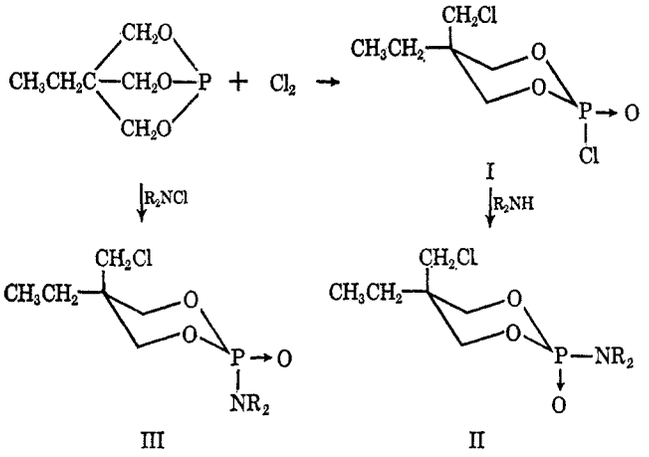
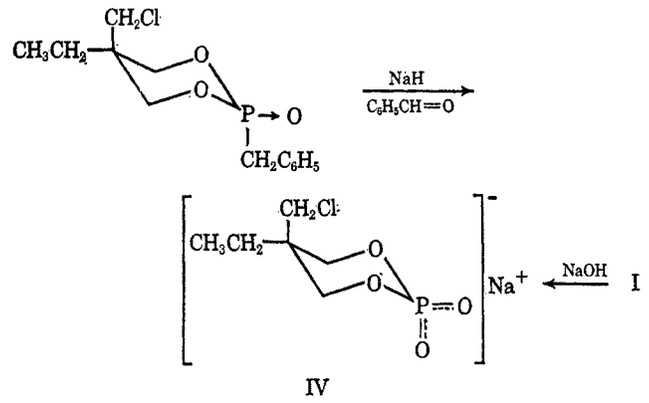
SCHEME I



there was little similarity. Thin layer chromatography showed both materials to be pure and uncontaminated by the other isomer. Heating both II and III independently to 200° produced no change in physical properties in either case. Treatment of I with 2 equiv of NaOH in CCl_4 gave the sodium salt of the cyclic phosphate, IV. An identical compound was ob-



tained by treating *cis*-2-chloromethyl-2-ethyl-1,3-propanediol benzylphosphonate with sodium hydride and benzaldehyde[5] further excluding the possibility that the different physical properties of II and III are due merely to conformational effects. In the first case inversion would be expected while in the second, if the accepted mechanism for the phosphonate–olefin reaction is correct, retention should predominate.

Westheimer[6] has postulated either a trigonal bipyramid or a square pyramid as likely transition states for the acid hydrolysis of cyclic phosphate esters, and similar transition states can be drawn for the present system. Since in our compounds inversion takes place exclusively and a square pyramid would lead to retention, a trigonal bipyramid where displacement takes place in the radial plane at a mutual angle of 120° would most likely represent the transition state. The ring would span one apical and one radial position. Further work with other nucleophiles and a study of solvent effects is currently in progress and will be reported at a later date.

(5) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

(6) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961); E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3432 (1966).

Experimental Section

2-Chloromethyl-2-ethyl-1,3-propanediol-N-cyclopentylene Phosphoramide (II).—Ethyl bicyclic phosphite (16.2 g, 0.1 mole) was dissolved in 100 ml of dry methylene chloride. Chlorine gas was bubbled into the solution at 20–30° until the solution took on the characteristic green color of chlorine. The solution was warmed to expel excess chlorine, and piperidine (17.0 g, 0.2 mole) dissolved in 50 ml of dry methylene chloride was added slowly at 20–30°. The solution was suction filtered and the filtrate was stripped under reduced pressure. The residue was recrystallized twice from heptane to give 14.35 g of a white crystalline solid, mp 161–162°.

Anal. Calcd for $C_{11}H_{21}ClNO_3P$: C, 46.89; H, 7.46; N, 4.97. Found: C, 47.09; H, 7.30; N, 4.96.

2-Chloromethyl-2-ethyl-1,3-propanediol-N-cyclopentylene Phosphoramide (III).—N-Chloropiperidine (0.2 mole), prepared from sodium hypochlorite, was dissolved in 100 ml of CCl_4 and the solution was added dropwise at 20–30° with stirring to ethyl bicyclic phosphite (24.3 g, 0.15 mole) dissolved in 100 ml of carbon tetrachloride. After standing overnight, solvent was removed under reduced pressure and the residue was recrystallized twice from heptane to give a white crystalline solid, 32.8 g, mp 99–100°.

Anal. Calcd for $C_{11}H_{21}ClNO_3P$: C, 46.89; H, 7.46; N, 4.97. Found: C, 46.73; H, 7.40; N, 5.04.

Registry No.—II [R = $(CH_2)_5$], 10212-39-2; III [R = $(CH_2)_5$], 10212-40-5.

Acknowledgment.—The author wishes to express his gratitude to Mr. Zale Puhlman who prepared some of the starting materials.

The Attempted Conversion of 1-Alkyl-4-(2-hydroxyethyl)-4-phosphorinanols into Bicylic Phosphonium Salts by a Quinuclidine Synthesis[1]

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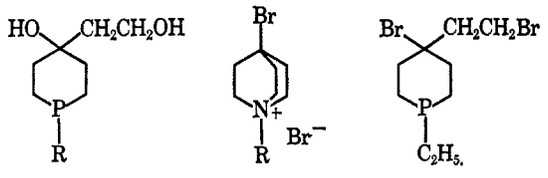
Received September 9, 1966

The cyclic phosphine (Ia) was recently subjected[2] to conditions used by Grob and Brenneisen[3] for converting the analogous nitrogen compound to a quinuclidine derivative (II). By analogy to II, the product of the first step (12 hr in 62% hydrobromic acid at 50–55°) should have been the dibromide (III). To effect cyclization, the product without isolation was placed in refluxing benzene;[3] a salt did indeed precipitate, but it contained hydroxyl and ionic bromine and could not be the phosphorus counterpart of II. The salt was assigned the bicyclic structure (IVa), which seemed best to fit the available data.[2] However, this structure would require the survival of a tertiary alcoholic function in 62% hydrobromic acid, and it was pointed out that such a unique event required further investigation. An alternative structure (V), which avoided this feature, was rejected on the basis of the proton magnetic resonance (pmr) spectrum, which failed to show a signal for CH_2CH_2OH.

(1) Supported by Research Grant CA-05507 from the National Cancer Institute, U. S. Public Health Service. Taken in part from the Ph.D. dissertation of H. E. Shook, Jr., 1966.

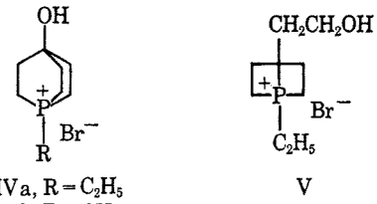
(2) L. D. Quin and D. A. Mathewes, *Chem. Ind.* (London), 210 (1963).

(3) C. A. Grob and P. Brenneisen, *Helv. Chim. Acta*, **41**, 1184 (1958).



Ia, R = C_2H_5
b, R = CH_3

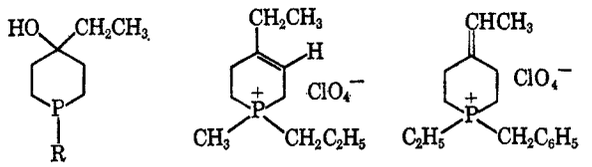
II III



IVa, R = C_2H_5
b, R = CH_3

V

A mixture of *cis* and *trans* isomers[4] of 1-methyl-4-ethyl-4-phosphorinanol (VIa) has now been treated with 62% hydrobromic acid (55–60° for 12 hr). After neutralization and extraction into ether, the product was gas chromatographed, and the complete absence of the alcohol (VIa) was observed. A similar result was obtained for 1,4-diethyl-4-phosphorinanol (VIb).[5] Unsaturated phosphines were isolated from each reaction mixture and identified as benzyl perchlorate salts (VII and VIII, respectively; see the Experimental Section). It is clear that a tertiary phosphorinanol is far from inert to 62% hydrobromic acid, and the structure (IVa) assigned to the product from diol Ia needs reconsideration.

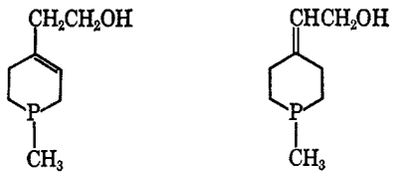


VIa, R = CH_3
b, R = C_2H_5

VII VIII

The Grob–Brenneisen procedure was then applied to a new diol (Ib). Analysis of the salt recrystallized from methanol, as well as analysis after exchange of bromide (all bromine was ionic) for perchlorate, suggested that, with respect to Ib, one hydroxyl had been replaced by bromine and at least a half of the second had been eliminated. The crude product had some characteristics of a hydrobromide (acidic aqueous solution; small infrared peak at 2360 cm^{-1} attributable to PH). However, after neutralization, only a trace of a phosphine was extractable. The infrared spectrum of the salt showed hydroxyl (OH stretch at 3400 and CO stretch at 1050 cm^{-1}) and unsaturation (weak C=C stretching peak at 1650 and strong absorption at 810–820 cm^{-1} possibly for CH bending of a trisubstituted double bond). The pmr spectrum of the bromide also indicated unsaturation (broad, unresolved signals at 5.3–6.5 ppm), as well as CH_2CH_2OH (partially resolved triplet at 4.0 ppm). The area ratio of vinyl to carbinol protons was about 1. These data clearly are not in accord with a bicyclic structure such as IVb, nor do they suggest a simple phosphorinane derivative. Difficulty in obtaining a pure specimen of the product has so far prevented the assignment of a structure.[6] It is clear however that, from Ib, the tertiary hydroxyl group has been lost, with introduction of unsaturation, that to some extent the primary hydroxyl has been retained in the product, and that the Grob–Brenneisen procedure has failed to give a bicyclic structure.

Alcohol X (containing about 12% of isomer XI)[7] was subjected to the 62% hydrobromic acid reaction; this compound would appear likely to give the same carbonium ion in acid medium as diol Ib, and similar subsequent changes might be anticipated. The salt obtained after the benzene reflux step had an infrared spectrum and other properties nearly identical with those for the product from diol Ib, supporting the assignment of a primary alcohol function in the latter product.

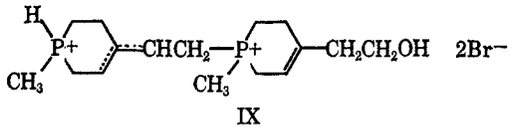


X XI

The reactions with diol Ia[2] were therefore repeated. The product had an infrared spectrum similar to the original,[2] but showed additionally a weak PH band (2360 cm^{-1}). A weak band at 1660 cm^{-1} in both spectra appears attributable to C=C. The pmr spectrum possessed the feature specifically sought for, but absent, in that of the original sample; there was a triplet (J = 5.65 cps) assignable to CH_2CH_2OH at 4.27 ppm. The triplet was well separated from other signals, and the failure to observe it for the original sample is not readily accounted for. Vinyl signals centered at 6.3 ppm were also present in the spectrum (apparent doublet, peak separation of 22 cps). The peaks were broad and shallow and could have been lost in the original spectrum[2] in the background noise. The area ratio of vinyl protons to the total of all other carbon-bound protons was about 1:17, and the ratio of vinyl to carbinol protons was about 1. The salt was acidic (equivalent weight 500). The new evidence, therefore, suggests similarity to the product from Ib and does not support the originally assigned bicyclic structure (IVa).[2,8] The synthesis of derivatives of the 1-phosphabicyclo[2.2.2]octane system remains to be accomplished.

(4) L. D. Quin and H. E. Shook, Jr., *Tetrahedron Letters*, 2193 (1965).
(5) H. E. Shook, Jr., and L. D. Quin, *J. Am. Chem. Soc.*, **89**, 1841 (1967).

(6) A dimeric alkylation product such as IX could account for acidity and spectral and solubility data. Analytical values for the bromide and the perchlorate fall slightly above the limits for IX, however.



IX

(7) H. E. Shook, Jr., and L. D. Quin, unpublished results.
(8) In the original work[2] the salt was converted to a perchlorate, whose cation was indicated by analysis to be that of IVa. The infrared spectrum of this salt has now been obtained; it shows unsaturation and a strong resemblance to that of the corresponding perchlorate of the P-methyl series. Insolubility of the perchlorate prevented taking its pmr spectrum. The correspondence of the analytical figures with that of a bicyclic perchlorate would now appear merely to have been fortuitous.

Experimental Section[9]

Reaction of 1-Methyl-4-ethyl-4-phosphorinanol (VIa) with 62% Hydrobromic Acid.—To 40 ml of 62% hydrobromic acid was added 3.34 g (21 mmoles) of a mixture of the *cis* and *trans* isomers of VIa,[5] and the solution was heated in an oil bath at 55–57° for 12 hr. After concentration on a rotary evaporator to a viscous oil, 50 ml of water was added, and the solution was neutralized by adding sodium hydrogen carbonate. The mixture was shaken with 100 ml of ether, and the resulting emulsion was broken by the addition of 100 ml of a saturated sodium sulfate solution. The layers were separated, and the aqueous layer was extracted with two 50-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, and the ether solution was concentrated to approximately 20 ml on a rotary evaporator. Gas chromatography of the ether solution showed that all of both isomers of the alcohol had reacted. Distillation of the residue gave a fraction boiling at 59–74° (2.3 mm) of 0.62 g (20.8%) of 1-methyl-4-ethyl-1,2,5,6-tetrahydrophosphorin mixed with a small amount of 1-methyl-4-phosphorinanone (an impurity in the VIa sample) as indicated by the infrared spectrum. A large, solid residue remained in the flask.

The benzyl bromide salt of the distilled material was prepared by mixing 0.62 g (4.4 mmoles) with 1.88 g (11 mmoles) of benzyl bromide in 25 ml of ether. The perchlorate was prepared by dissolving the white, crystalline bromide in distilled water and slowly adding 35% perchloric acid. The yield was 0.92 g. The analytical sample was crystallized from aqueous methanol as white leaflets, mp 108–110°. The infrared spectrum contained bands at 3020, 1665, and 835 cm^{-1} (assigned to a trisubstituted double bond). The pmr spectrum, run on a solution containing 200 mg in 0.5 ml of $CDCl_3$ using an internal TMS standard, showed phenyl protons at 7.4 ppm (singlet), vinyl proton (doublet, J = 22 cps) (similarly large values have been reported for a vinyl proton β to positive phosphorus[10,11]) centered at 5.4, benzylic protons (doublet, J = 16 cps) centered at 3.9, methylene protons at 2.0–3.0 (multiplet), PCH_3 protons (doublet, J = 14 cps) centered at 1.9, and CH_3CH_2 protons at 0.95 ppm (triplet, J = 7.0 cps). Peak areas agreed with the assigned structure (VII).

Anal. Calcd for $C_{15}H_{22}ClO_4P$: C, 54.14; H, 6.66; P, 9.31. Found: C, 54.06; H, 6.87; P, 9.50.

Reaction of 1,4-Diethyl-4-phosphorinanol (VIb) with 62% Hydrobromic Acid.—To 35 ml of 62% hydrobromic acid was added 1.3 g (7.5 mmoles) of a mixture of the *cis* and *trans* isomers of VIb.[5] The solution was heated on an oil bath at 55° for 13 hr. After the solution had been concentrated on a rotary evaporator, 50 ml of water was added, and the solution was neutralized by adding solid sodium hydrogen carbonate. The mixture was shaken with 100 ml of ether; the resulting emulsion was broken with 50 ml of a saturated sodium sulfate solution. The layers were separated, and the aqueous layer was extracted with two 50-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate. The ether solution was concentrated to approximately 10 ml. Gas chromatography showed that none of the original alcohol remained.

A benzyl bromide salt was prepared directly after diluting the concentrate with 40 ml of ether by adding 2.3 g (13 mmoles) of benzyl bromide. The benzyl bromide salt, an oil, was converted to the perchlorate by adding 35% perchloric acid to an aqueous solution. The dry perchlorate weighed 0.56 g (21.5%). The analytical sample was crystallized from aqueous methanol as white crystals, mp 134°. The infrared spectrum showed bands at 1660 and 810 cm^{-1}, assigned to a trisubstituted double bond. The pmr spectrum (96.8 mg in 0.5 ml of $CDCl_3$ using an internal TMS standard) showed phenyl protons at 7.4 (singlet), vinyl proton (quartet, J = 6.5 cps) centered at 5.4, benzylic protons (doublet, J_{PCH} = 15 cps) centered at 3.9, methylene protons at 2.0–3.0 (multiplet), CH_3CH= protons (doublet, J = 6.5 cps) centered at 1.55, and CH_3CH_2 protons (triplet, J = 8.0 cps) at 1.06 ppm. Peak areas agreed with the assigned structure (VIII) containing an exocyclic double bond. It is possible that some of the endocyclic isomer (corresponding to VII) may have also been formed but was not recovered by this different isolation procedure.

Anal. Calcd for $C_{16}H_{24}ClO_4P$: C, 55.41; H, 6.97; P, 8.93. Found: C, 55.53; H, 7.01; P, 8.96.

Reaction of 1-Methyl-4-(2-hydroxyethyl)-4-phosphorinanol (Ib) with 62% Hydrobromic Acid.—Diol Ib[5] (4.96 g, 28.2 mmoles) was dissolved in 50 ml of 62% hydrobromic acid, and the mixture was heated at 55–60° in an oil bath for 12 hr. The acid solution was concentrated in an all-glass rotary evaporator to a brown, viscous oil. The oil was dissolved in 30 ml of distilled water, and solid potassium carbonate was added to make the solution basic. Benzene (30 ml) and 25 ml of a saturated solution of sodium sulfate was added and the mixture extracted with three 25-ml portions of benzene. The benzene extracts were filtered through anhydrous potassium carbonate, and the solution was refluxed. As the solution approached reflux it became cloudy, and a solid began to precipitate. After 8 hr, the salt (1.8 g) was collected. The benzene filtrate was refluxed for an additional 24 hr, and 0.9 g of the same salt was obtained. The infrared spectrum showed a strong band at 3400 (OH stretch), a weak band at 2360 (PH), a band at 1650 (C=C), a band at 1050 (CO stretch), and a strong, broad band at 810–820 cm^{-1} (=CH bend). The pmr spectrum, run on a solution of 0.22 g in 0.3 ml of D_2O with an external TMS standard, showed a vinyl proton (doublet, J_{PCCH} = 23 cps) centered at 6.1, CH_2-CH_2OH protons (poorly resolved triplet) centered at 4.0, methylene protons (multiplet) at 1.5–3.6, and PCH_3 protons (doublet, J_{PCH} = 14.5 cps) centered at 2.3 ppm.

Anal. Calcd for $C_8H_{16}BrOP$ (IVb): C, 40.19; H, 6.74; P, 12.95. Calcd for $C_{16}H_{30}Br_2O_2P_2$ (Im): C, 41.78; H, 6.53; P, 13.47. Found: C, 42.33; H, 6.81; P, 13.73.

A portion of the hydrobromide was dissolved in water, and excess 35% perchloric acid was added to precipitate a hydroperchlorate salt. The analytical sample was crystallized from aqueous methanol. It decomposed above 200°.

Anal. Calcd for $C_8H_{16}ClO_5P$; P, 11.98. Calcd for $C_{16}H_{30}Cl_2O_9P_2$: P, 12.41. Found: P, 12.89.

Reaction of a Mixture of 1-Methyl-4-(2-hydroxyethyl)-1,2,5,6-tetrahydrophosphorin (X) and 1-Methyl-4-(2-hydroxyethylidene)-phosphorinane (XI) with 62% Hydrobromic Acid.—A mixture of 88% X–12% XI (4 g, 25.5 mmoles)[7] was dissolved in 80 ml of 62% hydrobromic acid and heated at 55–60° for 14 hr. The acid solution was concentrated in an all-glass rotary evaporator to a brown, viscous oil. The oil was dissolved in 25 ml of water, and solid potassium carbonate was added to make the solution basic. An oil separated from the basic layer. A saturated sodium sulfate solution (25 ml) was added, and the mixture was extracted with benzene. The benzene layer was filtered through anhydrous potassium carbonate. One-half of the benzene extract was refluxed for 24 hr. A white salt began to precipitate shortly after reflux began. After drying, the salt weighed 2.6 g. The infrared spectrum was identical with the spectrum obtained for the salt from the similar treatement of diol Ib with 62% hydrobromic acid. The pmr spectrum, run on a solution containing 0.1 g in 0.2 ml of D_2O using an external TMS standard, showed vinyl proton (doublet, J_{PCCH} = 24 cps) centered at 6.3, CH_2CH_2OH protons (triplet, J = 7.0 cps) centered at 4.2, methylene protons (multiplet) at 2.0–3.8, and PCH_3 protons (doublet, J_{PCH} = 16 cps) centered at 2.55 ppm.

A portion of the bromide was dissolved in water, and excess 35% perchloric acid was added to precipitate the perchlorate. The analytical sample was crystallized from aqueous methanol. It decomposed above 200°.

Anal. Calcd for $C_8H_{16}ClO_5P$: C, 37.15; H, 6.24; P, 11.98. Calcd for $C_{16}H_{30}Cl_2O_9P_2$: C, 38.51; H, 6.02; P, 12.41. Found: C, 38.82; H, 6.08; P, 12.80.

4-(Carbethoxymethyl)-1-ethyl-4-phosphorinanol.—The apparatus was first flamed and flushed with nitrogen; traces of water tended to retard or prevent the reaction. The Reformatsky reagent was prepared from ethyl bromoacetate (77 g, 0.46 mole). About 10 ml and a few iodine crystals were added to 60 g (0.92 g-atom) of zinc suspended in 150 ml of benzene–ether (1:1 v/v) (each dried and freshly distilled). A mildly exothermic reaction, not requiring cooling, occurred. The rest of the ester and an additional 60 g of zinc were added during a 3-hr period. The mixture was then refluxed for 1 hr. To the cooled solution was

(9) Operations involving phosphines were conducted in a nitrogen atmosphere. Melting points are corrected; boiling points are uncorrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Triangle Chemical Laboratories, Inc., Chapel Hill, N. C. Infrared spectra were obtained on films for liquids or potassium bromide pellets for solids; the Perkin-Elmer Model 137 or 237 spectrophotometer was used. Pmr spectra were obtained with a Varian A-60 spectrometer.

(10) H. Weitkamp and F. Korte, *Z. Anal. Chem.*, **204**, 245 (1964).

(11) L. D. Quin, J. A. Peters, C. E. Griffin, and M. Gordon, *Tetrahedron Letters*, 3689 (1965).

added 1-ethyl-4-phosphorinanone[12] (27.5 g, 0.19 mole) in 80 ml of benzene–ether during a 30-min period, while the mixture stirred vigorously. The exothermic reaction required no temperature control. The mixture was refluxed for 1 hr and allowed to stand overnight. The flask was then placed in an ice bath, and 200 ml of glacial acetic acid was added. After stirring for 30 min, liquid was decanted and the residue was dissolved in 100 ml of 7 *N* hydrochloric acid. The combined acidic solutions were adjusted to pH 9 with concentrated aqueous ammonia and extracted with five 100-ml portions of benzene. Distillation of the residue from stripping the solvent on a rotary evaporator was attempted, using a 15-cm Vigreux column. A forerun of the unreacted ketone (6.8 g) was collected at 51–60° (0.3–0.6 mm), but decomposition commenced before the product could be distilled. The pot residue was extracted with ether, and the material left from stripping the solvent had the same infrared spectrum as that obtained previously[2] when the distillation had been successful. The yield was 19.6 g (44%).

4-(2-Hydroxyethyl)-1-ethyl-4-phosphorinanol.—To a suspension of 11.5 g (0.30 mole) of lithium aluminum hydride in 400 ml of dry ether was added during 1 hr an ethereal solution (200 ml) of the undistilled Reformatsky product (19.6 g, 0.084 mole). The flask was cooled in an ice bath during the addition. The mixture was refluxed for 1 hr, and then excess hydride was destroyed by careful addition of cold water to the chilled mixture. After stirring for 1 hr, a saturated sodium sulfate solution was added and the ether layer was separated. The aqueous layer was extracted with three 200-ml portions of ether. The ether was stripped and the residue was distilled to give a forerun of 1.03 g [bp 108–132° (0.3 mm)] and then 9.17 g (42.3% based on ketone consumed in the Reformatsky reaction) of product [bp 132–142° (0.3 mm); lit.[2] bp 128–130° (0.15–0.2 mm)].

Reaction of 1-Ethyl-4-(2-hydroxyethyl)-4-phosphorinanol (Ia) with 62% Hydrobromic Acid.—The reaction procedure, applied to 9.2 g (48.3 mmoles) of Ia, was the same as for the diol (Ib). The benzene reflux step produced 4.65 g of salt after 8 hr. Some color was removed from the salt by treatment in water with charcoal. The salt was recovered by evaporation of the water. The infrared spectrum showed a weak band at 2360, assigned to P–H, a weak band at 1660, assigned to C=C, and a strong, broad band at 810–820 cm^{-1}. The pmr spectrum run on a solution containing 0.2 g in 0.2 ml of D_2O, using an external TMS standard, showed vinyl proton (doublet, J_{PCCH} = 22 cps) centered at 6.3 and CH_2CH_2OH protons (triplet, J = 6.5 cps) centered at 4.27 ppm, in the ratio 1:1. The combined area of the P-ethyl and ring methylene proton signals (poorly resolved) was about 16 with respect to the vinyl signal. A 0.070-g sample of the salt in 10 ml of water had pH 2.6; the titration curve with 0.05 *N* sodium hydroxide showed a break at 2.8 ml with pH 9.3. The equivalent weight was 500.

Registry No.—VII, 7781-76-2; VIII, 7781-77-3; Ib, 7781-78-4; 4-(carbethoxymethyl)-1-ethyl-4-phosphorinanol, 7781-79-5; Ia, 7781-80-8.

(12) R. P. Welcher, G. A. Johnson, and V. P. Wystrach, *J. Am. Chem. Soc.*, **82**, 4437 (1960).

Bimolecular Displacement Reactions. III. Reaction of Phenols with Triphenylphosphine and Bromine

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In 1959 Horner, Oediger, and Hoffmann[1] reported that the reaction of triphenylphosphine dihalides with alcohols produced alkyl halides and that the reaction was accompanied by a Walden inversion. In subsequent investigations the scope of this reaction was more clearly defined[2,3] and some mechanistic aspects of the reaction course have been elaborated.[4,5]

Although bimolecular displacement reactions on aromatic rings are relatively uncommon, they are feasible when the substituent is activated by an electron-withdrawing group or when the leaving group is exceptionally stable (*e.g.*, N_2). Since the formation of triphenylphosphine oxide is an energetically favorable process, triphenylphosphine dihalides and similar reagents[6] can be used to convert phenols to aryl halides. We have found that this reaction is general and is capable of producing aryl halides in high yields.

When a solution of triphenylphosphine in acetonitrile is treated with bromine at 0°, triphenylphosphine dibromide (1) is formed rapidly and quantitatively. Addition of an equimolar quantity of a phenol results in the formation of a complex which is readily decomposed on heating to the aryl halide, triphenylphosphine oxide, and hydrogen bromide. Utilizing this procedure, β-bromonaphthalene was obtained in yields of 82–86% from β-naphthol. The reaction is suitable for large-scale preparations and is currently the best method for preparing this compound, which is normally tedious to synthesize. Using similar conditions, α-naphthol was converted to α-bromonaphthalene in 72% yield.

The reaction is also applicable to heterocyclic systems. Treatment of 3-hydroxypyridine with 1 gave 3-bromopyridine in 76% yield. Similarly, 2-bromopyridine could be isolated in 61% yield from 2-hydroxypyridine, and 8-hydroxyquinoline was converted to the corresponding bromide in 48% yield.

Although many simple aryl halides are readily available through direct halogenation of the aromatic nucleus, cases frequently arise when isomer formation makes this route impractical. In these cases and those in which heterocycles are normally inert to direct halogenation, reaction of the appropriate phenols with 1 presents a practical alternative. For example, from *o*-cresol, *o*-bromotoluene was isolated in 72% yield.

Experimental Section

The following procedure is typical of those used. When the product was a liquid, distillation was used to purify the halide.

2-Bromonaphthalene.—A 500-ml three-necked, round-bottom flask was equipped with a Trubore stirrer, a pressure-compensating dropping funnel, and a reflux condenser with drying tube. The flask was charged with 144 g of triphenylphosphine (0.55 mole) and 125 ml of acetonitrile. With stirring, the solution was cooled in an ice bath and 88 g (0.55 mole) of bromine was added dropwise over a period of 20–30 min. After the addition of the bromine, the ice bath was removed, 72 g (0.50 mole) of β-naphthol in 100 ml of acetonitrile was added in one portion, and the reaction mixture was heated to 60–70° for at least 30 min. The flask was then fitted for a simple distillation and the acetonitrile was distilled under water aspirator pressure until the oil bath temperature reached 110°. After all the acetonitrile had been removed, the condenser was replaced with a short, large-diameter glass tube connected to a 500-ml flask half-filled with water and the oil bath was replaced with a Wood's metal bath. The bath temperature was raised to 200–220° and kept at this temperature

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