

The sample of IIIb was recovered unchanged by chilling the solution.

1,3-Diacetyl-4-imidazoline.—Imidazole (20 g), 2 g of platinum oxide, and 400 ml of acetic anhydride were placed in a stainless steel bomb and pressurized to 500 psi with hydrogen. The bomb was rocked for 7 hr at room temperature, then opened the contents were poured over 1 kg of crushed ice. The resulting solution was evaporated *in vacuo* and the residue dissolved in ethanol. This solution was cooled and the resulting precipitate filtered. Usually, two or three crops of product were obtained with a total yield of 50%. The white, crystalline solid was recrystallized from ethanol and melted at 239–240°.

The nmr spectrum of 1,3-diacetyl-4-imidazoline in deuterium oxide at 80° consisted of singlets at 6.78, 5.48 (br), and 2.26 (sharp) ppm. The integral tracing checked very closely with the theoretical number of protons.

Anal. Calcd C₇H₁₀N₂O₂: C, 54.55; H, 6.49; N, 18.18. Found: C, 54.80; H, 6.50; N, 18.01.

1,3-Diacetylimidazolidine.—The third or fourth crop of crystals obtained from the ethanol solution in the synthesis of 1,3-diacetyl-4-imidazoline was a hygroscopic white solid, melting at 90–95° and identified as 1,3-diacetylimidazolidine (lit.⁵ mp 95°).

Hydroxylation of 1,3-Diacetyl-4-imidazoline.—To 5.1 g of 90% formic acid was added 2.3 g of 30% hydrogen peroxide. To this solution was added slowly 1.6 g of 1,3-diacetyl-4-imidazoline. An exotherm was encountered, but the temperature of the solution was not allowed to go above 60°. After standing at room temperature for 1 hr, the solution was heated on the steam cone for 5–10 min. The solution was chilled overnight but no solids were obtained. Since the solution still contained peroxides, it was heated for 30 min on the steam cone with air blowing into the solution. On testing with potassium iodide solution, the reaction mixture was found to be almost clear of peroxides. The mixture was then evaporated to dryness under vacuum only and triturated with absolute ethanol. The solids, obtained in 30% yield, melted at 173–175° and produced an infrared spectrum identical with one from the product isolated from the addition of methylenebisacetamide to glyoxal (lit.⁸ mp 176–177° for 1,3-diacetyl-4,5-dihydroxyimidazolidine).

(8) S. L. Vai., C. M. Moran, H. B. Moore, and R. M. H. Kullman, *J. Org. Chem.*, **27**, 2071 (1962).

Trialkyl Phosphates. II. Chlorination of Elemental Phosphorus in the Presence of Alcohols¹

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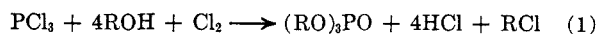
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In part I we showed that trialkyl phosphates could be prepared by the halogenation of trialkyl phosphites in the presence of alcohols.¹ Dialkyl phosphites could also be used, but they reacted more slowly. A logical development of this work was to extrapolate the synthesis back to phosphorus trihalides, and perhaps even to elemental phosphorus itself, generating the required P(III) halides and esters *in situ*. Until recently there were very few syntheses of organic phosphorus compounds in which elemental phosphorus was employed directly, but their number is growing rapidly.³

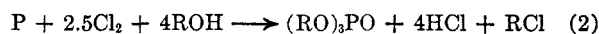
A reaction of phosphorus trichloride with chlorine and methanol, employing the preferred procedure¹

in which the P(III) compound and the chlorine are added simultaneously but separately to a large excess of the ice-cold alcohol, gave a 62% yield of trimethyl phosphate. This was less than the 88% yield obtained with trimethyl phosphite, but not disappointing in view of the large quantity of hydrogen chloride liberated (eq 1) and the known sensitivity of the methyl ester to acid cleavage.^{1,4}



Triethyl phosphate, which is less sensitive to acid cleavage, was obtained in 89% yield from phosphorus trichloride, compared to 91% from triethyl phosphite. Bliznyuk and Kolomiets⁵ have since described this same reaction, obtaining an 82% yield of triethyl phosphate from phosphorus trichloride, chlorine, and ethanol at 20–25°, and have extended it to the propyl, butyl, pentyl, and octyl esters, which they obtained in 83–88% yields. The first step in our extrapolation was established.

The next step was to prepare the phosphorus trichloride *in situ* by the chlorination of elemental phosphorus in the presence of an alcohol. The formal stoichiometry of this reaction is shown in eq 2.



The insolubility of elemental phosphorus in alcohols posed an immediate problem. Experiments in which chlorine was passed into white phosphorus dispersed in ethanol by means of a high-speed stirrer gave a 43% yield of triethyl phosphate at –10 to 0° and a 66% yield at 25–30° (Table I).

TABLE I

CHLORINATION OF WHITE PHOSPHORUS IN ETHANOL	
Reaction temp, °C	Yield of (C ₂ H ₅ O) ₃ P, %
–10 to 0	43
25–30	66
45–50	85
78 (reflux)	46

The outcome was considerably better when the reaction was carried out at 45–50°, slightly above the melting point of white phosphorus (44.1°). The yield of triethyl phosphate was 85% (Table I), and the reaction was easier to run as it did not require a high-speed stirrer. At reflux, however, the yield of triethyl phosphate dropped to 46%.

Another problem, which caused some concern in the early stages of the investigation, was a yellow flashing which was observed when the chlorine was passed in without dilution. This phenomenon was believed to be the result of a chemiluminescent reaction between the chlorine and the phosphorus.⁶ It also appeared to be the cause of a brown discoloration which sometimes made it difficult to determine the end point of the reaction. The flashing could be suppressed by diluting the chlorine with nitrogen.

(4) H. D. Orloff, C. J. Worrel, and F. X. Markley, *J. Am. Chem. Soc.*, **80**, 734 (1958).

(5) N. K. Bliznyuk and A. F. Kolomiets, *Zh. Obshch. Khim.*, **34**, 1169 (1964); USSR Patent 148,407 (July 13, 1962); *Chem. Abstr.*, **58**, 8906 (1963).

(6) See, for example, "Gmelins Handbuch der Anorganischen Chemie. Phosphor. Teil B," 8th ed, Verlag Chemie, Weinheim, Germany, 1964, p 283. A referee suggested that the flashing might result from an interaction of the alcohol and the chlorine alone, but we have only observed it when elemental phosphorus was present.

(1) Part I: A. W. Frank and C. F. Baranauckas, *J. Org. Chem.*, **31**, 872 (1966).

(2) To whom correspondence should be addressed.

(3) See review by M. M. Rauhut in "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, p 1.

Other variables we investigated were the alcohol:phosphorus ratio, the presence of hydrogen chloride and of water in the reaction mixture, the use of red phosphorus in place of white, and the scale of the reaction. One problem encountered in the halogenation of trialkyl phosphites in alcohols, isomerization of the trialkyl phosphite to a dialkyl alkylphosphonate, was not encountered in the present work.

An excess of the alcohol over the stoichiometric 4:1 ratio was believed to be necessary, its function being to complex the hydrogen chloride as the oxonium salt.⁴ A reduction of the ethanol:phosphorus ratio from 30:1 to 15:1 had no appreciable effect, the yield of triethyl phosphate being 80%, but further reduction gave a product contaminated with chlorine. The chlorination of a 5:1 mixture of ethanol and white phosphorus, for example, using benzene as a solvent, gave a crude product containing 4.9% of hydrolyzable chlorine. This reaction could be made to give pure triethyl phosphate by distilling the solvent at atmospheric pressure or by adding more ethanol, but in either case the yield was low (41–45%).

An experiment was performed in which the reaction was carried out under reduced pressure, with the intention of removing as much as possible of the hydrogen chloride during the reaction proper. The pressure was adjusted to 200 mm so that the ethanol would reflux at 45–50°. Analysis of the reaction mixture before stripping, however, showed that little if any of the hydrogen chloride had been removed. The complexing power of the alcohol for the hydrogen chloride was enough to overcome the reduction in pressure.

The effect of water on the reaction of white phosphorus with chlorine and ethanol was tested by substituting the regular 95.6% ethanol–water azeotrope for the anhydrous ethanol. At the ethanol:phosphorus ratio used, 20:1, the water:phosphorus ratio was 2.3:1, but triethyl phosphate was obtained nevertheless in 67% yield.

The chlorination of red phosphorus in ethanol at 45–50° gave triethyl phosphate in high yield, but considerable difficulty was experienced with flashing, aggravated perhaps by the fine state of subdivision of the phosphorus.

A large-scale laboratory preparation of triethyl phosphate was accomplished without difficulty. The yield of triethyl phosphate from 155 g of white phosphorus, 100 moles of ethanol, and 16.9 moles of chlorine was 81%.

The synthesis of other trialkyl phosphates was also accomplished without difficulty, by chlorinating white phosphorus in the presence of the appropriate alcohol at 45–50°. Trimethyl phosphate, tributyl phosphate, and tristearyl phosphate were prepared in high yield. The tristearyl phosphate was isolated as a crystalline 1:1 adduct with stearyl alcohol.¹

The mechanism of the reaction of elemental phosphorus with chlorine is probably the same as the mechanism of the trialkyl phosphite reaction,¹ *i.e.*, chlorination of the phosphorus to a chlorophosphonium species followed by alcoholysis and dealkylation (eq 3). With so many reactive species present at once, it would be idle to speculate as to whether phosphorus

trichloride or trialkyl phosphites are actually present as discrete entities during the reaction.

At the time our work was nearing completion, an interesting paper appeared in which trialkyl phosphates were prepared from red phosphorus by an electrochemical method involving the electrolysis of hydrogen chloride.⁷ The equation given for the reaction was as follows.



It seems clear that while this equation represents the over-all process, the actual reaction taking place at the anode is that given by eq 2.

Experimental Section⁸

Reagents.—The reagents were all obtained from commercial sources and used without further purification.

Methods of Analysis.—Trialkyl phosphite and dialkyl phosphite contents were measured by iodine titration.⁹ Gas chromatographic analyses were run on a Burrell K-2 instrument using the 20% SE-30/Chromosorb W column described for trimethyl phosphite.¹⁰ Infrared spectra were taken on a Beckman IR-4 spectrophotometer.

Trialkyl Phosphates from Phosphorus Trichloride.—Chlorine gas was passed into 414 g (9.0 moles) of anhydrous ethanol at –10 to –20° at a steady rate through a gas dispersion tube. When the solution was visibly yellow, phosphorus trichloride (45.8 g, 0.3 mole) was run in through a capillary tube attached to a dropping funnel and extending under the surface of the liquid, at such a rate that a faint yellow tinge was maintained and the temperature did not rise above –10°. The addition took 30 min. The solution was then purged with nitrogen for 1 hr at –10 to –20°, stripped of solvent under reduced pressure, and distilled, giving 48.6 g (89%) of triethyl phosphate,¹¹ bp 84–85° (5 mm), n_D^{20} 1.4058, d_4^{20} 1.070.

Anal. Calcd for $C_6H_{15}O_4P$: P, 17.0. Found: P, 17.6.

Tests for purity showed that the product was quite pure: by gas chromatographic analysis, over 99%; by iodine titration, no diethyl phosphite or triethyl phosphite; by infrared, no diethyl ethylphosphonate. A titration for acidity gave 1.1 mg of KOH/g, corresponding to 0.3% of diethyl phosphate.

A similar reaction between 68.8 g (0.5 mole) of phosphorus trichloride, 480 g (15.0 moles) of methanol, and chlorine gave 41.6 g (62%) of trimethyl phosphate,¹¹ bp 64° (6 mm), n_D^{20} 1.3958.

Anal. Calcd for $C_3H_9O_4P$: P, 22.1. Found: P, 21.8.

The residue from the distillation was a viscous light brown oil (18.1 g).

Trialkyl Phosphates from White Phosphorus. General Procedure.—In each of the following experiments, the phosphorus was weighed in a beaker containing water, dipped into two successive beakers containing the appropriate alcohol, and then transferred to the reaction flask containing the reagent alcohol. Before adding the phosphorus, the reagent alcohol was flushed with nitrogen by means of a gas dispersion tube. An inert atmosphere was maintained throughout. Chlorine was admixed with nitrogen in the required ratio and passed in at such a rate that most of it was absorbed, except in the rapid chlorination experiments where part of the gas was allowed to escape. The ratio of chlorine to nitrogen in most cases was 3:2 at the start, and was gradually increased to 10:1 as the reaction progressed. The chlorination was stopped when a silver nitrate

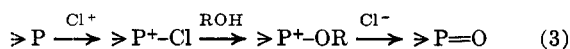
(7) S. L. Varshavskii, A. P. Tomilov, and Yu. D. Smirnov, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva*, **7**, 598 (1962); *Chem. Abstr.*, **58**, 3097 (1963).

(8) Melting points were determined using a Fisher-Johns apparatus and are corrected. The C and H microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(9) Technical Data Sheet No. 819A, "Analytical Methods for Tridecyl Phosphite," Hooker Chemical Corp., Niagara Falls, N. Y., 1959.

(10) A. Davis, A. Roaldi, J. G. Michalovic, and H. M. Joseph, *J. Gas Chromatog.*, **1**, No. 8, 23 (1963).

(11) A. I. Vogel and D. M. Cowan, *J. Chem. Soc.*, 16 (1943), gave bp 62° (5 mm), n_D^{20} 1.39630 for trimethyl phosphate; bp 75.5° (5 mm), n_D^{20} 1.40533, d_4^{20} 1.0695 for triethyl phosphate; and bp 138.5° (6 mm), n_D^{20} 1.42496 for tributyl phosphate.



test¹² for unreacted phosphorus was negative. *Caution: White phosphorus is highly poisonous and ignites when exposed to the air.*¹³

Reaction Temperature.—A dispersion of white phosphorus (6.2 g, 0.2 g-atom) in anhydrous ethanol (276 g, 6.0 moles) was prepared by warming the mixture to 45° in a 1-l. Morton flask and dispersing the phosphorus when molten with a high-speed stirrer. The dispersion was cooled to -10° and chlorinated with a 1:1 mixture of chlorine and nitrogen at -10 to 0° until a test for unreacted phosphorus was negative (3 hr). Constant stirring was required, as the phosphorus tended to settle out when the stirring was stopped. Occasional flashing was observed. The reaction mixture, which was greenish black in color, was allowed to warm to room temperature, stripped of solvent under reduced pressure, and distilled, giving 15.6 g (43%) of triethyl phosphate,¹¹ bp 66–68° (2 mm), n_D^{20} 1.4050.

Anal. Calcd for $C_6H_{16}O_4P$: P, 17.0. Found: P, 16.7.

The infrared spectrum of the product showed no diethyl ethylphosphonate. A gas chromatographic analysis gave its purity as 99.7%, with 0.2% of ethanol and 0.1% of another impurity.

The effect of higher reaction temperatures on the yield of triethyl phosphate is shown in Table I. The experimental procedure was the same including the 3-hr reaction time, except for the use of a regular mechanical stirrer in place of the high-speed stirrer in the last two experiments. The product of the 45–50° experiment, which gave the highest yield (85%), was a colorless liquid, bp 69° (1–2 mm), n_D^{20} 1.4048.

Anal. Calcd for $C_6H_{16}O_4P$: P, 17.0; Cl, nil. Found: P, 16.9; Cl, 0.8.

Ethanol:Phosphorus Ratio.—A slurry of 37.2 g (1.2 g-atoms) of white phosphorus, 276 g (6.0 moles) of anhydrous ethanol, and 600 g of benzene was chlorinated with 218 g (3.1 moles) of chlorine over a 1.5-hr period at 45–50°. Hydrogen chloride evolution was brisk. The resulting solution, which gave a negative test for unreacted phosphorus, was purged with nitrogen and split into four equal portions.

One portion was worked up in the preferred manner, by stripping carefully under vacuum at temperatures not exceeding 40°. Distillation gave 46.1 g (84%) of product, bp 60–63° (0.7 mm), n_D^{20} 1.4074, which was high in acidity and hydrolyzable chlorine (P, 16.8; acidity, 41.9 ml of 0.1 N NaOH/g, of which one-third was accounted for by chlorine: 13.9 ml of 0.1 N $AgNO_3$ /g, or Cl, 4.9).

Another portion was stripped of solvent at atmospheric pressure. The product, 24.9 g, bp 60–63° (0.7 mm), n_D^{20} 1.4038, now showed an analysis of almost pure triethyl phosphate (P, 17.1; Cl, 0.05; acidity, 1.3 ml of 0.1 N NaOH/g), but the yield had dropped to 45% and a large undistilled residue remained. It appeared that the chlorine-containing by-product was destroyed at the expense of some of the triethyl phosphate.

Reduced Pressure.—An experiment was carried out in an apparatus modified to accommodate a vacuum of 200 mm in order to have the ethanol at reflux. The vapor pressure of ethanol is 174.0 mm at 45° and 222.2 mm at 50°. The chlorine and nitrogen were premixed and admitted through a capillary tube extending under the surface of the alcohol. Vacuum was applied by means of a water aspirator. The chlorination of 6.2 g (0.2 g-atom) of white phosphorus in 276 g (6.0 moles) of anhydrous ethanol under these conditions required 1 hr at 45–50° (200 mm). The resulting solution was purged with nitrogen, analyzed for hydrolyzable chlorine and acidity, and stripped of excess ethanol under reduced pressure. Distillation of the product gave 32.0 g (88%) of triethyl phosphate, bp 70–80° (1.5 mm), n_D^{20} 1.4041.

Analysis of the purged solution before stripping gave 33.71 ml of 0.1 N $AgNO_3$ /g and 34.62 ml of 0.1 N NaOH/g, corresponding to 1.02 moles of HCl and 1.06 moles of total acidity (HCl and P-OH). The theoretical value is 0.80 mole of acid, all as HCl.

Scale-Up.—A large-scale laboratory run was made without difficulty, employing 155 g (5.0 g-atoms) of white phosphorus and 4600 g (100 moles) of anhydrous ethanol in a 12-l. flask. The chlorination took 6.5 hr at 45–50° and required 1200 g of chlo-

rine, vs. the calculated 887.5 g (12.5 moles). Distillation of the product remaining after stripping off the excess ethanol gave a small forecut (45 g, n_D^{20} 1.4219) followed by 740 g (81%) of triethyl phosphate, bp 77° (1.0 mm), n_D^{20} 1.4049.

Anal. Calcd for $C_6H_{16}O_4P$: P, 17.0. Found: P, 16.7.

The undistilled residue was a brown, viscous oil, 110 g, n_D^{20} 1.4042, with a phosphorus content (P, 26.1) approaching that of diethyl pyrophosphate (P, 26.5).

Other Alcohols.—Several other trialkyl phosphates were prepared by the chlorination of white phosphorus in the appropriate alcohol at 45–50°, the actual experimental conditions being modified to suit the alcohol.

Trimethyl phosphate,¹¹ bp 51–52° (2 mm), n_D^{20} 1.3956, was prepared in 34% yield following the procedure used for the ethyl ester in Table I, *i.e.*, a 3-hr reaction time at 45–50° with a 30:1 ratio of methanol:phosphorus.

Anal. Calcd for $C_3H_9O_3P$: P, 22.1. Found: P, 22.1.

A faster chlorination time (1.5 hr) improved the yield of trimethyl phosphate to 61%. No dimethyl methylphosphonate was detected in either product (infrared).

Tributyl phosphate,¹¹ bp 88–90° (0.005 mm), n_D^{20} 1.4238, was also prepared by the procedure used for the ethyl ester in Table I. The yield was quantitative.

The preparation of **tristearyl phosphate**¹⁵ required more extensive modification, since the alcohol itself was a solid. A solution of 1.0 g (0.032 g-atom) of white phosphorus, 64.8 g (0.24 mole) of stearyl alcohol, and 250 ml of benzene was chlorinated over a 25-min period at 45–50°, filtered, and stripped of volatiles under vacuum. The residue, which was partly solid, was triturated in a mortar under acetone, filtered, washed with acetone, and dried, giving 35.7 g (98%) of product, mp 55.5–57.5° after recrystallization from ethanol. The product was found to be a 1:1 adduct of tristearyl phosphate and stearyl alcohol.

Anal. Calcd for $C_{72}H_{146}O_5P$: C, 76.80; H, 13.34; P, 2.75. Found: C, 76.61; H, 13.31; P, 2.74.

The presence of stearyl alcohol in the product was verified by gas chromatographic analysis (calcd, 24.0; found, 24.0).

Acknowledgment.—We are indebted to Mr. Leon A. Zengierski for capable technical assistance, to Mr. Rex A. Schad and Mr. William L. Schall for some of the starting materials, and to the members of our analytical and spectral laboratories under the direction of Mr. Richard L. McCullough and Mr. Abram Davis for their cooperation.

(15) W. Davey, *Ind. Eng. Chem.*, **42**, 1841 (1950), gave mp 72° for tristearyl phosphate.

Electrolytic Reductive Coupling. X.¹ Reactions of Allylic Tautomers of Activated Olefins

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Electrolysis of the allylic tautomers of activated olefins under conditions similar to those used in the electrolytic reductive coupling of the activated olefins themselves¹ promises to provide a new tool for investigating the problems associated with the "three-carbon shift." We report here the results of a limited experimental study in this area.

The base-catalyzed equilibration of β,γ - α,β -unsaturated systems (I, II, and III, where X = an electron-attracting group) has been studied extensively.² At

(12) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., London, 1961, p 793.

(13) For proper handling, see "Phosphorus and Its Compounds," Vol. II, J. R. Van Wazer, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p 1202.

(14) "International Critical Tables," Vol. III, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 217.

(1) Paper IX: M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 3138 (1965).

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 562–556.