pigment. Attempts to demethylate this material by various methods were unsuccessful.

Dihydroosajaxanthone (7).—A mixture of the synthetic dihydroosajaxanthone monomethyl ether[7] (**6**, 240 mg), aluminum bromide (500 mg), and anhydrous benzene (20 ml) was saturated with dry hydrogen chloride and refluxed for 2 hr. The mixture was poured into ice and dilute hydrochloric acid and stirred for 1 hr. Evaporation of the benzene left a precipitate in the aqueous layer which was collected. Thick layer chromatography [silica gel, petroleum ether (bp 65–110°)–benzene–ethyl acetate, 4:4:1 (v/v) developer] followed by recrystallization from ethanol gave yellow crystals: yield 35 mg (15%), mp 299–300° dec (lit.[7] 299–300° dec); mmp 299–300° dec; X-ray powder diffraction data[16] 11.79 m, 10.40 s, 9.41 s, 6.81 s, 5.91 s, 5.22 w, 4.55 w, 4.29 m, 4.00 vs (3), 3.85 vs (2), 3.24 vs (1), and 3.00 m.

X-ray powder diffraction pattern and infrared spectra of the reaction product with the dihydro derivative of the natural pigment showed the two to be identical.

Osajaxanthone (8).—A mixture of the above synthetic dihydroosajaxanthone (**7**, 35 mg), sodium acetate (308 mg), and acetic anhydride (4 ml) was refluxed for 2 hr and poured into water. The resulting precipitate was collected and dried. A mixture of the compound (40 mg), *N*-bromosuccinimide (18.4 mg), potassium carbonate (20 mg), and benzoyl peroxide (1 mg) in carbon tetrachloride (25 ml) was refluxed for 9 hr. The solution was cooled and filtered, and the filtrate was evaporated. The residue was dissolved in pyridine and heated under nitrogen at 100° for 1 hr. The pyridine was evaporated under reduced pressure and the syrup that was obtained was dissolved in 1% ethanolic sodium hydroxide solution (30 ml) and heated at 75° for 1 hr. The solution was acidified with 2 *N* hydrochloric acid and the resulting precipitate was chromatographed on thick layer plates [silica gel, petroleum ether (bp 65–110°)–benzene–ethyl acetate, 4:4:1 (v/v) developer]. Recrystallization from methanol yielded yellow needles [yield 10 mg (30%), mp 264° (lit.[9] mp 264–265°), with the natural pigment mmp 264°]. The X-ray powder diffraction pattern and the infrared spectra of the compound and the natural pigment[5] were identical.

Registry No.—**8**, 1043-08-9; **2**, 7661-00-9; **3**, 7661-01-0; **4**, 7661-02-1; **5**, 7661-03-2; **8** (**7**=OMe), 3257-07-6; **7**, 3257-10-1.

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Reaction of Tetraalkylphosphonium Salts with Anhydrous Sodium Hydroxide

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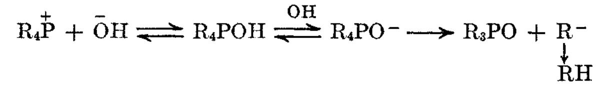
The reaction of anhydrous sodium hydroxide with tetraalkylphosphonium halides to produce trialkylphosphine oxides and alkanes has been shown to proceed under considerably milder conditions and permit more facile isolation of the phosphine oxides than when aqueous sodium hydroxide is used. Anhydrous dodecyltrimethylphosphonium hydroxide is surprisingly unstable and decomposes rapidly at 25–28°. By contrast, a 0.25 *M* aqueous solution of this phosphonium hydroxide was refluxed for 40 hr without apparent decomposition. A marked difference in reactivity of the various dodecyltrimethylphosphonium halides with anhydrous sodium hydroxide was observed. Reaction temperatures of 68–80° are required for the chloride, 80–110° for the bromide, and 140–150° for the iodide. An interpretation of these differences based on relative stabilities of ion pairs is suggested. Methyl groups are cleaved faster than dodecyl groups from dodecyltrimethylphosphonium halides by a factor of about 50:1. This corresponds to a difference in activation energies of about 2.9 kcal between transition states leading to methane and dodecane. This energy difference is attributed largely to the energy difference between the methyl and higher alkyl carbanions.

The reaction of aqueous base with phosphonium salts has long been known to give tertiary phosphine oxides and the hydrocarbons resulting from the most stable carbanion.[1,2] Early workers[3] visualized this reaction as proceeding *via* a pentacovalent phosphorus intermediate (R_4POH) whose formation was rate determining. Subsequently, it was shown that the reaction of benzyl-[4,5] and phenylphosphonium[6,7] salts in dilute solution is generally second order in hydroxide ion and first order in the phosphonium salt. These facts are best explained by a series of rapidly established equilibria followed by the slow decomposition of the pentacovalent phosphorus anion (R_4PO^-) to the tertiary phosphine oxide and the most stable carbanion, which rapidly forms the hydrocarbon.[8]



$$R_4\overset{+}{P} + \overset{-}{O}H \rightleftharpoons R_4POH \underset{}{\overset{\overset{-}{O}H}{\rightleftharpoons}} R_4PO^- \longrightarrow R_3PO + \underset{\displaystyle RH}{\underset{\downarrow}{R^-}}$$

Since a polar protic solvent such as water, capable of strong solvation of ions and hydrogen bonding with hydroxide ion, should retard the reaction,[6,9,10] and because alkyl-substituted phosphonium salts are less reactive to hydroxide ion than benzyl- or phenyl-substituted phosphonium salts,[5,7] the reaction of anhydrous sodium hydroxide with tetraalkylphosphonium salts was investigated. In addition, the use of anhydrous sodium hydroxide was investigated because frequently tertiary phosphine oxides are hygroscopic and very difficult to isolate from aqueous solution.[11]

Results and Discussion

The reactions of dodecyltrimethylphosphonium chloride, bromide, and iodide, methyltridodecylphosphonium bromide, and dodecyltriethylphosphonium chloride with anhydrous sodium hydroxide were generally car-

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(1) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).

(2) K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).

(3) L. Hey and C. K. Ingold, *J. Chem. Soc.*, 531 (1933).

(4) M. Zanger, C. A. Vander Werf, and W. E. McEwen, *J. Am. Chem. Soc.*, **81**, 3806 (1959).

(5) G. Aksnes and J. Songstad, *Acta Chem. Scand.*, **16**, 1426 (1962).

(6) H. Hoffmann, *Ann.*, **634**, 1 (1960).

(7) G. Aksnes and L. J. Brudvik, *Acta Chem. Scand.*, **17**, 1616 (1963).

(8) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. Vander Werf, *J. Am. Chem. Soc.*, **86**, 2378 (1964).

(9) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(10) M. R. V. Sahyun and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1263 (1963).

(11) C. Screttas and A. F. Isbell, *J. Org. Chem.*, **27**, 2573 (1962).

ried out by heating the powdered reactants until gas evolution was complete. The conditions required for these reactions are recorded in Table I. Experiments in aqueous solution are included for comparison.

TABLE I

TEMPERATURES REQUIRED FOR REACTION OF TETRAALKYLPHOSPHONIUM SALTS WITH SODIUM HYDROXIDE

Phosphonium salt[a]	Reacn temp, °C
1. $[RP(CH_3)_3]^+OH^-$ (anhydrous)	$<25^b$
2. $[RP(CH_3)_3]^+OH^-$ (0.25 M aq soln)	No reaction up to 95–100°
3. $[RP(CH_3)_3]^+Cl^-$ (anhydrous)	68–80
4. $[RP(CH_3)_3]^+Cl^-$ (0.9 M aq soln)	No reaction up to 95–100°[c]
5. $[RP(CH_3)_3]^+Br^-$ (anhydrous)	80–110
6. $[RP(CH_3)_3]^+I^-$ (anhydrous)	140–150
7. $[R_3PCH_3]^+Br^-$ (anhydrous)	100–130
8. $[RP(C_2H_5)_3]^+Cl^-$ (anhydrous)	85–113

[a] R is n-$C_{12}H_{25}$ in all cases. [b] Decomposition of a small sample was complete in about 20–30 min at 25°. [c] Reaction was not observed after refluxing for 2.5 hr. Upon distilling the water from the mixture, reaction occurred at bath temperatures of 130–135°, at approximately 4 M concentrations. At this point the reaction accelerated and was uncontrollable owing to foaming.

With the exceptions noted, the trialkylphosphine oxides recorded in Table II were isolated by vacuum distillation from the residual sodium halide and a slight excess of anhydrous sodium hydroxide. Use of anhydrous sodium hydroxide made isolation of the trialkylphosphine oxides in this manner quite simple, particularly the hygroscopic trialkylphosphine oxides (*e.g.*, trimethylphosphine oxide, triethylphosphine oxide, and diethyldodecylphosphine oxide).

TABLE II

PRODUCTS AND YIELDS FROM THE REACTION OF TETRAALKYLPHOSPHONIUM SALTS WITH SODIUM HYDROXIDE

Phosphonium salt[a]	Products, %		
	$R\overset{\overset{O}{\uparrow}}{P}(CH_3)_2$	$+\ CH_4$	$+\ \underbrace{(CH_3)_3\overset{\overset{O}{\uparrow}}{P} + RH}$
$[RP(CH_3)_3]^+Cl^-$	94–96	99	0.7–1.1
$[RP(CH_3)_3]^+Br^-$	93	99	Not determined
$[RP(CH_3)_3]^+I^-$	92–97	99	0.5–0.6
$[R_3PCH_3]^+Br^-$	$\underbrace{R_3\overset{\overset{O}{\uparrow}}{P} + CH_4{}^b}_{88} + \underbrace{R_2\overset{\overset{O}{\uparrow}}{P}CH_3 + RH^b}_{12}$		
$[RP(C_2H_5)_3]^+Cl^-$	$\underbrace{R\overset{\overset{O}{\uparrow}}{P}(C_2H_5)_2 + C_2H_6}_{75} + \underbrace{(C_2H_5)_3\overset{\overset{O}{\uparrow}}{P} + RH}_{25}$		

[a] R is n-$C_{12}H_{25}$ in all cases. [b] Tridodecylphosphine oxide was isolated by recrystallization from acetone. The didodecylmethylphosphine oxide was concentrated in the mother liquor.

The rate-retarding effect of water on the reaction of tetraalkylphosphonium ions with hydroxide ion is most evident in the decomposition of the intermediate tetraalkylphosphonium hydroxides (Table I, entries 1 and 2). Anhydrous dodecyltrimethylphosphonium hydroxide decomposed within 30 min at 25° to methane and dimethyldodecylphosphine oxide. In contrast, an aqueous solution of this phosphonium hydroxide (0.25 M) was refluxed for 40 hr without apparent decomposition. Upon distillation of the solution, decomposition of the dodecyltrimethylphosphonium hydroxide occurred at 130–140°[12] after most of the water had been removed. Similarly the reaction of dodecyltrimethylphosphonium chloride with sodium hydroxide was markedly retarded by dissolution in water (Table I, entries 3 and 4).

A marked difference in the reactivity of dodecyltrimethylphosphonium chloride, bromide, and iodide with anhydrous sodium hydroxide was observed (Table I, entries 3, 5, and 6). Finely powdered dodecyltrimethylphosphonium chloride and sodium hydroxide began evolving methane smoothly at 68–70° and upon further heating to 80° the evolution was complete in less than 2 hr. In contrast, dodecyltrimethylphosphonium iodide and sodium hydroxide required temperatures of 140 to 150° for a comparable rate of reaction. The corresponding bromide was intermediate in reactivity, requiring temperatures of 80–110°. Similar reaction temperatures were also required when the phosphonium salt and sodium hydroxide were dissolved in absolute alcohol, the alcohol was removed at room temperature, and the reactants were heated.

The difference in reactivity of the various dodecyltrimethylphosphonium halides with sodium hydroxide can be explained in terms of the relative association energies of the ion pairs involved in the following manner. Since the intermediate tetraalkylphosphonium hydroxide decomposes rapidly to products at 25°, the reaction of the different phosphonium halides with sodium hydroxide presumably depends on the tendency of the following ion-exchange reaction to proceed to the right.[13] Because the Na^+OH^- and $R_4P^+OH^-$ ion

$$R_4\overset{+}{P}X^- + Na^+OH^- \rightleftharpoons Na^+X^- + R_4\overset{+}{P}OH^-$$

pairs are common to all the reactions, the ease with which $R_4P^+OH^-$ is formed depends on the relative stability of the ion pairs, $R_4P^+X^-$ and Na^+X^-. Since the association energies of Na^+ with X^- can be assumed to increase at a faster rate in the series I < Br < Cl than do the association energies of R_4P^+ with X^-,[14] it follows that the tendency to form $R_4P^+OH^-$ should increase in the order $Cl^- > Br^- > I^-$.

A quantitative study of the products from dodecyltrimethylphosphonium halides and sodium hydroxide

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(12) Earlier workers[1] reported decomposition temperatures of 100–140° for alkyltrimethylphosphonium hydroxides during distillation of aqueous solutions. Since the analogous phosphonium alkoxides[3] decomposed under approximately the same conditions they concluded that the slow step in both reactions was the formation of the pentacovalent intermediate, R_4POR', where R′ = H or alkyl. Subsequent kinetic evidence has corrected this idea; however, dodecyltrimethylphosphonium methoxide was prepared and heated for comparison purposes. The phosphonium methoxide was thermally stable to about 160–170°, at which time decomposition occurred to give chiefly dimethyl ether, methane, and dimethyldodecylphosphine oxide.

(13) The assumption of extensive ion association is reasonable in view of the near absence of solvent. Under these conditions the reaction mixture is heterogeneous and consists of a molten phase and powdered sodium hydroxide. The rate of reaction is somewhat dependent upon the particle size of the sodium hydroxide in the sense that pellets react very slowly. However, the same reaction temperatures are observed when the finely powdered reactants are heated and when the reactants are first dissolved in ethanol followed by removal of the ethanol under reduced pressure, then heated. That the observed reactivities are not directly related to the crystallinity of the phosphonium salts is evident from their melting points. The more reactive dodecyltrimethylphosphonium chloride is much higher melting than the corresponding iodide (mp 210° for the chloride, mp 87–88° for the iodide).

(14) This statement is supported by inspection of table, p 235, in O. K. Rice, "Electronic Structure and Chemical Binding with Special Reference to Inorganic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940. The crystal-lattice energies of the alkali metal halides increase at a faster rate for a small than for a large metal ion in the series MI < MBr < MCl < MF.

showed that methyl and dodecyl groups are cleaved at a relative rate of about 50/1, respectively. The relative rate of cleavage was somewhat lower (22/1) for methyltridodecylphosphonium bromide. These relative rates correspond to a difference of 2.5 to 2.9 kcal of activation energy in the transition states leading to cleavage of a dodecyl group and a methyl group. This energy difference is believed to represent principally the energy difference between methyl and higher alkyl carbanions.

It is of interest that the energy differences between benzyl-, phenyl-, and methylcarbanions are apparently large enough that competitive cleavage of these groups from benzylphenylphosphonium salts[8] and phenylmethylphosphonium salts[7] is not observed.

Dodecyltriethylphosphonium chloride reacted with sodium hydroxide to give the expected statistical yields of diethyldodecylphosphine oxide, ethane, triethylphosphine oxide, and dodecane.[1]

Experimental Section

Tetraalkylphosphonium Salts and Trialkylphosphine Oxides.—The preparation and characterization of the phosphonium halides and phosphine oxides involved in this study are reported elsewhere.[15] Identification of all the phosphine oxides was made by comparison of melting points, infrared spectra, and proton and P^{31} nmr spectra with those of authentic samples.

Reaction of Dodecyltrimethylphosphonium Salts with Sodium Hydroxide.—The general procedure consisted of placing the finely powdered phosphonium halide (0.1 mole) and dry, powdered, sodium hydroxide[16] (0.1–0.2 mole) in a 200-ml flask equipped with a magnetic stirrer, metallic thermometer, and condenser attached to a calibrated 2.5-l. gas trap. An argon atmosphere was employed. The reactants were stirred and heated with an oil bath until the evolution of methane, identified by its infrared spectrum,[17] was complete. The amount of methane evolved in all cases was nearly quantitative. At this point the condenser was replaced by a large-bore distilling head and the products were distilled under reduced pressure. Generally a few milligrams of trimethylphosphine oxide,[1] mp 139–140°, sublimed and collected in the condenser. After this hygroscopic phosphine oxide was removed, further distillation gave 92–97% yields of analytically pure dimethyldodecylphosphine oxide, bp 150–170° (0.5–1.0 mm), mp 83–84°. An infrared lamp was used to prevent solidification of the solid during distillation. Isolation of the dodecane was accomplished in the following manner. The condenser (Dry Ice cooled in these cases) was washed with 10 g or less of either tridecane or dodecylmethylether and then replaced by a distillation head. About 5 g of forerun was collected from the distillation and analyzed by gas chromatography on a polyester column. Standard solutions of 1–10% dodecane in the respective solvent were used to determine the per cent dodecane present. In two experiments, at 100° bath temperatures, dodecyltrimethylphosphonium chloride and sodium hydroxide gave 0.7 and 1.1% yields of dodecane. Dodecyltrimethylphosphonium iodide and sodium hydroxide gave 0.5 and 0.6% yields of dodecane. In the two experiments that gave 0.7, and 0.6% yields, a 1.5% yield of 1-dodecene was added to the reactants as a standard and carried through the entire experiment. The yield of dodecane was then calculated from the relative areas of the dodecene and dodecane peaks.

Using dry reactants, the reaction temperatures of dodecyltrimethylphosphonium halides with sodium hydroxide were found to be 68–80° for the chloride, 80–110° for the bromide, and 140–150° for the iodide. Reaction was complete in less than 2 hr, provided that the reactants were finely powdered and well stirred. Higher reaction temperatures resulted in considerably shorter reaction times with no adverse effects. The same reaction temperatures were observed when ethanol solutions of the reactants were evaporated under reduced pressure and the solid reactants were subsequently heated. Attempts to treat dodecyltrimethylphosphonium chloride with aqueous sodium hydroxide were not successful until the concentration of the base exceeded about 15%. In one such experiment a solution of this quaternary salt and sodium hydroxide (0.9 *M* in both reactants) was heated to 130–140° bath temperatures for 2.5 hr, without apparent reaction. Upon distillation of the water, reaction began to occur when the sodium hydroxide concentration became about 4 *M*. At this point the reaction began accelerating as more water distilled, and the gas evolution through the aqueous mixture of the phosphonium salt and the phosphine oxide resulted in uncontrollable foaming.

Reaction of Methyltridodecylphosphonium Bromide with Sodium Hydroxide.—Methyltridodecylphosphonium bromide (35 g, 0.055 mole) and 2.2 g of anhydrous sodium hydroxide (0.055 mole) were powdered and heated to 100–130° until methane evolution was complete. Distillation of the dodecane with a small amount of dodecanol and analysis of the mixture by gas chromatography on a polyester column showed a 12% yield of dodecane. The P^{31} nmr spectrum of the crude product was consistent with an 88:12 ratio of tridodecylphosphine oxide and didodecylmethylphosphine oxide. Tridodecylphosphine oxide, mp 59.5–60°, was isolated by recrystallization from acetone, whereas the didodecylmethylphosphine oxide was concentrated in the acetone solution.

Reaction of Dodecyltriethylphosphonium Chloride with Sodium Hydroxide.—A dry, powdered mixture of 32 g of dodecyltriethylphosphonium chloride (0.1 mole) and 8 g of sodium hydroxide (0.2 mole) was heated to 85–113° until ethane evolution was complete. Approximately 850 ml of ethane (78% yield) was collected and identified by its gas phase infrared spectrum.[18] A P^{31} nmr spectrum of the crude product showed a 75:25 ratio of diethyldodecylphosphine oxide and triethylphosphine oxide. Addition of 5 ml of tridecane and distillation gave a forerun that analyzed for a 25 ± 2% yield of dodecane and a 21 ± 2% yield of triethylphosphine oxide.[1] Further distillation gave a 62% yield of diethyldodecylphosphine oxide. Both tertiary phosphine oxides are very hygroscopic.

Anhydrous Dodecyltrimethylphosphonium Hydroxide.—A solution of 28 g of dodecyltrimethylphosphonium chloride (0.1 mole) in 100 ml of absolute ethanol was mixed and stirred overnight with 12 g of freshly prepared silver oxide[19] (0.05 mole) in 50 ml of 95% ethanol. The silver chloride was filtered and the ethanol was removed rapidly on a rotary evaporator without heating. A considerable amount of dodecyltrimethylphosphonium chloride was not converted to the phosphonium hydroxide, as evidence by the infrared and P^{31} nmr spectra and a positive chloride test. Upon warming to room temperature the semisolid dodecyltrimethylphosphonium hydroxide rapidly evolved methane[17] to product dimethyldodecylphosphine oxide. Over a period of 30 min the infrared spectra of samples showed an increased in intensity of the 8.63-μ phosphoryl band and a decrease in intensity of the broad intense band at 10.3 μ, characteristic of dodecyltrimethylphosphonium compounds.

Dodecyltrimethylphosphonium hydroxide is an intermediate in the hydrolysis of dodecyltrimethylphosphonium methoxide. Although this methoxide is thermally stable to about 150°, exposure to the moist atmosphere at room temperature resulted in rapid hydrolysis and decomposition to methanol, methane, and dimethyldodecylphosphine oxide. A thin film of dodecyltrimethylphosphonium methoxide required about 20 min for hydrolysis and decomposition at 28°.

Aqueous Dodecyltrimethylphosphonium Hydroxide.—A solution of 37 g of dodecyltrimethylphosphonium iodide (0.1 mole) in 100 ml of water was added dropwise to 24 g of freshly prepared silver soxide (0.1 mole) in 100 ml of water. Considerable heat evolution was observed. After stirring overnight the silver iodide was filtered. A P^{31} nmr spectrum of the aqueous solution showed a singlet at −26 ppm, characteristic of dodecyltrimethylphosphonium compounds. The proton nmr spectrum showed a methyl triplet at τ 9.12, a methylene singlet at 8.70, and a phosphonium methyl doublet centered at 8.15 (J = 14 cps). Integration of the peaks gave a ratio of 3.3:22.5:9, respectively. Potentiometric titration of a sample of the aqueous solution of

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[15] H. R. Hays, *J. Org. Chem.*, **31**, 3817 (1966).

[16] Baker Analyzed reagent grade sodium hydroxide was ground with a mortar and pestle in a drybox.

[17] "The Sadtler Standard Spectra," Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 4063.

[18] Reference 17, Spectrum No. 7989.

[19] B. Helferich and W. Klein, *Ann.*, **450**, 219 (1926).

dodecyltrimethylphosphonium hydroxide with 1.0025 *N* hydrochloric acid gave a value of 0.26 *N*. Subsequent titration curves did not change even after refluxing 40 hr. Evaporation of a small sample led to decomposition to dimethyldodecylphosphine oxide.

Dodecyltrimethylphosphonium Methoxide.—A solution of 28 g of dodecyltrimethylphosphonium chloride (0.1 mole) in 40 ml of anhydrous methanol was added dropwise to a freshly prepared solution of potassium methoxide (0.1 mole) in 100 ml of methanol under argon. After stirring for 1 hr the potassium chloride was filtered under argon and the methanol was removed under vacuum overnight. The viscous liquid gave an infrared spectrum with a medium P^+CH_3 band at 7.73, a strong CH_3O band at 9.49, and a medium strong band at 10.2 μ characteristic of other dodecyltrimethylphosphonium compounds. The P^{31} nmr spectrum showed a singlet at −27.5 ppm relative to 85% phosphoric acid, characteristic of dodecyltrimethylphosphonium compounds. The proton nmr spectrum suggested the presence of about 3:1 ratio of methanol to dodecyltrimethylphosphonium methoxide. Care was required to prevent exposure to atmospheric moisture because hydrolysis and subsequent decomposition are rapid. Under a dry, inert atmosphere the dodecyltrimethylphosphonium methoxide showed little decomposition up to 160–170°. At this point, methane and dimethyl ether[20] (identified by their infrared spectra) were evolved. Upon heating to 200°, about 1.8 l. of gas was collected. Distillation gave 3.9 g of methanol, bp 67°, containing a trace of trimethylphosphine. Addition of excess methyl iodide and evaporation gave 0.4 g of tetramethylphosphonium iodide, mp >400°. The infrared spectrum was identical with that of an authentic sample of tetramethylphosphonium iodide prepared from trimethylphosphine and methyl iodide. Distillation of the remainder of the product under reduced pressure gave a 62% yield of slightly impure dimethyldodecylphosphine oxide, mp 78–81. The melting point was raised to 83–84° after recrystallization from hexane.

Registry No.—**1** and **2**, 7641-69-2; **3** and **4**, 7641-70-5; **5**, 2071-59-2; **6**, 7641-72-7; **7**, 7641-73-8; **8**, 7688-11-1.

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[20] Reference 17, Spectrum No. 1128.

A New Synthesis of Monoalkyl Phosphates

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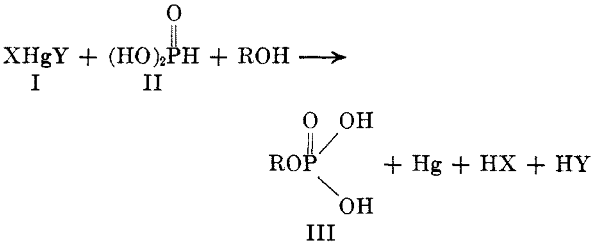
Various monoalkyl dihydrogen phosphates were prepared in good yields by the reaction of alcohols with inorganic phosphorous acid and mercury compounds in the presence of tertiary amines. The reaction can be explained by assuming an intermediate, metaphosphate, which reacts with alcohols to yield alkyl dihydrogen phosphates.

Various methods[1] have been reported for the phosphorylation of alcohols; however, there are few[2] which are well suited to the preparation of monoalkyl phosphates. One of the most simple and effective methods available is that of Kirby[3] in which the direct iodine oxidation of inorganic phosphorous acid in alcohols gives the corresponding monoalkyl phosphates in excellent yields, but this procedure is not applicable to most solid alcohols or those available in only small amounts, since the reaction has to be carried out in the presence of a large excess of alcohol.

It was found in our laboratory[4] that phosphorylation of simple alcohols by the use of monobenzyl phosphite or inorganic phosphorous acid and monobromocyanoacetamide gave the corresponding monoalkyl dihydrogen phosphates in good yields. However, when a slight excess of an alcohol was treated with either of these acids and monobromocyanoacetamide, the expected monoalkyl phosphates were always accompanied by small amounts of phosphoric acid and polyphosphoric acids which made the purification of the resulting phosphates more difficult.

The phosphorylation of alcohols was therefore investigated further by studying the use of some mercury compounds (I) as oxidizing reagents in the place of monobromocyanoacetamide in the above-mentioned experiment.

When mercuric acetate (I, X = Y = OAc) was brought into reaction with dry phosphorous acid (II) in refluxing ethanol, monoethyl phosphate (III, R = C_2H_5) was detected by paper chromatography together with orthophosphoric and unidentified polyphosphoric acids. Among various compounds examined, mercuric chloride, acetate, and sulfate, and mercurous chloride were found to be effective for this type of reaction, while mercuric cyanide and dialkyl or diaryl mercury were ineffective. In view of these results, it might be said that mercuric compounds capable of releasing stable anions are effective for this reaction.



$$\underset{\text{I}}{\text{XHgY}} + \underset{\text{II}}{(\text{HO})_2\overset{\text{O}}{\overset{\|}{\text{P}}}\text{H}} + \text{ROH} \longrightarrow \underset{\text{III}}{\text{RO}\overset{\text{O}}{\overset{\|}{\text{P}}}(\text{OH})_2} + \text{Hg} + \text{HX} + \text{HY} \qquad (1)$$

When mercuric chloride was treated with phosphorous acid in refluxing ethanol, a good deal of monoethyl phosphate and a small amount of unreacted phosphorous acid were detected by paper chromatography. On the other hand, when the reaction was carried out in the presence of more than 4 mole equiv of triethylamine, a quantitative yield of metallic mercury was deposited within a few minutes, and, in this case, chromatographically pure monoethyl dihydrogen phosphate (IV) was obtained as the bis(cyclo-

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(1) D. M. Brown, "Advances in Organic Chemistry: Methods and Results," Vol. 3, Interscience Publishers, Inc., New York, N. Y., 1963, p 75.

(2) F. Cramer and G. Weimann, *Chem. Ber.*, **94**, 996 (1961).

(3) A. J. Kirby, *Chem. Ind.* (London), 1877 (1963).

(4) T. Obata, M. Ueki, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, **39**, 1040 (1966).