to the mark and the contents mixed thoroughly.[14] The solution was transferred to a reaction flask and heated to reflux (93 ± 1°) as quickly as possible. Refluxing was continued for 3–4 days (7 days in the case of di-2-ethylhexyl lauroylphosphonate). Ten-milliliter aliquots were removed by pipet frequently during the first 8 hours, then once a day until hydrolysis was complete. The aliquot was transferred to 60–70 ml. of absolute ethanol and titrated immediately with 0.1 *N* NaOH.

Polarographic Studies.—Details of the polarographic procedure and the solvent system have been reported in previous publications.[10,15] Methanol–benzene was the only solvent system used.

Infrared Studies.—Infrared absorption spectra were obtained with a Beckman IR-3 spectrophotometer, using sodium chloride prisms. For the pure liquid samples a spacer approximately 0.02 mm. thick was used between two sodium chloride windows. A single sodium chloride window was used for the tape-recorded blank.

Ultraviolet Studies.—The instrument was the Carey Model 11 recording spectrophotometer. Samples were dissolved in isoöctane at levels of 1 and 0.1%, and measured in a cell of 1 cm. thickness.

Acknowledgment.—The authors wish to thank Dr. Constantine Ricciuti for the polarographic studies, Mrs. Ruth B. Kelly, Mrs. Katherine M. Zbinden and Dr. Clyde L. Ogg for the analytical work, and Miss Anne M. Smith and Dr. George C. Nutting for the ultraviolet spectroscopy. The authors also wish to thank Mr. E. T. Roe for helpful discussions.

PHILADELPHIA, PA.

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(14) Twenty ml. additional dioxane was necessary in the case of di-2-ethylhexyl lauroylphosphonate because of incomplete solubility in the above solution.

(15) W. E. Parker, C. Ricciuti, C. L. Ogg and D. Swern, THIS JOURNAL, **77**, 4037 (1955).

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORIES, THE LUBRIZOL CORPORATION]

Aromatic Phosphinic Acids and Derivatives. II. Direct Esterification of Diphenylphosphinodithioic Acid[1]

BY T. ROBERT HOPKINS AND PAUL W. VOGEL

RECEIVED MAY 7, 1956

Alkyl diphenylphosphinodithioates have been prepared in good yields by the direct esterification of diphenylphosphinodithioic acid with certain alcohols in the absence of a catalyst. The reaction proceeds readily with primary alcohols, higher boiling secondary alcohols and tertiary alcohols. Phenol yields a monothioester.

Very little work has been reported on the chemistry of the diarylphosphinodithioic acids and their derivatives. The first member of this series, diphenylphosphinodithioic acid, can now be conveniently prepared by the reaction of benzene with phosphorus pentasulfide in the presence of anhydrous aluminum chloride.[2] Esters of this acid have not been reported previously.

In the present investigation it was found that diphenylphosphinodithioic acid can be esterified directly either by addition of the thiol group to an olefin or by reaction with certain alcohols in the absence of a catalyst. The latter is a novel reaction in that water, rather than hydrogen sulfide, is eliminated and a dithioester is formed.

Esters possessing primary alkyl groups are obtained from primary alcohols. An 85% yield of the *n*-octyl ester was obtained from the reaction of *n*-octyl alcohol with the acid at 180°. The alcohol was not first dehydrated since, if this were the case, the 2-octyl ester would result. This was demonstrated by the reaction of diphenylphosphinodithioic acid with 1-octene to give a 90% yield of the 2-octyl ester as shown in reaction (2). The addition of the thiol group to the olefin followed Markownikoff's rule. The structures of the esters were proven by saponification to the corresponding mercaptan and diphenylphosphinothioic acid. The mercaptans were identified by their 2,4-dinitrophenyl thioethers prepared by the procedure of Bost.[3]

$$\mathrm{Ph_2PSSH} + n\text{-}\mathrm{C_8H_{17}OH} \longrightarrow \mathrm{Ph_2PSS{-}C_8H_{17}} + \mathrm{H_2O} \quad (1)$$

$$\mathrm{Ph_2PSSH} + \text{1-octene} \longrightarrow \mathrm{Ph_2PSS{-}CH(CH_3){-}C_6H_{13}} \quad (2)$$

$$\mathrm{Ph_2PSSR} + \mathrm{H_2O} \xrightarrow{\mathrm{NaOH}} \mathrm{Ph_2POSNa} + \mathrm{RSNa} \quad (3)$$

The esterification of carboxylic acids requires the removal of a hydroxyl group from the acid. The relative order of reactivity of alcohols in this type of esterification is $R^{\mathrm{I}} > R^{\mathrm{II}} > R^{\mathrm{III}}$. When a strong acid is esterified, the hydroxyl group is believed to be removed from the alcohol. No definite proof of this is known except in the case of the hydrogen halide acids where there is no alternative. The relative reactivity rates for alcohols in the "esterification" of these acids are in the order $R^{\mathrm{III}} > R^{\mathrm{II}} > R^{\mathrm{I}}$. Diphenylphosphinodithioic acid may be classified as a strong acid, and as such it removes the hydroxyl group from the alcohol during esterification. One would, therefore, expect the relative reactivity rates of the alcohols to be $R^{\mathrm{III}} > R^{\mathrm{II}} > R^{\mathrm{I}}$. Actually, the order seems to be $R^{\mathrm{III}} \gtrless R^{\mathrm{I}} > R^{\mathrm{II}}$. Primary alcohols react readily while the lower secondary alcohols give little or no reaction at their boiling points. Only one tertiary alcohol, *t*-butyl alcohol, has been studied.

The reactivity rates of primary, secondary and tertiary alcohols were compared by the esterification of a series of butyl alcohols. *n*-Butyl alcohol reacted with the acid at 117° for 28 hr. to give a 63% yield of the *n*-butyl ester. When *sec*-butyl alcohol was employed, little or no reaction occurred after 30 hr. at the reflux temperature (100°), and 90% of the starting acid was recovered unchanged. The fact that *t*-butyl alcohol gave a 66% yield of the

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(1) Presented before the Division of Organic Chemistry at the 125th A.C.S. Meeting, Kansas City, Mo., March, 1954.

(2) W. Higgins, P. Vogel and W. Craig, THIS JOURNAL, **77**, 1864 (1955).

(3) R. W. Bost, J. D. Turner and R. D. Norton, *ibid.*, **54**, 1985 (1932).

TABLE I

GENERAL FORMULA—Ph_2PSSR

R	Hours	Reaction temp., °C.	Yield, %	B.p. °C.	Mm.	M.p., °C.	n^{20}_D	d^{20}_4	Phosphorus, % Calcd.	Phosphorus, % Found	Sulfur, % Calcd.	Sulfur, % Found
CH_3–	16	65	98[a]			82–83			11.8	11.7	24.2	24.4
C_2H_5–	36	80	65	166–167	0.3		1.6611	1.1919	11.15	11.06	23.03	22.84
i-C_3H_7–	20	80	No reaction									
n-C_4H_9–	28	100	63	162–164	.07		1.6370	1.1471	10.11	10.26	20.95	20.75
sec-C_4H_9–	36	100	No reaction									
t-C_4H_9–	16	80	66			91–92			10.11	10.10	20.95	20.82
n-C_6H_{13}–	8	155	87	190–192	.1	43–44			9.26	9.35	19.17	19.37
n-C_8H_{17}–	6	185	86	197–199	.2		1.5972	1.0845	8.54	8.52	17.69	17.64
2-C_8H_{17}–	6	180	88[a]	100–110[b]	.015		1.6050	1.0895	8.54	8.62	17.69	17.78
n-$C_{10}H_{21}$–	10	180	97[a]	155[b]	.04		1.5864	1.0640	7.93	8.01	16.41	16.46
n-$C_{12}H_{25}$–	10	180	95[a]	158[b]	.20		1.5726	1.0267	7.40	7.10	15.32	15.02

[a] Crude yield from which small samples were purified for analysis. [b] These products were distilled from a still having a short distillation path.

t-butyl ester after heating for 16 hr. at 83° indicates that a different mechanism is probably involved when tertiary alcohols are employed. When simple tertiary alcohols are dehydrated, the olefin formed may react with the acid to form the same ester as that expected by direct esterification with the alcohol. This view is supported by a reaction in which isobutylene was passed into a benzene solution of the acid at 80° for 7 hr. to produce a 50% yield of the *t*-butyl ester. It is probable that the lower secondary alcohols would react if pressures and higher temperatures were employed. The higher boiling secondary alcohols do react. 2-Octyl alcohol gave a 79% yield of the 2-octyl ester after 6 hr. at 180°.

The esters which have been identified are shown in Table I. It was necessary to distil the higher members of the series from a still having a short distillation path as some decomposition occurs in the neighborhood of 200°. In general, the dithioesters are relatively stable and possess a characteristic odor.

In the reaction of diphenylphosphinodithioic acid with phenol, hydrogen sulfide was eliminated and a monothioester II was obtained. This can be explained by the sequence in reactions (4) to (6).

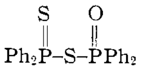
$$Ph_2PSSH \xrightarrow{\Delta} \underset{\text{I}}{(Ph_2PS)_2S} + H_2O \qquad (4)$$

$$\text{I} + PhOH \longrightarrow \underset{\text{II}}{Ph_2PSOPh} + Ph_2PSSH \qquad (5)$$

$$Ph_2PSSH \xrightarrow{\Delta} \text{I} \qquad (6)$$

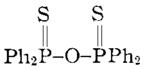
When heated, the acid was converted to diphenylphosphinodithioic thioanhydride (I), and hydrogen sulfide was evolved. Further heating in the presence of phenol cleaved the anhydride with the formation of the monothioester II and liberated the acid which was free to re-enter the cycle. When a sample of the thioanhydride was heated with phenol the product was identified as phenyl diphenylphosphinothionate (II).

In the reactions with 2-octyl alcohol and *n*-dodecyl alcohol, a solid by-product III which melted at 197–198° was isolated. Analytical data indicated this material was a monomeric compound whose empirical formula was $C_{24}H_{20}OS_2P_2$ and further suggested the anhydride of diphenylphosphinothioic acid. This anhydride could have either structure IIIA or IIIB. Hydrolysis of a compound with



$$\overset{S}{\overset{\|}{Ph_2P}}-S-\overset{O}{\overset{\|}{P}}Ph_2$$

IIIA



$$\overset{S}{\overset{\|}{Ph_2P}}-O-\overset{S}{\overset{\|}{P}}Ph_2$$

IIIB

structure IIIA could be expected to yield either a mixture of diphenylphosphinic acid with the dithio analog or the monothio acid only, depending on which P–S bond was ruptured. Hydrolysis of a material with structure IIIB could produce only diphenylphosphinothioic acid. From the hydrolysis of the anhydride formed in these esterification reactions, diphenylphosphinothioic acid was obtained in a 90% yield.

When a sample of diphenylphosphinodithioic thioanhydride I was oxidized with a large excess of dilute nitric acid, a quantitative yield of diphenylphosphinic acid was obtained. However, when a 6:1 molar ratio was employed, there was obtained, in addition to diphenylphosphinic acid, a 37% yield of the anhydride of diphenylphosphinothioic acid. The melting point of a mixture of this material and the anhydride obtained in the esterification reactions show no depression from the individual melting points. The exact structure of this anhydride is not known. It will be the subject of a future communication.

$$\text{I} + \text{excess } HNO_3(\text{dil.}) \longrightarrow \underset{\text{IV}}{Ph_2POOH} \qquad (7)$$

$$\text{I} + 6HNO_3(\text{dil.}) \longrightarrow \underset{\text{IIIA or IIIB}}{C_{24}H_{20}OS_2P_2} + \text{IV} \qquad (8)$$

Experimental[4]

Diphenylphosphinodithioic Acid.—The diphenylphosphinodithioic acid used in this work was prepared by the method of Higgins, Vogel and Craig.[2] For use in these reactions, the acid was not purified by recrystallization. The neutralization equivalent on different samples of acid varied from 215 to 230 (theory, 224).

Methyl Diphenylphosphinodithioate.—The following procedure describing the preparation of the methyl ester of diphenylphosphinodithioic acid is general for the synthesis of the low molecular weight esters.

Thirty-seven grams (0.15 mole) of diphenylphosphinodithioic acid and 150 ml. of methanol were heated at the reflux temperature for 16 hr. The decrease in acidity of the reaction solution as shown by titration with standard potassium hydroxide solution indicated that 95% of the acid had reacted. Most of the unreacted methanol was removed by distillation. The residue was cooled and a white crys-

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(4) All melting points are uncorrected.

talline product (38 g., 98% crude) was obtained by filtration with suction. An analytical sample prepared by recrystallization from naphtha (60–70°) melted at 82–83°.

t-Butyl **Diphenylphosphinodithioate.**—Diphenylphosphinodithioic acid (50 g., 0.2 mole), 80 ml. (0.8 mole) of *t*-butyl alcohol and 50 ml. of benzene were refluxed at 80° for 16 hr. During this time 4.0 ml. of an azeotrope was separated by means of a reflux trap (theory 3.2 g. of water). Nearly all of the solvent was removed by distillation. The residue was cooled, diluted with ethyl ether and washed with 5% sodium bicarbonate solution, then with water until neutral. The ether was removed by distillation and the solid residue was dissolved in naphtha (60–70°), treated with Nuchar, filtered and the filtrate concentrated. The white needles which separated on cooling were collected by filtration. The product weighed 40 g. (66%) and melted at 92–93°.

Isobutylene was passed into a solution of 50 g. (0.2 mole) of diphenylphosphinodithioic acid in 200 g. of benzene at the reflux temperature for 7 hr. The material was washed with an aqueous 18% solution of sodium bicarbonate. The solvent was removed by distillation at reduced pressure and the residue was recrystallized from naphtha (fraction boiling at 60–70°) to yield 30 g. (50%, no attempt was made to improve on this yield) of white needles melting at 90–92°. A sample of this product mixed with a sample of the product obtained from *t*-butyl alcohol melted at 91–92°.

n-Octyl **Diphenylphosphinodithioate.**—This procedure is representative of the method used for the synthesis of the higher molecular weight esters. Yields were found to be better when the reaction temperature did not exceed 185°.

Diphenylphosphinodithioic acid (250 g., 1.0 mole) and 260 g. (2.0 moles) of *n*-octyl alcohol were heated at 185° for 6 hr. During this time 15 ml. of water was separated by means of a reflux trap. The decrease in acidity of the reaction solution indicated that over 99% of the acid had reacted. This material was washed with 5% sodium bicarbonate solution, then with water until neutral. The excess alcohol was removed by distillation *in vacuo*, the final conditions being 150° (0.5 mm.). The residue, a light yellow liquid, weighed 340 g. (99% crude). A portion (86 g.) of the residue was distilled at reduced pressure. A sample weighing 75 g. (87%) was collected at 197–200° (0.2 mm.).

n-**Octyl Mercaptan.**—*n*-Octyl diphenylphosphinodithioate (182 g., 0.5 mole) was heated under reflux with 600 ml. of aqueous 10% sodium hydroxide solution until a homogeneous reaction mixture resulted. This required about 2 hr. The mixture was cooled; concentrated hydrochloric acid was added to give a *p*H 7 and solid sodium bicarbonate was added until a saturated solution occurred. The material was extracted with ether several times and the organic layers combined. The combined extract was dried over anhydrous sodium sulfate, filtered and the ether removed on a steam-bath. The residue, which weighed 76 g., was distilled. A fraction weighing 52 g. (71%) was collected at 95–98° (33 mm.).

Anal. Calcd. for $C_8H_{18}S$: S, 21.8. Found: S, 21.3.

The 2,4-dinitrophenol thioether derivative was prepared by the procedure of Bost, Turner and Norton[3] and melted at 75–77°. This material showed no melting point depression when mixed with the corresponding derivative of *n*-octyl mercaptan (m.p. 74–76°) prepared by the method of Frank and Smith.[5]

The aqueous layer from the saponification was made acid to a *p*H 3 with hydrochloric acid and filtered. The crude diphenylphosphinothioic acid was air-dried and recrystallized from toluene to give 96 g. (82%) of diphenylphosphinothioic acid which melted at 140–143°.

2-Octyl Diphenylphosphinodithioate (A).—Diphenylphosphinodithioic acid (125 g., 0.5 mole) and 1-octene (168 g., 1.5 moles) were heated with stirring for 3 hr. at 130°. At the end of this time, the mixture was neutral. The excess octene was removed under reduced pressure, the final conditions being 80° (0.5 mm.). The residue weighed 170 g. (99% crude). A small portion (55 g.) was distilled on a short path molecular still. A fraction weighing 31 g. (56%) was collected at 100–110° (0.01–0.015 mm.).

(B).—Diphenylphosphinodithioic acid (125 g., 0.5 mole) and 2-octyl alcohol (165 g., 1.25 moles) were heated at 175–185° for 6 hr. At the end of this period, 8.0 ml. of water had been collected in a reflux trap. The mixture was allowed to cool and was filtered to remove a white solid (A).

The filtrate containing the ester and excess alcohol was concentrated *in vacuo*, the final conditions being 150° (0.5 mm.). A residue, crude ester, weighing 143 g. (83%) was obtained. This product was not distilled but was characterized by saponification to form 2-octyl mercaptan as described below.

The solid (A) was washed with naphtha (fraction boiling at 40–60°) and recrystallized three times from benzene. A white crystalline material weighing 18 g. and melting at 197–198° was obtained.

Anal. Calcd. for $C_{24}H_{20}OP_2S_2$: P, 13.75; S, 14.21; sapn. equiv., 226. Found: P, 13.40; S, 14.30; sapn. equiv., 227.

2-Octyl Mercaptan.—The saponification of 2-octyl diphenylphosphinodithioate (181 g., 0.5 mole) obtained in procedure (A) from the acid and unsaturate was carried out as described previously for the preparation of *n*-octyl mercaptan. A yield of 51 g. (69%) of 2-octyl mercaptan, b.p. 83–85° (27 mm.), was obtained. The 2,4-dinitrophenyl thioether derivative was prepared by the procedure of Bost, Norton and Turner[3] and melted at 47–48°.

The saponification of 181 g. (0.5 mole) of the ester obtained by procedure (B) above gave 50 g. (68%) of 2-octyl mercaptan, b.p. 83–85° (27 mm.). The 2,4-dinitrophenyl thioether melted at 47–48°.

The mixed melting points of the two 2,4-dinitrophenyl thioethers was 47–48° and the mixed melting points with a known 2,4-dinitrophenyl thioether derivative of 2-octyl mercaptan (m.p. 47–48°) showed no depression.

Diphenylphosphinothioic Acid by Hydrolysis of Diphenylphosphinothioic Anhydride.—Diphenylphosphinothioic anhydride (III) (8 g., 0.016 mole) and 60 ml. of 10% aqueous potassium hydroxide were heated at reflux for 4 hr. The reaction mixture was made acid (*p*H 2) with dilute hydrochloric acid and filtered. The solid was air-dried to give 8.8 g. of white powder. The product was recrystallized twice from toluene. The white needles of diphenylphosphinothioic acid weighed 7.4 g. (87%) and melted at 141–143°.

Anal. Calcd. for $C_{12}H_{10}OPS$: P, 13.25; S, 13.68. Found: P, 13.21; S, 13.56.

Preparation of Diphenylphosphinodithioic Thioanhydride (I).—Diphenylphosphinodithioic acid (50 g., 0.2 mole) was heated slowly to 170° for 10 hr. At the end of this time, titration indicated 91% reaction. The mixture was cooled, diluted with 100 ml. of benzene and filtered. The filtrate was washed three times with aqueous 10% sodium bicarbonate, dried azeotropically and diluted with isopropyl alcohol. The solution was allowed to cool and was filtered. The solid material was recrystallized twice from isopropyl alcohol to give 31 g. (67%) of a white product melting at 118–121°.

Anal. Calcd. for $C_{24}H_{20}P_2S_3$: P, 12.90; S, 20.66. Found: P, 13.15; S, 20.55.

Oxidation of Diphenylphosphinodithioic Thioanhydride.—Diphenylphosphinodithioic thioanhydride (10 g., 0.02 mole) was dissolved in 15 ml. of benzene and the solution treated (with shaking) with 15 ml. of aqueous 6 *N* nitric acid. The temperature rose to 40–50° and was maintained for 30 minutes. The white solid was washed several times with cold water and was air-dried to yield 8.4 g. of crude product. A 5-g. sample of this material was washed thoroughly with an aqueous 5% sodium bicarbonate solution and then with water. When this product was dried, it weighed 2.2 g. and melted at 194–197°. A mixed melting point with the by-product from the esterification of diphenylphosphinodithioic acid with 2-octyl alcohol showed no depression.

Anal. Calcd. for $C_{24}H_{20}OP_2S_2$: P, 13.7; S, 14.2. Found: P, 13.3; S, 14.5.

Phenyl Diphenylphosphinothionate (II).—One hundred twenty-five grams (0.5 mole) of diphenylphosphinodithioic acid and 143 g. (1.5 moles) of phenol were heated at 190° for 10 hr. The mixture was cooled and poured into 450 ml. of aqueous 10% sodium hydroxide solution. The solid ester was collected on a suction funnel, thoroughly washed with water and air-dried. It weighed 143 g. (92%), m.p. 118–124°. A sample of this material was recrystallized several times from naphtha (60–70°) to give a product melting at 123–125°.

Anal. Calcd. for $C_{18}H_{15}OPS$: P, 9.98; S, 10.32. Found: P, 9.76; S, 10.41.

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(5) R. L. Frank and P. V. Smith, This Journal, **68**, 2103 (1946).

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

BY RICHARD L. MCCONNELL AND HARRY W. COOVER, JR.

RECEIVED MARCH 21, 1956

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]

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

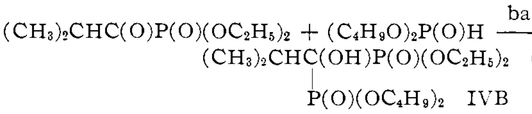
While studying the reaction of acetyl chloride and sodium diethyl phosphite, Arbuzov and Azanovskaya obtained tetraethyl 1-acetoxyethylidenediphosphonate, $CH_3C(OCOCH_3)[P(O)(OC_2H_5)_2]_2$.[15] They postulated that sodium diethyl phosphite added to the carbonyl group of $CH_3C(O)P(O)(OC_2H_5)_2$, initially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

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



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

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).

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