).

[3] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, N. Y., 1950, p. 50.