composition contained 0.09 m. of hydrogen, 1.60 m. of iso-butane, and 0.06 m. of isobutylene. The reaction mixture was filtered and the aluminum salts were washed several times with methanol. The filtrate was distilled to give 12.3 g. (70% yield) of trans-2-butene-1,4-diol boiling at 86–88°/0.5 mm.; n_D^{25} 1.4758.

Bromine (12.2 g., 0.076 m.) was added dropwise over 4 hr. to a stirred mixture of trans-2-butene-1,4-diol (6.6 g., 0.075 m.) in chloroform maintained at 5–10°. The product was filtered and recrystallized from chloroform to give 14.2 g. of meso-2,3-dibromo-1,4-butanediol[12] melting at 130.0–130.6°.

Anal. Calcd. for $C_4H_8O_2Br_2$: Br, 64.5. Found: Br, 64.5.

Reduction of diethyl fumarate. Diethylaluminum hydride (0.2 m.) was added under nitrogen over 1 hour to a stirred solution of diethyl fumarate (8.6 g., 0.05 m.) in benzene (300 ml.). The temperature rose to 45° during the reaction. After stirring an additional 2 hr., the reaction mixture was decomposed at room temperature by the slow addition of methanol (25.6 g., 0.8 m.) in benzene (55 ml.) followed by water (15 g., 0.8 m.). The gas evolved during the decomposition contained 0.39 m. of ethane and 0.02 m. of ethylene. The decomposed reaction mixture was filtered and the aluminum salts were washed several times with methanol. The filtrates were combined and distilled to give 2.9 g. (66% yield) of trans-2-butene-1,4-diol boiling at 86–88°/0.5 mm.; n_D^{25} 1.4752.

Reduction of 2-butyne-1,4-diol with lithium aluminum hydride. 2-Butyne-1,4-diol (43.2 g., 0.5 m.) in tetrahydrofuran (300 ml.) was added dropwise to lithium aluminum hydride (39.0 g., 1.0 m.) in anhydrous ether (1 l.). The reaction mixture was refluxed for 18 hr., cooled, and decomposed by the addition of water (72 g., 4.0 m.). The resulting slurry was filtered, the ether dried and concentrated. Distillation of the residue (6.1 g.) gave 2-butene-1,4-diol (3.3 g., 7.5% yield) boiling at 112–114°/3 mm.

Anal. Calcd. for $C_4H_8O_2$: Hydrogen No., 1.00; Hydroxyl No.,[13] 2.0. Found: Hydrogen No., 1.05; Hydroxyl No., 1.9.

(12) C. Prevost, Compt. rend., 183, 1292 (1926).

(13) S. Siggia, Quantitative Organic Analysis via Functional Groups, p. 9, John Wiley & Sons, New York, 1954.

This was confirmed as the trans isomer by its infrared spectrum and dibromo derivative (m.p. 129–130°).

Reduction of 2-butyne-1,4-diol with diisobutylaluminum hydride. Diisobutylaluminum hydride (0.2 m.) was added over 4 hr. to a stirred slurry of 2-butyne-1,4-diol (25.8 g., 0.3 m.) in benzene (160 ml.). The volume of gas evolved during this addition indicated that the reaction of the diisobutylaluminum hydride with the hydroxyl groups of 2-butyne-1,4-diol was practically quantitative. After stirring at 45° for 6 hr., a second portion of diisobutylaluminum hydride (0.3 m.) was added over 0.5 hr. The mixture was stirred for 8 hr. and then was decomposed by the addition of methanol (32.0 g., 1.0 m.) in benzene (35 m.) followed by water (27.0 g., 1.5 m.) in methanol (30 ml.). The reaction mixture was filtered and concentrated under reduced pressure leaving 19.7 g. of solid residue. Recrystallization from ethyl acetate produced unreacted 2-butyne-1,4-diol (15.0 g.) melting at 55–56°.

Reduction of 1-ethynylcyclohexanol. Diisobutylaluminum hydride (0.2 m.) was added under nitrogen to a stirred solution of 1-ethynylcyclohexanol (12.4 g., 0.1 m.) in 150 ml. of benzene over 1.1 hr. The temperature rose to 40° during the addition. The reaction mixture was stirred at 60° for 8 hr., cooled and decomposed by the addition of methanol (19.2 g., 0.6 m.) in benzene (50 ml.) followed by water (10.8 g., 0.6 m.) in methanol (25 ml.). The product was filtered and concentrated to give 9.7 g. of residue which gave a hydrogen number of 1.52 and a methynyl hydrogen number[14] of 0.51. Therefore, this crude product contained 52% of unreacted 1-ethynylcyclohexanol and 48% of 1-vinylcyclohexanol.

Acknowledgment. The authors are indebted to Dr. E. H. Dobratz for the generous supply of diisobutyl- and diethylaluminum hydrides.

Pittsburgh, Pa.

(14) S. Siggia, Quantitative Organic Analysis via Functional Groups, p. 86, John Wiley & Sons, New York, 1954.

[Contribution from the Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company]

Phosphorus-Containing Derivatives of 2,2-Dimethyl-1,3-propanediol

RICHARD L. McCONNELL AND H. W. COOVER, JR.

A number of phosphorus-containing esters were made from 2,2-dimethyl-1,3-propanediol. Phosphoryl chloride gave a cyclic phosphorochloridate which could be treated with an alcohol or phenol to produce a neutral ester. Phosphonic dichlorides gave cyclic neutral esters directly. When phosphorus trichloride was used, a cyclic bisphosphite was produced; however, when this reaction was carried out in the presence of an alcohol, a cyclic hydrogen phosphite was formed. Treatment of 2,2-dimethyl-1,3-propanediol with diethyl phosphorochloridate gave a neutral bisphosphate which on pyrolysis liberated triethyl phosphate to yield a cyclic neutral ester. In general, these derivatives of 2,2-dimethyl-1,3-propanediol are stable, white, crystalline compounds.

This investigation was undertaken to study the preparation and properties of phosphorus-containing esters derived from 2,2-dimethyl-1,3-propanediol, a derivative of isobutyraldehyde. These esters were made using phosphoryl chloride, phosphonic dichlorides, phosphorus trichloride, and diethyl p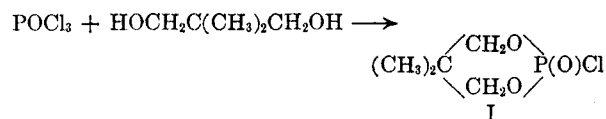hosphorochloridate. Treatment of a 1,2- or 1,3-glycol with a phosphorus dihalide or trihalide usually results in the formation of cyclic esters.[1-13]

(1) A. D. F. Toy (to Victor Chemical Works), U. S. Patent 2,382,622 (1945).

(2) A. E. Arbuzov and M. M. Azanovskaya, Izvest. Akad. Nauk S. S. S. R., 473 (1949); Chem. Abstr., 44, 1905b (1950).
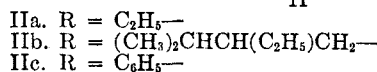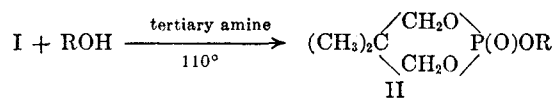
2,2-Dimethyl-1,3-propanediol is particularly prone to form cyclic derivatives. These new phosphorus-containing heterocyclic compounds are usually much more stable than the analogous alkyl esters. In general, these products are white, crystalline solids.

When 2,2-dimethyl-1,3-propanediol was treated with phosphoryl chloride, the cyclic phosphorochloridate I was produced. I does not hydrolyze

$$POCl_3 + HOCH_2C(CH_3)_2CH_2OH \longrightarrow$$

$$(CH_3)_2C \begin{matrix} CH_2O \\ \diagdown \\ CH_2O \end{matrix} P(O)Cl$$

$$I$$

very readily since it is insoluble in water; however, it may be hydrolyzed to 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphate by dissolving it in a moist organic solvent.

I is less reactive toward alcohols than a typical dialkyl phosphorochloridate; for example, diethyl phosphorochloridate reacts readily with an alcohol at 75–80° in the presence of pyridine to form the neutral phosphate, whereas only a negligible amount of I reacted with ethyl alcohol when refluxed for 6 hr. in benzene in the presence of pyridine. The reaction was also incomplete when I was dissolved in pyridine and treated with a large excess of ethyl alcohol at 80° for 16 hr. 2,2-Dimethyl-1,3-propanediol cyclic phosphorochloridate does react with alcohols in the presence of tertiary amines at higher temperatures; for example, treatment of I with an alcohol or phenol in the presence of pyridine in refluxing toluene gave the neutral ester II.

$$I + ROH \xrightarrow[110°]{\text{tertiary amine}} (CH_3)_2C \begin{matrix} CH_2O \\ \diagdown \\ CH_2O \end{matrix} P(O)OR$$

$$II$$

IIa. R = C_2H_5—
IIb. R = $(CH_3)_2CHCH(C_2H_5)CH_2$—
IIc. R = C_6H_5—

(3) H. J. Lucas, F. W. Mitchell, Jr., and C. N. Scully, *J. Am. Chem. Soc.*, **72**, 5491 (1950).

(4) A. E. Arbuzov and M. M. Azanovskaya, *Izvest. Akad. Nauk S. S. S. R.*, 544 (1951); *Chem. Abstr.*, **47**, 98c (1953).

(5) A. F. McKay, R. O. Braun, and G. R. Vavasour, *J. Am. Chem. Soc.*, **74**, 5540 (1952).

(6) A. E. Arbuzov and V. M. Zoroastrova, *Bull. Acad Sci. U. S. S. R., Div. Chem. Sci. S. S. R. (Eng. Translation)*, 697 (1952); *Chem. Abstr.*, **48**, 4496a (1954).

(7) A. E. Arbuzov and V. M. Zoroastrova, *Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci. S. S. R. (Eng. Translation)*, 705 (1952); *Chem. Abstr.*, **48**, 4496a (1954).

(8) H. R. Gamrath and R. E. Hatton (to *Monsanto Chemical Co.*), U. S. Patent **2,661,365** (1953).

(9) A. F. McKay, R. A. B. Bannard, R. O. Braun, and R. L. Benness, *J. Am. Chem. Soc.*, **76**, 3546 (1954).

(10) R. C. Morris and J. L. Van Winkle (to Shell Development Co.), U. S. Patent **2,744,128** (1956).

(11) W. M. Lanham (to Union Carbide and Carbon Corp.), British Patent **762,125** (1956).
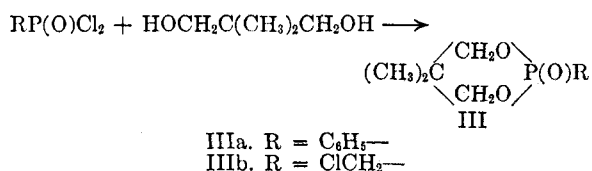
(12) E. L. Gefter, *J. Gen. Chem. U. S. S. R. (Eng. Translation)*, **26**, 1619 (1956).

(13) T. Ukita, K. Nagasawa, and M. Irie, *Pharm. Bull. Tokyo*, **5**, 121 (1957); *Chem. Abstr.*, **51**, 17735b (1957).
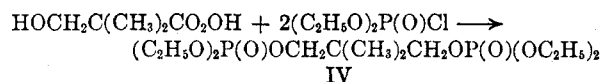
It was also possible to prepare esters of type II by treating phosphoryl chloride with one mole of an alcohol or a phenol to produce the alkyl or aryl phosphorodichloridate. The crude intermediate phosphorodichloridate was subsequently treated with 2,2-dimethyl-1,3-propanediol to produce II. These reactions could be effected without using a tertiary base to absorb the liberated hydrogen chloride.

$$ROH + POCl_3 \xrightarrow{-HCl}$$

$$ROP(O)Cl_2 \xrightarrow[-2 HCl]{HOCH_2C(CH_3)_2CH_2OH} II$$
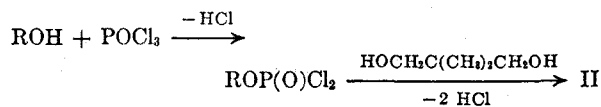
Phenylphosphonic and chloromethylphosphonic dichlorides reacted as expected when treated with 2,2-dimethyl-1,3-propanediol to produce the cyclic phosphonates III.

$$RP(O)Cl_2 + HOCH_2C(CH_3)_2CH_2OH \longrightarrow$$

$$(CH_3)_2C \begin{matrix} CH_2O \\ \diagdown \\ CH_2O \end{matrix} P(O)R$$

$$III$$

IIIa. R = C_6H_5—
IIIb. R = $ClCH_2$—

2,2-Dimethyl-1,3-propanediol reacted with diethyl phosphorochloridate to form 2.2-dimethyl-1,3-propanediol bis(diethyl phosphate) IV. IV

$$HOCH_2C(CH_3)_2CO_2OH + 2(C_2H_5O)_2P(O)Cl \longrightarrow$$

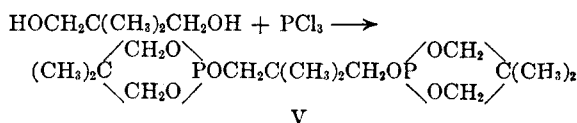$$(C_2H_5O)_2P(O)OCH_2C(CH_3)_2CH_2OP(O)(OC_2H_5)_2$$

$$IV$$

could be successfully distilled at low pressures (3 mm.). However, attempts to distill IV at higher pressures (64 mm.) led to pyrolysis. Under these conditions, triethyl phosphate was liberated and 2,2-dimethyl-1,3-propanediol cyclic ethyl phosphate was liberated and 2,2-dimethyl-1,3-propanediol cyclic ethyl phosphate was formed. This again illustrates the great tendency for these 2,2-dimethyl-1,3-propanediol derivatives to cyclize.

$$IV \xrightarrow{\Delta} (C_2H_5O)_3P(O) + (CH_3)_2C \begin{matrix} CH_2O \\ \diagdown \\ CH_2O \end{matrix} P(O)OC_2H_5$$
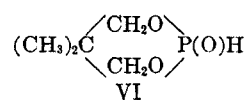
$$IIa$$
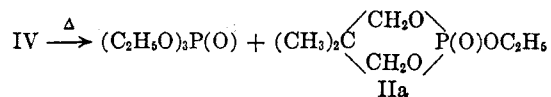
This pyrolysis reaction represents an alternative path for the preparation of esters of type II.

Somewhat unusual results were obtained when 2,2-dimethyl-1,3-propanediol was treated with phosphorus trichloride. The predominant product was 2,2-dimethyl-1,3-propanediol bis(cyclic 2,2-dimethyltrimethylene phosphite) V whether or not a tertiary base was used.

$$HOCH_2C(CH_3)_2CH_2OH + PCl_3 \longrightarrow$$

$$(CH_3)_2C \begin{matrix} CH_2O \\ \diagdown \\ CH_2O \end{matrix} POCH_2C(CH_3)_2CH_2OP \begin{matrix} OCH_2 \\ \diagdown \\ OCH_2 \end{matrix} C(CH_3)_2$$

$$V$$

and

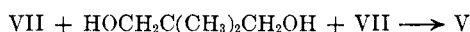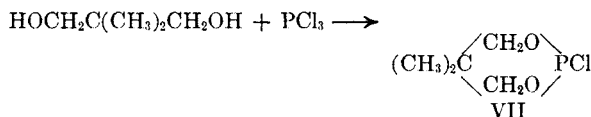$$(CH_3)_2C \begin{matrix} CH_2O \\ \diagdown \\ CH_2O \end{matrix} P(O)H$$

$$VI$$

VI was probably formed by hydrolysis of VII, a likely intermediate, when traces of moisture were present in the reaction mixture. In one experiment without a tertiary base and when moisture was apparently absent, only V was obtained. It should be pointed out that 2,2-dimethyl-1,3-propanediol is extremely hygroscopic. The presence of moisture can be minimized by mixing this glycol with toluene or benzene and removing the water present as the azeotrope before beginning the reaction.

It seems likely that V may form by the following mechanism. 2,2-Dimethyl-1,3-propanediol cyclic phosphorochloridite VII could form rapidly and subsequently react with another molecule of VII and 2,2-dimethyl-1,3-propanediol. The pro-

$$HOCH_2C(CH_3)_2CH_2OH + PCl_3 \longrightarrow$$

$$(CH_3)_2C \underset{CH_2O}{\overset{CH_2O}{\diagup\hspace{-0.3em}\diagdown}} PCl$$
$$VII$$

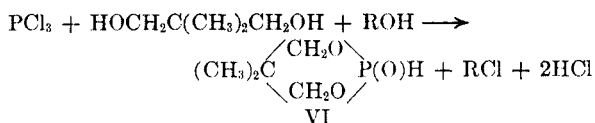$$VII + HOCH_2C(CH_3)_2CH_2OH + VII \longrightarrow V$$

duction of V appeared to be independent of the molar ratio of phosphorus trichloride to 2,2-dimethyl-1,3-propanediol.

The difficulty in forming 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphite VI from the interaction of phosphorus trichloride and 2,2-dimethyl-1,3-propanediol may possibly be explained by the blocking effect of the two methyl groups adjacent to the carbon-oxygen bond. This blocking would tend to prevent dealkylation of V or 2,2-dimethyl-1,3-propanediol cyclic 3-

$$(CH_3)_2C \underset{CH_2O}{\overset{CH_2O}{\diagup\hspace{-0.3em}\diagdown}} POCH_2C(CH_3)_2CH_2OH$$

hydroxy-2,2-dimethylpropyl phosphite, by the liberated hydrogen chloride to form the cyclic hydrogen phosphite VI.

It was found that good yields of VI could be obtained by treating phosphorus trichloride with an equimolar mixture of 2,2-dimethyl-1,3-propanediol and an alcohol. Ethyl alcohol, isobutyl alcohol, and

$$PCl_3 + HOCH_2C(CH_3)_2CH_2OH + ROH \longrightarrow$$

$$(CH_3)_2C \underset{CH_2O}{\overset{CH_2O}{\diagup\hspace{-0.3em}\diagdown}} P(O)H + RCl + 2HCl$$
$$VI$$

2-ethyl-1-hexanol were used successfully in this reaction. The reaction was not successful when cetyl alcohol was used. It is probable that a 2,2-dimethyl-

$$(CH_3)_2C \underset{CH_2O}{\overset{CH_2O}{\diagup\hspace{-0.3em}\diagdown}} POR$$
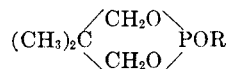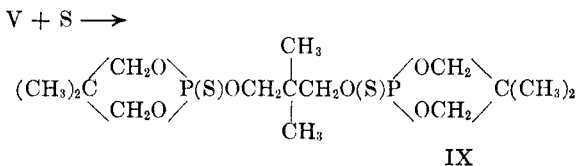
1,3-propanediol cyclic alkyl phosphite, is an intermediate which is dealkylated by the liberated hydrogen chloride. The cetyl radical may prevent the dealkylation to the cyclic hydrogen phosphite by a blocking effect similar to that proposed above for the 3-hydroxy-2,2-dimethylpropyl radical.

VI reacts as a typical hydrogen phosphite with chloral or chlorine. Treatment of VI with chloral forms 2,2-dimethyl-1,3-propanediol cyclic 2,2,2-trichloro-1-hydroxyethylphosphonate VIII. Treat-

$$VI + CCl_3CHO \longrightarrow (CH_3)_2C \underset{CH_2O}{\overset{CH_2O}{\diagup\hspace{-0.3em}\diagdown}} P(O)CHOHCCl_3$$
$$VIII$$
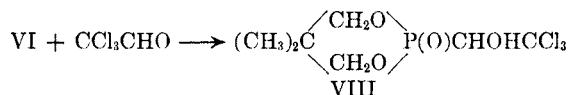
ment of VI with chlorine results in the formation of the cyclic phosphorochloridate I.

A cyclic bis(phosphorothionate) IX was obtained when V was treated with sulfur.

$$V + S \longrightarrow$$

$$(CH_3)_2C \underset{CH_2O}{\overset{CH_2O}{\diagup\hspace{-0.3em}\diagdown}} P(S)OCH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2O(S)P \underset{OCH_2}{\overset{OCH_2}{\diagup\hspace{-0.3em}\diagdown}} C(CH_3)_2$$
$$IX$$

Thus, this investigation demonstrated the ease with which 2,2-dimethyl-1,3-propanediol forms cyclic esters. In general, these derivatives are stable, white, crystalline materials that undergo reactions typical of organophosphorus esters.

EXPERIMENTAL

2,2-Dimethyl-1,3-propanediol cyclic phosphorochloridate (I). *Method A.* 2,2-Dimethyl-1,3-propanediol (104 g., 1.0 mole) was dissolved in 400 ml. of anhydrous dioxane, and phosphoryl chloride (153 g., 1.0 mole) was added dropwise with vigorous stirring. After a short induction period, the temperature of the reaction mixture rose to about 80°. The temperature was not allowed to exceed 80°, and it was controlled by occasional external cooling using chilled water. After all the phosphoryl chloride had been added and the mixture had cooled to room temperature, stirring was continued for 8 hr. while dry nitrogen was bubbled in through a fritted glass disk to sweep out the liberated hydrogen chloride. The dioxane was removed by distillation at atmospheric pressure, leaving an oil which crystallized as it cooled. This material was washed with cold cyclohexane and then recrystallized from a 50/50 mixture of cyclohexane and benzene. It could also be recrystallized from a 75/25 mixture of cyclohexane and 1,2-dichloroethane. The purified material was obtained as white crystals (115 g., 62.4%), m.p. 102-103°. The product was soluble in acetone, benzene, and 1,2-dichloroethane and insoluble in water, ether, and cyclohexane.

Anal. Calcd. for $C_5H_{10}ClO_3P$: C, 32.54; H, 5.46; Cl, 19.21. Found: C, 32.60; H, 5.53; Cl, 19.20.

This compound was also prepared using 1,2-dichloroethane as the solvent rather than dioxane. In this case, the yield of recrystallized product was 65%.

Method B. 2,2-Dimethyl-1,3-propanediol cyclic hydrogen phosphite VI (15 g., 0.1 mole) was dissolved in 100 ml. of chloroform, and chlorine was bubbled in through a fritted glass disk with stirring. The solution became warm and the chlorine was absorbed rapidly. The reaction mixture was cooled externally with cold water while the chlorine was added. After 30 min., the yellow color of chlorine persisted. The flow of chlorine was stopped and the solution was stirred for 1 hr. at 25°. Next, nitrogen was bubbled through the solution for 4 hr. to remove excess chlorine and the liberated hydrogen chloride. The solvent was removed under reduced pressure, leaving the product as a white mass. Recrystallization of a small sample of crude material from a mixture of cyclohexane and benzene gave white crystals,

m.p. 102–103°. The melting point of a mixture with product obtained by Method A was not depressed.

A small sample of the 2,2-dimethyl-1,3-propanediol cyclic phosphorochloridate was dissolved in a 50/50 mixture of acetone and water. After the mixture had stood for 2 days, some of the solvent had evaporated and a white, crystalline material had deposited, m.p. 170–173°. Recrystallization of this compound from a mixture of benzene and ethyl alcohol gave long, slender needles, m.p. 174–176°. Analysis of this product indicated it to be the monohydrate of 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphate.

Anal. Calcd. for $C_5H_{11}O_4P \cdot H_2O$: P, 16.82; neut. equiv., 184.1. Found: P, 16.87; neut. equiv., 174.1.

2,2-Dimethyl-1,3-propanediol cyclic ethyl phosphate (IIa). *Method A.* 2,2-Dimethyl-1,3-propanediol (31.2 g., 0.3 mole) was treated with diethyl phosphorochloridate (103.0 g., 0.6 mole) in the presence of pyridine (55.3 g., 0.7 mole) in 200 ml. of dioxane according to the procedure used for the preparation of IV. After the pyridine hydrochloride and solvent had been removed, the crude 2,2-dimethyl-1,3-propanediol bis(diethyl phosphate) was heated at 150–175° (64 mm.) for 8 hr. Distillation through an 18-in. Vigreux column gave two fractions: (1) 27.5 g., b.p. 97–136° (4.0–3.0 mm.), n_D^{20} 1.4101; and (2) 38 g., b.p. 136–145° (3.0–2.7 mm.), n_D^{20} 1.4242.

Fraction 2 was redistilled to give the following fractions: (1) 17.8 g., b.p. 77–78° (5.3 mm.), n_D^{20} 1.4055 (n_D^{20} of triethyl phosphate is 1.4053); (2) 10.0 g., b.p. 112–139° (5.3 mm.), n_D^{20} 1.4410; and (3) 3.4 g., b.p. 139–146° (5.3 mm.), n_D^{20} 1.4434. The infrared spectrum of Fraction 1 was identical with that of an authentic sample of triethyl phosphate. Analyses of Fractions 2 and 3 indicated the material to be 2,2-dimethyl-1,3-propanediol cyclic ethyl phosphate.

Anal. Calcd. for $C_7H_{15}O_4P$: C, 43.30; H, 7.79. Found: C, 43.19; H, 7.75.

Method B. Ethyl alcohol (23 g., 0.5 mole) was added dropwise with stirring to phosphoryl chloride (76.6 g., 0.5 mole) dissolved in 250 ml. of dioxane while the reaction flask was cooled in an ice bath. The reaction mixture was stirred for 30 min. with cooling, then 2,2-dimethyl-1,3-propanediol (52 g., 0.5 mole) dissolved in 150 ml. of dioxane was added dropwise with stirring. The reaction mixture was stirred at 25° for 4 hr., and then it was allowed to stand overnight. Most of the solvent was removed by distillation at atmospheric pressure, and then a small amount of 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphate precipitated. This material was filtered off and recrystallized from benzene and ethyl alcohol to obtain long, slender, white needles, m.p. 175–176°. There was no depression in the melting point of a mixture with material obtained from hydrolysis of the 2,2-dimethyl-1,3-propanediol cyclic phosphorochloridate as described above.

Anal. Calcd. for $C_5H_{11}O_4P \cdot H_2O$: P, 16.82; neut. equiv., 184.1. Found: P, 16.90; neut. equiv., 186.5.

The oil obtained after removal of the cyclic hydrogen phosphate impurity was fractionated *in vacuo* through a short Vigreux column. When the forerun had been removed, 21 g. (22%) of product was obtained, b.p. 129–137° (3.2 mm.), n_D^{20} 1.4388.

Anal. Calcd. for $C_7H_{15}O_4P$: C, 43.30; H, 7.79; P, 15.95. Found: C, 43.59; H, 8.05; P, 15.98.

2,2-Dimethyl-1,3-propanediol cyclic 2-ethyl-4-methylpentyl phosphate (IIb). *Method A.* Pyridine (47.4 g., 0.6 mole) and 2,2-dimethyl-1,3-propanediol cyclic phosphorochloridate (50.3 g., 0.3 mole) were placed in 400 ml. of toluene and stirred while 2-ethyl-4-methyl-1-pentanol (39 g., 0.3 mole) dissolved in 100 ml. of toluene was added dropwise with stirring. No temperature rise was noted. The reaction mixture was stirred at 25° for 5 hr., then heated to reflux for 5 hr. After the mixture had stood overnight, the precipitated pyridine hydrochloride (29.8 g.; theor., 34.7 g.) was removed by filtration. The toluene solution was washed twice with water and dried over sodium sulfate. The toluene was removed, and then 1 g. of anhydrous sodium carbonate was

added to the oil which remained. The crude product was distilled through an 8-in. Vigreux column to obtain 31.8 g. (38%) of a clear, colorless oil, b.p. 153–159° (1.3 mm.), n_D^{20} 1.4483.

Anal. Calcd. for $C_{13}H_{27}O_4P$: C, 56.09; H, 9.78; P, 11.13. Found: C, 56.03; H, 9.95; P, 11.41.

Method B. Phosphoryl chloride (76.6 g., 0.5 mole) was placed in a flask and cooled externally to 5°. 2-Ethyl-4-methyl-1-pentanol (65 g., 0.5 mole) was added dropwise over a 1-hr. period with stirring and cooling so that the temperature remained at 5°. The reaction mixture was stirred for 30 min. at 5° and then for 1.5 hr. at 25°. The mixture was allowed to stand overnight, and then was stirred for 2 hr. while nitrogen was passed through the product to remove the liberated hydrogen chloride. At this point, 2,2-dimethyl-1,3-propanediol (52 g., 0.5 mole) was added, and the mixture was stirred at 25° for several hours. Then it was heated gently on the steam bath while nitrogen was passed through the reaction mixture to remove hydrogen chloride. When no more could be detected emerging from the condenser, the reaction mixture was distilled *in vacuo* through a 6-in. Vigreux column. After the forerun had been removed up to a temperature of 159° at 1.2 mm., the product was cooled and 0.5 g. of anhydrous sodium carbonate was added. Vacuum distillation was then resumed, and 33.4 g. (24%) of product was collected at 159–161° (1.2–1.9 mm.), n_D^{20} 1.4485.

Anal. Calcd. for $C_{13}H_{27}O_4P$: C, 56.09; H, 9.78. Found: C, 56.08; H, 9.85.

When cooled, the distillation residue deposited a white, crystalline solid. This material, when recrystallized from a mixture of benzene and absolute ethyl alcohol, gave large, transparent prisms, m.p. 170–174°. This product was the monohydrate of 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphate which was probably formed by the loss of 2-ethyl-4-methylpentene from the above product.

Anal. Calcd. for $C_5H_{11}O_4P \cdot H_2O$: P, 16.82. Found: P, 16.82.

2,2-Dimethyl-1,3-propanediol cyclic phenyl phosphate (IIc). *Method A.* Phenol (56.6 g., 0.6 mole), 2,2-dimethyl-1,3-propanediol cyclic phosphorochloridate (11 g., 0.6 mole), pyridine (95 g., 1.2 moles), and toluene (500 ml.) were mixed and heated to reflux with stirring for 16 hr. After the mixture had stood overnight, the precipitated pyridine hydrochloride was removed by filtration. The toluene solution was washed with water and then distilled *in vacuo*. After much of the toluene solution had been removed, a crystalline precipitate formed and was removed by filtration. This product was crude 2,2-dimethyl-1,3-propanediol cyclic phenyl phosphate containing 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphate as an impurity. A small portion of this material was stirred in a hot mixture of benzene and cyclohexane. The insoluble part was removed by filtration, and analysis of this white, crystalline material indicated it to be 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphate, m.p. 189–192°.

Anal. Calcd. for $C_5H_{11}O_4P$: P, 18.65. Found: P, 19.07.

When crystallization had occurred in the benzene-cyclohexane solution, the crystals were removed by filtration and recrystallized from cyclohexane containing a small amount of ethyl alcohol. The product was obtained as short, white fluffy needles, m.p. 130–131°. The melting point of a mixture of the product with material obtained by Method B was not depressed.

Method B. Phenol (18.8 g., 0.2 mole), phosphoryl chloride (30.6 g., 0.2 mole), and anhydrous magnesium chloride (0.1 g.) were mixed with stirring and heated to approximately 125° over a 9-hr. period. The crude phenyl phosphorodichloridate was a yellow liquid. 2,2-Dimethyl-1,3-propanediol (20.8 g., 0.2 mole) was added to this crude product with stirring. The reaction was weakly exothermic. The mixture was stirred for 5 hr., and then heated on a steam bath with stirring for 3 additional hours. The steam bath was then removed and nitrogen was passed through

the reaction mixture. The reaction mixture solidified immediately to a white, crystalline mass, which was recrystallized from a mixture of benzene and cyclohexane. An analytical sample, m.p. 133–135°, was obtained by recrystallization of a small amount of this material from a 75/25 mixture of benzene and cyclohexane.

Anal. Calcd. for $C_{11}H_{15}O_4P$: C, 54.54; H, 6.24; P, 12.79. Found: C, 54.53; H, 6.44; P, 12.89.

2,2-Dimethyl-1,3-propanediol cyclic phenylphosphonate (IIIa). 2,2-Dimethyl-1,3-propanediol (31.2 g., 0.3 mole) and pyridine (55.3 g., 0.7 mole) were dissolved in 250 ml. of dry dioxane. Phenylphosphonic dichloride (58.5 g., 0.3 mole) was added dropwise with stirring while the reaction vessel was cooled externally with ice water. Then the reaction mixture was stirred at 25° for 1.5 hr. After the precipitated pyridine hydrochloride had been filtered off, the dioxane was removed under reduced pressure. The residual white, crystalline solid was washed well with water. The yield was 31 g. (46%) of product, m.p. 103–105°, that was soluble in acetone and methanol but insoluble in water.

Anal. Calcd. for $C_{11}H_{15}O_3P$: C, 58.40; H, 6.68. Found: C, 57.93; H, 6.66.

2,2-Dimethyl-1,3-propanediol cyclic chloromethylphosphonate (IIIb). This compound was prepared from 2,2-dimethyl-1,3-propanediol (31.2 g., 0.3 mole), pyridine (47.5 g., 0.6 mole), and chloromethylphosphonic dichloride (50.3 g., 0.3 mole) using 240 ml. of dioxane as the solvent. The procedure used was that described for preparation of 2,2-dimethyl-1,3-propanediol cyclic phenylphosphonate, except that the reaction mixture was stirred for 6 hr. instead of 1.5 hr. After the pyridine hydrochloride and the solvent had been removed, a crystalline residue was obtained. The residue was recrystallized from a 50/50 mixture of benzene and cyclohexane to yield 25 g. (42%) of snow-white crystals, m.p. 115–116°. The product was soluble in benzene, acetone, ethyl alcohol, and water but insoluble in cyclohexane.

Anal. Calcd. for $C_6H_{12}ClO_3P$: C, 36.28; H, 6.09. Found: C, 36.47; H, 6.32.

2,2-Dimethyl-1,3-propanediol bis(diethyl phosphate) (IV). 2,2-Dimethyl-1,3-propanediol (31.2 g., 0.3 mole) and pyridine (55.3 g., 0.7 mole) were dissolved in 300 ml. of dioxane. The mixture was stirred and cooled externally with ice water while diethyl phosphorochloridate (103 g., 0.6 mole) was added dropwise over a period of 30 min. The mixture was stirred for 2 hr. at 25°, and the precipitated pyridine hydrochloride was removed by filtration. The filtrate was distilled *in vacuo* through a short Vigreux column. A forerun of 42.5 g., b.p. 90–182° (3.0 mm.), was removed and then 43.6 g. (38.6%) of colorless oil was collected at 183–188° (3.1 mm.), n_D^{20} 1.4278.

Anal. Calcd. for $C_{13}H_{30}O_8P_2$: C, 41.49; H, 8.04. Found: C, 41.31; H, 8.00.

2,2-Dimethyl-1,3-propanediol bis(cyclic 2,2-dimethyltrimethylene phosphite) (V). 2,2-Dimethyl-1,3-propanediol (364 g., 3.5 moles) was dissolved in 1500 ml. of anhydrous dioxane. Pyridine (474 g., 6.0 moles) was added, and then phosphorus trichloride (274 g., 2.0 moles) was added dropwise with stirring while the reaction vessel was cooled externally with an ice bath. After all of the phosphorus trichloride had been added, the reaction mixture was stirred at room temperature for 5 hr. The pyridine hydrochloride was filtered off and the filtrate was fractionated *in vacuo* using a short Vigreux column. After a small amount of unreacted 2,2-dimethyl-1,3-propanediol had been removed, 45 g. (15% based on phosphorus trichloride) of 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphite, b.p. 140–145° (2.2–2.5 mm.), was obtained. When cooled, this material formed white crystals, m.p. 48–50°. The infrared spectrum of this material was identical with that of the product prepared as described below (see VI).

After an intermediate fraction of 38 g., b.p. 153–167° (2.5 mm.), had been removed, 98 g. (27% based on phosphorus trichloride) of 2,2-dimethyl-1,3-propanediol bis(cyclic 2,2-dimethyltrimethylene phosphite) was obtained, b.p. 167–

177° (2.6 mm.), n_D^{20} 1.4689. This material solidified into large, transparent crystals after standing for several days. The product was low-melting and insoluble in water.

Anal. Calcd. for $C_{15}H_{30}O_6P_2$: C, 48.91; H, 8.21. Found: C, 48.66; H, 8.23.

When the above reaction was repeated using 0.4 mole of 2,2-dimethyl-1,3-propanediol and 0.2 mole of phosphorus trichloride without pyridine, no cyclic hydrogen phosphite was found. A small amount of 2,2-dimethyl-1,3-propanediol was recovered, and a 72% yield of 2,2-dimethyl-1,3-propanediol bis(cyclic 2,2-dimethyltrimethylene phosphite), n_D^{20} 1.4687, was obtained. The distillate solidified to a low-melting solid after standing for 2 days.

Anal. Calcd. for $C_{15}H_{30}O_6P_2$: C, 48.91; H, 8.21. Found: C, 48.61; H, 8.06.

In a separate reaction in which 3.0 moles of 2,2-dimethyl-1,3-propanediol dissolved in 700 ml. of 1,1,2,2-tetrachloroethane was treated with 2.0 moles of phosphorus trichloride, both V and VI were isolated. The presence of moisture in the reaction mixture probably accounted for the formation of VI.

2,2-Dimethyl-1,3-propanediol cyclic hydrogen phosphite (VI). Ethyl alcohol (13.8 g., 0.3 mole) and 2,2-dimethyl-1,3-propanediol (31.2 g., 0.3 mole) were mixed and stirred while phosphorus trichloride (41.3 g., 0.3 mole) was added dropwise. The reaction flask was cooled externally so that the temperature did not rise above 25°. After all the phosphorus trichloride had been added and the exothermic reaction had subsided, the reaction mixture was stirred at 25° while nitrogen was passed through to remove the liberated hydrogen chloride and ethyl chloride. Finally, the reaction mixture was warmed on the steam bath to complete the removal of the by-products. The evolved ethyl chloride (14 g., theor. = 19.4 g.) was collected in a Dry Ice trap. After a forerun of 2.5 g. had been removed, 28 g. (62%) of product was collected at 142–145° (2.9 mm.) through a short Vigreux column. This distillate solidified to a white, crystalline solid, m.p. 48–50°. The infrared spectrum of this compound was in agreement with the cyclic hydrogen phosphite structure. It had a P—H absorption band at 4.2 μ. The compound discolored both bromine and potassium permanganate solutions. The molecular weight, as determined by treatment of a sample with excess alkali followed by back titration with acid, was 153.7 (calculated molecular weight = 150.12).

Anal. Calcd. for $C_5H_{11}O_3P$: C, 40.00; H, 7.39; P, 20.64. Found: C, 39.62; H, 7.44; P, 20.57.

When the above reaction was repeated using isobutyl alcohol and 2-ethyl-1-hexanol instead of ethyl alcohol, the yields of 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphite were 68.5% [b.p. 117–119° (1.3 mm.)] and 75% [b.p. 117–120° (0.8 mm.)], respectively. In these two cases the reaction mixture was not cooled during the addition of the phosphorus trichloride; however, the temperature of the reaction mixture was moderated by the rate of addition of the phosphorus trichloride so that the temperature never exceeded 70°. None of the cyclic hydrogen phosphite was obtained when cetyl alcohol was used instead of ethyl alcohol.

2,2-Dimethyl-1,3-propanediol cyclic 2,2,2-trichloro-1-hydroxyethylphosphonate (VIII). Chloral (14.7 g., 0.1 mole) and 2,2-dimethyl-1,3-propanediol cyclic hydrogen phosphite (15.0 g., 0.1 mole) were mixed with stirring. Even though the flask was cooled in an ice bath, the temperature of the reaction mixture rose to 120°. At this temperature the system solidified to a white solid. A small sample of this material was recrystallized from ethyl alcohol to obtain transparent, square platelets, m.p. 209–210°. The compound was insoluble in cyclohexane, benzene, chloroform, and water. The infrared spectrum was compatible with the proposed structure and indicated that the —OH group present was hydrogen-bonded.

Anal. Calcd. for $C_7H_{12}Cl_3O_4P$: C, 28.25; H, 4.07; P, 10.41. Found: C, 28.25; H, 4.09; P, 10.30.

2,2-Dimethyl-1,3-propanediol bis(cyclic 2,2-dimethyltrimethylene phosphorothionate) (IX). 2,2-Dimethyl-1,3-propanediol bis(cyclic 2,2-dimethyltrimethylene phosphite) (18.4 g., 0.05 mole), sulfur (3.2 g., 0.1 mole), and 70 ml. of benzene were mixed with stirring. A weakly exothermic reaction occurred. The reaction mixture was stirred at 25° for 48 hr., refluxed for 8 hr., and then cooled. A cream-colored solid (3.3 g.) crystallized from the benzene solution. Recrystallization of this material from benzene gave white crystals, m.p. 163–164°.

Anal. Calcd. for $C_{15}H_{30}O_6P_2S_2$: P, 14.33; S, 14.83. Found: P, 14.13; S, 14.74.
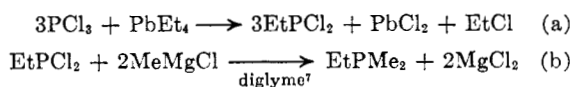
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Preparation and Characterization of Vinyldichlorophosphine, Vinyldimethylphosphine, and Ethyldimethylphosphine[1,2]

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The air and moisture sensitive compound vinyldichlorophosphine (b.p. 104°/760 mm.) is readily obtained by heating a mixture of phosphorus trichloride and divinylmercury. Treatment of methylmagnesium chloride in diglyme with vinyldichlorophosphine afforded vinyldimethylphosphine (b.p. 69.0°/760 mm.) Ethyldimethylphosphine (b.p. 73.3°/760 mm.) was similarly prepared from ethyldichlorophosphine. The vapor tensions of four phosphines are reported.

As part of a study[5] on the relative electron-pair donor power of several organophosphines it was necessary to prepare and characterize vinyldimethylphosphine and ethyldimethylphosphine. The latter compound has been reported by Collie[6] but has not been mentioned in the chemical literature since its discovery in 1888. Ethyldimethylphosphine was prepared by us by the sequence of reactions:

$$3PCl_3 + PbEt_4 \longrightarrow 3EtPCl_2 + PbCl_2 + EtCl \quad (a)$$

$$EtPCl_2 + 2MeMgCl \xrightarrow[\text{diglyme}^7]{} EtPMe_2 + 2MgCl_2 \quad (b)$$

Reaction (a) was carried out exactly as described by Kharasch *et al.*[8] The normal boiling point of ethyldimethylphosphine is 11° less than that reported earlier.[6] The hitherto unreported compound vinyldimethylphosphine was obtained from the reaction between vinyldichlorophosphine and methylmagnesium chloride. Before this reaction could be carried out, however, it was necessary to prepare a vinyldihalophosphine. Although trivinylarsine and trivinylstibine undergo redistribution to the vinylhalo derivatives when mixed with the trichlorides or tribromides of the respective elements, trivinylphosphine and phosphorus trihalides yield only black solids.[9] Similarly, excellent yields of vinylhaloarsines were obtained by Seyferth[9,10] by treating arsenic trihalides with dibutyldivinyltin, but when the "mixed" redistribution method was applied to phosphorus trihalides the desired vinylhalophosphines were not obtained. It is still possible that vinyldihalophosphines could be obtained from these reactions by empirically varying the experimental techniques until the correct conditions are found, but meanwhile, as described in the experimental section, the recently discovered divinylmercury[11] provides a ready route to such compounds.

$$(CH_2:CH)_2Hg + PCl_3 \xrightarrow{\text{heat}}$$
$$CH_2:CHPCl_2 + CH_2:CHHgCl$$
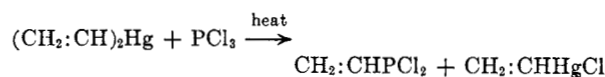
Vinyldichlorophosphine (b.p. 104°/760 mm.) is very sensitive to air and to moisture. Even when sealed in evacuated ampoules it will decompose unless the ampoules have been thoroughly baked during evacuation. The gas-phase infrared spectrum of vinyldichlorophosphine has been studied[3] over the region 650–3500 cm.$^{-1}$. It shows the typical absorption C—H stretches at 3050 and 3110 cm.$^{-1}$; an overtone of a 968 cm.$^{-1}$ band at 1930 cm.$^{-1}$; C—H deformations at 1400, 1324 and 968 cm.$^{-1}$; and the P—C stretch frequency at 728 and 671

(1) This work was made possible by the award of a grant (G5106) from the National Science Foundation.

(2) Presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959.

(3) Taken from the thesis of H. D. Kaesz submitted to the Graduate School of Arts and Sciences, Harvard University, in partial fulfillment of the requirements of the Ph.D. degree. Other parts of the dissertation are published elsewhere.

(4) Public Health Predoctoral Fellow of the National Heart Institute.

(5) H. F. Kaesz and F. G. A. Stone, abstracts of papers presented at the 135th Meeting of the American Chemical Society held in Boston, Mass., April 1959, p. 11M.

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