Diphenylphosphinodithioic thioanhydride (23.3 g., 0.05 mole) and phenol (14.1 g., 0.15 mole) were heated to 190° and stirred at that temperature for 5 hr. The reaction mixture was cooled and poured into 80 g. of cold 10% NaOH solution. The solid material was thoroughly washed with water, filtered and dried. The product (30 g., 93% crude) was recrystallized from naphtha several times to obtain a pure sample (15.0 g., 48.4%) of phenyl diphenylphosphinothionate melting at 123–124°. A mixture of this white crystalline product with the ester obtained above by direct esterification of the acid gave no melting point depression.

Anal. Calcd. for $C_{18}H_{15}OPS$: P, 9.98; S, 10.32. Found: P, 10.02; S, 10.51.

Acknowledgment.—The authors wish to thank Mr. Harry Ferber for the analytical work reported throughout this paper.

CLEVELAND 17, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, TENNESSEE EASTMAN COMPANY, DIVISION OF EASTMAN KODAK COMPANY]

Preparation of 1-Hydroxyalkylidenediphosphonates

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Dialkyl hydrogen phosphites react with acylphosphonic acid esters in the presence of basic catalysts to produce tetraalkyl 1-hydroxyalkylidenediphosphonates. β-Propiolactone reacts with diethyl hydrogen phosphite to produce tetraethyl 1,3-dihydroxypropylidenediphosphonate. Diethyl 3-hydroxypropionylphosphonate is an intermediate in this reaction.

The base-catalyzed addition of dialkyl hydrogen phosphites to aldehydes and ketones to form 1-hydroxyalkylphosphonates is well known.[1–10]

$$CH_3CHO + (C_2H_5O)_2P(O)H \xrightarrow{\text{base}} \underset{\text{I}}{CH_3CHOHP(O)(OC_2H_5)_2} \quad (1)$$

$$CH_3C(O)CH_3 + (C_2H_5O)_2P(O)H \xrightarrow{\text{base}} \underset{\text{II}}{(CH_3)_2C(OH)P(O)(OC_2H_5)_2} \quad (2)$$

With a strongly negatively substituted aldehyde such as chloral, no catalyst is required.[11–14]

$$CCl_3CHO + (CH_3O)_2P(O)H \longrightarrow \underset{\text{III}}{CCl_3CHOHP(O)(OCH_3)_2} \quad (3)$$

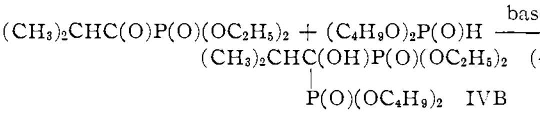
While studying the reaction of acetyl chloride and sodium diethyl phosphite, Arbuzov and Azanovskaya obtained tetraethyl 1-acetoxyethylidenediphosphonate, $CH_3C(OCOCH_3)[P(O)(OC_2H_5)_2]_2$.[15] They postulated that sodium diethyl phosphite added to the carbonyl group of $CH_3C(O)P(O)(OC_2H_5)_2$, initially formed, to give $CH_3C(ONa)[P(O)(OC_2H_5)_2]_2$ which was followed by acetylation of the ONa group by the acetyl chloride.

We have found that dialkyl hydrogen phosphites will add readily to acylphosphonates in the presence of a base to form 1-hydroxyalkylidenediphosphonates as

$$CH_3C(O)P(O)(OC_2H_5)_2 + (C_2H_5O)_2P(O)H \xrightarrow{\text{base}} \underset{\text{IV}}{CH_3C(OH)[P(O)(OC_2H_5)_2]_2} \quad (4)$$

The mechanism of the reaction probably involves the nucleophilic attack of the dialkyl phosphite on the electropositive carbon of the carbonyl group in the acetylphosphonate molecule. The electropositive nature of the carbonyl carbon atom is probably enhanced by the electron-withdrawing power of the adjacent phosphoryl group, thus promoting the reaction. Use of basic catalysts, such as amines, for the addition of certain carbonyl reagents is well known.[16]

$$(CH_3)_2CHC(O)P(O)(OC_2H_5)_2 + (C_2H_5O)_2P(O)H \xrightarrow{\text{base}} \underset{\text{IVA}}{(CH_3)_2CHC(OH)[P(O)(OC_2H_5)_2]_2} \quad (4a)$$



$$(CH_3)_2CHC(O)P(O)(OC_2H_5)_2 + (C_4H_9O)_2P(O)H \xrightarrow{\text{base}} (CH_3)_2CH\underset{\substack{|\\ P(O)(OC_4H_9)_2}}{C}(OH)P(O)(OC_2H_5)_2 \quad (4b)$$

IVB

It is somewhat surprising that the diethyl- and dibutylphosphono groups enter the isobutyrylphosphonate molecule very readily since one might expect some steric hindrance from the isopropyl- and diethylphosphono groups which bracket the carbonyl group. Reactions 4a and 4b are almost as vigorous as 4, however. 1-Hydroxyalkylidenediphosphonates can be obtained with different alkoxy groups on the two phosphorus atoms as shown in equation 4b.

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(2) A. N. Pudovik and Yu. P. Kitaev, *J. Gen. Chem.* (*U.S.S.R.*) (Consultants Bureau English Translation), **22**, 531 (1952).

(3) V. S. Abramov, *ibid.*, **22**, 709 (1952).

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(10) V. S. Abramov and N. S. Kuznetsov, *ibid.*, 398 (1953); *C. A.*, **49**, 839 (1955).

(11) W. E. Craig and W. F. Hester (to Rohm and Haas Company), U. S. Patent 2,485,573 (1949).

(12) W. F. Barthel, P. A. Giang and S. A. Hall, THIS JOURNAL, **76**, 4186 (1954).

(13) W. Lorenz (to Farbenfabriken Bayer Akt.), U. S. Patent 2,701,225 (1955).

(14) W. Lorenz, A. Henglein and G. Schrader, THIS JOURNAL, **77**, 2554 (1955).

(15) A. E. Arbuzov and M. M. Azanovskaya, *Doklady Akad. Nauk S.S.S.R.*, **58**, 1961 (1947); *C. A.*, **46**, 8606 (1952).

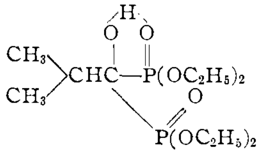
(16) R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 379.

We would expect other phosphorus compounds containing a P–H group to add to acylphosphonates in a similar manner. This would include hypophosphorous acid, sodium hypophosphite and phosphinous acids.

In contrast to the sensitivity of 1-hydroxyalkylphosphonates to distillation,[4–6] the above 1-hydroxyalkylidenediphosphonates are quite stable to distillation at reduced pressures.

When an aldehyde or ketone is treated with a dialkyl hydrogen phosphite in the presence of a primary or secondary amine, an aminoalkylphosphonate results.[17] Even though diethylamine was used as the catalyst in equation 4, no amino-substituted diphosphonate, $CH_3C[N(C_2H_5)_2][P(O)(OC_2H_5)_2]_2$, was observed. Perhaps the diphosphonate molecules are too sterically hindered to allow the diethylamino group to exist in the 1-position.

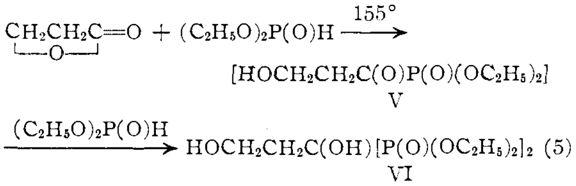
The infrared spectrum of IV had an –OH band of medium intensity while the spectra of IVA and IVB had –OH bands of weak intensity. This weak hydroxyl band in IVA and IVB is probably indicative of hydrogen bonding between the –OH group and one of the phosphoryl (P=O) groups as shown in the structure



IVA

It seems probable that the branched chains in IVA and IVB would force the bond angles closer together, thus promoting the hydrogen bonding. Compound IV does not have this chain branching.

We were also able to obtain 1-hydroxyalkylidenediphosphonates from the interaction of dialkyl hydrogen phosphites with lactones such as β-propiolactone.



$$\underbrace{CH_2CH_2C}_{—O—}{=}O + (C_2H_5O)_2P(O)H \xrightarrow{155°} \underset{V}{[HOCH_2CH_2C(O)P(O)(OC_2H_5)_2]}$$

$$\xrightarrow{(C_2H_5O)_2P(O)H} \underset{VI}{HOCH_2CH_2C(OH)[P(O)(OC_2H_5)_2]_2} \quad (5)$$

Reaction 5 can be explained by an attack of the phosphite molecule on the carbonyl group of the lactone causing an acyl–oxygen cleavage of the lactone ring to produce V. This intermediate 3-hydroxypropionylphosphonate then reacts similarly to equation 4 above to give VI. Temperatures in the range of 155–160° are required to open the β-propiolactone ring. At this temperature, the dialkyl phosphite adds to the carbonyl of V without the presence of a catalyst. This is not too surprising since chloral (equation 3) reacts at 25° without a catalyst and the intermediate V also contains a negatively substituted carbonyl group. Also, Stiles has reported the addition of dialkyl phosphites to simple aldehydes and ketones at 130° without the use of a catalyst.[18]

The reaction of diethyl hydrogen phosphite with the carbonyl group of an acylphosphonate is rapid compared to the opening of the lactone ring. Therefore, diethyl hydrogen phosphite would add to V as rapidly as the latter forms and none of the intermediate V would be present in the final reaction mixture. As shown below, however, V is formed by a thermal splitting of VI during distillation of the product.

Product VI distils with decomposition at 116–120° (0.5–0.8 mm.). Although the elemental analysis of the distillate agreed with the theoretical values, it was shown by infrared analysis that this distillate contained diethyl hydrogen phosphite and diethyl 3-hydroxypropionylphosphonate (V) in addition to VI. This sensitivity is in marked contrast to the stability of the 1-hydroxyalkylidenediphosphonates (IV, IVA and IVB), which could be distilled without decomposition at reduced pressures (1–4 mm.). Thus the sensitivity of the 1,3-dihydroxypropylidenediphosphonates is comparable to the sensitivity of the 1-hydroxyalkylphosphonates, which readily cleave to the starting dialkyl phosphite and carbonyl compound. Another factor pointing to the cleavage of VI during distillation was the low boiling point. Also, ebulliometric molecular weight determinations in benzene were intermediate (251.8, 243.3) between the values calculated. for V (210.17) and VI (348.28).

Reaction 5 was repeated using sodium diethyl phosphite in addition to diethyl hydrogen phosphite and β-propiolactone. In this case, the reaction was quite exothermic and had to be controlled with external cooling. After neutralization, again the mixture of V, VI and diethyl hydrogen phosphite was obtained after all unreacted starting materials had been removed. This demonstrates that diethyl hydrogen phosphite and sodium diethyl phosphite open the lactone ring in the same manner; however, the lactone ring is opened much more readily by the sodium diethyl phosphite. Tertiary organic bases such as triethylamine were also effective in catalyzing the reaction of β-propiolactone with diethyl hydrogen phosphite at room temperature to produce VI.

Experimental

Diethyl Acetylphosphonate.[19]—Triethyl phosphite (83.1 g., 0.5 mole) was added dropwise with stirring to acetyl chloride (39.2 g., 0.5 mole) over a period of about 30 minutes while the temperature of the reaction mixture was maintained below 30° by cooling with an ice-bath. After the addition of triethyl phosphite was complete, the reaction mixture was stirred at 25° for 1 hour and then heated gently on a steam-bath until the evolution of ethyl chloride had ceased. A total of 28 ml. of ethyl chloride was collected in a Dry Ice trap (theoretical = 35 ml.). Distillation of the reaction mixture gave 60 g. (67%) of product, b.p. 62–65° (1.5 mm.), $n^{20}\mathrm{D}$ 1.4231.

Anal. Calcd. for $C_6H_{13}O_4P$: C, 40.00; H, 7.28. Found: C, 40.10; H, 7.23.

Diethyl Isobutyrylphosphonate.—Triethyl phosphite (49.8 g., 0.3 mole) was added dropwise with stirring to isobutyryl chloride (31.8 g., 0.3 mole) while the temperature of the reaction mixture was moderated by external cooling with cold water. The reaction mixture was stirred at 25° for 1 hour, and the evolved ethyl chloride (15 ml., theoretical = 21 ml)

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[17] E. K. Fields, THIS JOURNAL, **74**, 1528 (1952).

[18] A. R. Stiles (to Shell Development Company), U. S. Patent 2,593,213 (1952).

[19] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 158.

was collected in a Dry Ice trap. Finally the reaction mixture was heated on the steam-bath with stirring for 1 hour to complete the evolution of the ethyl chloride. Distillation of the reaction mixture gave 48 g. (77%) of product, b.p. 92–97° (3.9 mm.), n^{20}D 1.4272.

Anal. Calcd. for $C_8H_{17}O_4P$: C, 46.15; H, 8.23. Found: C, 46.29; H, 8.26.

Tetraethyl 1-Hydroxyethylidenediphosphonate (IV).—Diethyl hydrogen phosphite (13.8 g., 0.1 mole) and diethylamine (7.3 g., 0.1 mole) were mixed in a round-bottom flask and diethyl acetylphosphonate (18.0 g., 0.1 mole) was added dropwise with stirring. The reaction was exothermic and the temperature rose rapidly to 70°. About 15 minutes were required to add the phosphonate. The mixture was stirred for 2 hours, and then was distilled under reduced pressure. The forerun (14.5 g.) was collected from 43 to 133° (1.1 mm.). The product IV distilled at 140–150° (0.7 mm.), n^{20}D 1.4311, and amounted to 18.3 g. (58%).

Anal. Calcd. for $C_{10}H_{24}O_7P_2$: C, 37.74; H, 7.60; P, 19.46. Found: C, 37.96; H, 7.61; P, 19.29, 19.51.

The following characteristic absorption bands were observed from the infrared spectrum of IV

Absorption band, μ	Assignment	Absorption band, μ	Assignment
2.85	-OH	9.7	C–OP
8.0	P═O	10.2	P–OC
8.6	P–O–C_2H_5		

Tetraethyl 2-Methyl-1-hydroxypropylidenediphosphonate (IVA).—Diethyl hydrogen phosphite (20.0 g., 0.145 mole), diethyl isobutyrylphosphonate (20.8 g., 0.1 mole) and triethylamine (7.0 g., 0.07 mole) were treated according to the procedure given above for IV. When the reaction mixture was fractionated, 25.2 g. (73% yield) of product boiling at 142–145° (1.2 mm.), n^{20}D 1.4359, was obtained.

Anal. Calcd. for $C_{12}H_{28}O_7P_2$: C, 41.74; H, 7.88; P, 17.94. Found: C, 41.97; H, 8.20; P, 18.02.

The following characteristic absorption bands were observed from the infrared spectrum of this compound

Absorption band, μ	Assignment	Absorption band, μ	Assignment
2.9 (weak)	-OH	9.8	C–OP
7.9	P═O	10.4	P–OC
8.6	P–O–C_2H_5		

Dibutyl Diethyl 1-Hydroxy-2-methylpropylidenediphosphonate (IVB).—Dibutyl hydrogen phosphite (8.35 g., 0.043 mole), diethyl isobutyrylphosphonate (8.9 g., 0.043 mole) and triethylamine (3.5 g., 0.035 mole) were treated according to the procedure given above for IV. When the reaction mixture was fractionated, 7.0 g. (40.5% yield) of product boiling at 180–187° (3.4 mm.), n^{20}D 1.4400, was obtained.

Anal. Calcd. for $C_{16}H_{36}O_7P_2$: C, 47.75; H, 9.02. Found: C, 46.95; H, 8.96.

The following characteristic absorption bands were observed from the infrared spectrum of this compound

Absorption bands, μ	Assignment	Absorption bands, μ	Assignment
2.9 (weak)	-OH	9.8	C–OP
7.9	P═O	10.3	P–OC
8.6	P–O–C_2H_5		

The weak-OH bands in the spectra of IVA and IVB probably indicate hydrogen bonding with one of the phosphoryl groups. There was no indication of —C═O or P–H bands in the spectra of IV, IVA or IVB.

Tetraethyl 1,3-Dihydroxypropylidenediphosphonate (VI). (Method A).—Diethyl hydrogen phosphite (110.4 g., 0.8 mole) and β-propiolactone (28.8 g., 0.4 mole) were mixed and heated to 160° with stirring. At this point, an exothermic reaction took place and the temperature climbed rapidly to 200°. The heating mantle was removed and the temperature was allowed to drop to 155°. The temperature was then maintained in the 155–160° range for 14 hours. Fractionation of the reaction mixture gave 36 g. of unchanged diethyl hydrogen phosphite and an intermediate cut of 28 g., b.p. 58–120° (1.3 mm.). Then 16.5 g. (12%) of product distilled at 116–120° (0.5–0.8 mm.), n^{20}D 1.4165, before decomposition became so great that the distillation had to be stopped.

Anal. Calcd. for $C_{11}H_{26}O_8P_2$: C, 37.93; H, 7.53; P, 17.79. Found: C, 38.13; H, 7.82; P, 17.98.

Infrared analysis indicated the presence of $(C_2H_5O)_2P(O)H$, $HOCH_2CH_2C(O)P(O)(OC_2H_5)_2$ (V) and $HOCH_2CH_2C(OH)[P(O)(OC_2H_5)_2]_2$ (VI) in the fraction which distilled at 116–120° (0.5–0.8 mm.). The characteristic absorption bands observed in the spectrum of this sample are listed below.

Absorption band, μ	Assignment
2.95	-OH
4.18	P–H [from $(C_2H_5O)_2P(O)H$]
5.78	C═O [from $HOCH_2CH_2C(O)P(O)(OC_2H_5)_2$]
8.0	P═O
9.7	C–OP
10.3	P–OC

It should be noted that the carbon, hydrogen and phosphorus content of this 3-component mixture would be the same as that for VI since V and $(C_2H_5O)_2P(O)H$ are formed by a simple cleavage of VI at the distillation temperature. The distillation residue was a viscous yellow oil and amounted to 33.5 g. The phosphorus content of this oil was found by analysis to be 18.05%; therefore, it was probably mostly VI.

When the 116–120° (0.5–0.8 mm.) fraction was redistilled, diethyl hydrogen phosphite, b.p. 50–52° (2.8 mm.), n^{20}D 1.4078, and a fraction which boiled at 85–100° (2.8 mm.), n^{20}D 1.4140, were obtained. The latter probably was chiefly $HOCH_2CH_2C(O)P(O)(OC_2H_5)_2$ but still contained a small amount of diethyl hydrogen phosphite.

(Method B).—Diethyl hydrogen phosphite (75 g., 0.54 mole) was treated with sodium (4.6 g., 0.2 mole) while the reaction mixture was stirred and cooled externally with cold water. After all of the sodium had reacted, β-propiolactone (14.4 g., 0.2 mole) was added dropwise with stirring while still cooled externally with cold water. The reaction was extremely vigorous and a viscous, transparent oil was obtained. The mixture was stirred for 6 hours at 25°, and then neutralized with concentrated hydrochloric acid while being chilled in an ice-bath. Benzene (150 ml.) was added to the white slurry, and the precipitated sodium chloride was removed by filtration. The upper layer was separated, dried and distilled at reduced pressure. After removing the benzene and unreacted diethyl phosphite, the following fractions were obtained: 1, b.p. 100–108° (2.8 mm.), 4 g., n^{20}D 1.4149; 2, b.p. 115–123° (2.8 mm.), 3.8 g., n^{20}D 1.4204; 3, b.p. 124–127° (2.8 mm.), 4.4 g., n^{20}D 1.4240.

The infrared spectra of fractions 2 and 3 were very similar to that of the fraction boiling at 116–120° (0.5–0.8 mm.) in method A above. The intensities of the bands indicated that fraction 2 of method B contained more V and less VI than the product of method A.

Anal. Calcd. for $C_7H_{15}O_5P$: P, 14.74. Found on fraction 2: P, 15.35, 15.36.

The lower layer contained water. 11.0 g. of diethyl phosphite (b.p. 55° (2.6 mm.)), and about 2 g. of an undistillable oil.

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