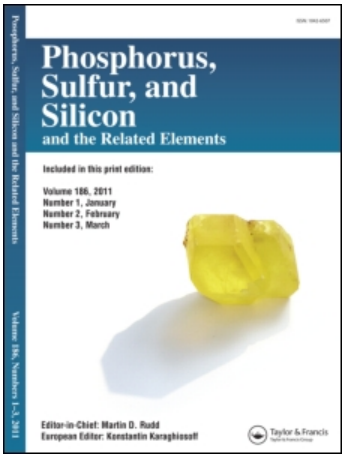

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SYNTHESIS AND CHEMICAL PROPERTIES OF SUBSTITUTED 2-HYDROXY-2-PHOSPHONYLETHANALS AND 1,2-DIHYDROXY-1,2-BISPHOSPHONYLETHANES

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SYNTHESIS AND CHEMICAL PROPERTIES OF SUBSTITUTED 2-HYDROXY-2-PHOSPHONYLETHANALS AND 1,2-DIHYDROXY-1,2-BISPHOSPHONYLETHANES

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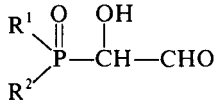
The syntheses of 2-hydroxy-2-(dialkoxyphosphonyl)ethanals **1a–1h,** and of 1,2-dihydroxy-1,2-bis(dialkoxyphosphonyl)ethanes **2a–2h** by reactions of glyoxal with phosphorous acid diesters in acidic medium are reported. The base catalyzed isomerization of 2-hydroxy-2-(dialkoxyphosphonyl)ethanals **1** to formylmethylphosphates **3** was demonstrated by ^{31}P NMR spectroscopy. The stability of 1,2-dihydroxy-1,2-bis-(dialkoxyphosphonyl)ethanes **2** towards bases was demonstrated and interpreted on the basis of their structural features. The reactions of glyoxal with O-(*n*-butyl)phenylphosphonite, diethyl- and diphenylphosphineoxide and the identification of their products are reported as well as the synthesis of 1,2-dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane **2m** by acid-catalyzed hydrolysis of 1,2-dihydroxy-1,2-bis(dialkoxyphosphonyl)ethanes and by hydrogenation of 1,2-dihydroxy-1,2-bis(dibenzyloxyphosphonyl)ethane **2f**. The rate constant of the hydrogenation of **2f** and the pKa values of the 1,2-dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane **2m** are also reported.

INTRODUCTION

In connection with our interest in the development of new organophosphorus flame retardants[1] we carried out the syntheses of substituted 2-hydroxy-2-phosphonylethanals **1** and 1,2-dihydroxy-1,2-bisphosphonylethanes **2**. Moreover, 1,2-dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane **2m,** a promising complexing agent, was synthesized.



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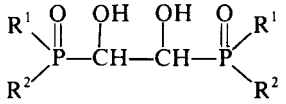


2

1a, 2a: R^1, $R^2 = CH_3O$
1b, 2b: R^1, $R^2 = CH_3CH_2O$
1c, 2c: R^1, $R^2 = (CH_3)_2CHO$
1d, 2d: R^1, $R^2 = n\text{-}C_4H_9O$
1e, 2e: R^1, $R^2 = ClCH_2CH_2O$
1f, 2f: R^1, $R^2 = C_6H_5CH_2O$
1g, 2g: R^1, $R^2 = C_6H_{11}O$
1h, 2h: R^1, $R^2 = C_6H_5O$
1i, 2i: $R^1 = n\text{-}C_4H_9O$, $R^2 = C_6H_5$
2k: R^1, $R^2 = C_2H_5$
2l: R^1, $R^2 = C_6H_5$
2m: R^1, $R^2 = OH$

* All correspondence to this author.

RESULTS AND DISCUSSION

The synthesis of 2-hydroxy-2-(dialkoxyphosphonyl)ethanals **1a–1h** and of 1,2-dihydroxy-1,2-bis(dialkoxyphosphonyl)ethanes **2a–2h** were carried out in acid medium by reacting glyoxal or glyoxal trimer dihydrate, which releases glyoxal in situ,[2] or vacuum condensed glyoxal aqueous solutions with phosphorous acid diesters neat or in the presence of solvent according to the following reactions:

$$OHCCHO + (RO)_2P(O)H \rightleftharpoons (RO)_2P(O)CH(OH)CHO$$

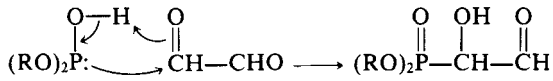
1a–1h

$$(RO)_2P(O)CH(OH)CHO + (RO)_2P(O)H \longrightarrow (RO)_2P(O)CH(OH)CH(OH)P(O)(OR)_2$$

2a–2h

Addition reactions of phosphorous acid diesters to other carbonyl compounds catalyzed by bases have been previously reported.[3–6] Reactions taking place in the absence of catalyst with compounds possessing a strongly electrophilic carbonyl group such as of chloral[7,8] have also been reported.[9] On the other hand addition reactions taking place under acidic conditions have been scarce in the literature.[10] In the present investigation all the reactions were carried out under acidic conditions resulting from the presence in the reaction media of phosphorous acid diesters and of the products of their partial hydrolysis[11] occuring during the course of the reactions.

It is known that in an acid medium the glyoxal carbonyl can be protonated to form the corresponding conjugate acid[12] thus facilitating the nucleophilic attack by phosphorous acid diesters. On the other hand, phosphorous acid diesters are found in two equilibrating tautomeric forms $(RO)_2P(O)H$ and $(RO)_2POH$.[13a] Spectroscopic data have shown that the pentavalent phosphorus structure predominates.[14,15] It has also been found that the conversion of the pentavalent phosphorus structure to the trivalent structure is catalyzed by acids.[16,17] This conversion favors the nucleophilic addition to the carbonyl since this reaction is believed to occur via an initial trivalent phosphorus attack followed by a proton transfer that stabilizes the adduct.[13b]



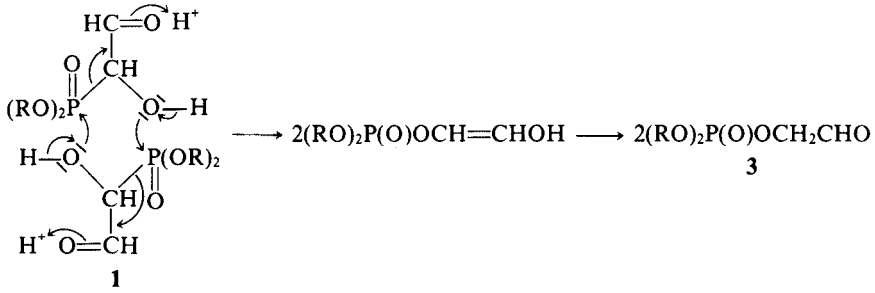
1a–1h

Substituted 2-hydroxy-2-phosphonylethanals **1a–1h**

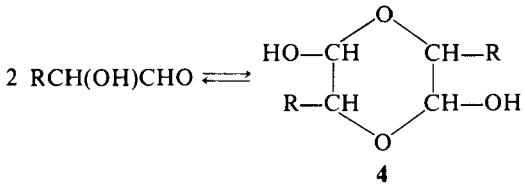
Attempts to isolate the phosphonylethanals **1a–1h** by vacuum distillation were unsuccessful due to their decomposition. A number of investigators have previously reported the tendency of some α-hydroxyphosphonates to decompose.[4,18,19] The IR spectra of the reaction mixtures revealed the decrease of the sec. phosphite concentration during the reaction and the generation of a hydrogen bonded carbonyl (6.11μ) assigned to the 2-hydroxy-2-phosphonylethanals **1a–1h**.

The ^{31}P NMR spectra of the reaction mixtures revealed the presence of **1a–1h** and of minor amounts of **2a–2h** in addition to small amounts of other phosphorus nuclei assigned to hydrolysis products. The bisphosphonylethanes **2a–2h** were isolated and identified. The spectra indicated also the presence of the corresponding formylmethylphosphates **3** arising from the isomerizations of the phosphonylethanals **1**. Thermal and base catalyzed isomerizations of other α-hydroxyphosphonates to

phosphates have been previously reported.[20–25] Further evidence for the presence of **1** and **3** in the mixture was derived by recording the ^{31}P NMR spectrum of the product after its treatment with Et_3N at 50°C for 10 min. It revealed that the peak assigned to **1** vanished and that the peak assigned to **3** increased in intensity presumably due to isomerization of **1** to **3**. A possible mechanism for the isomerization of **1** to **3** is the following:

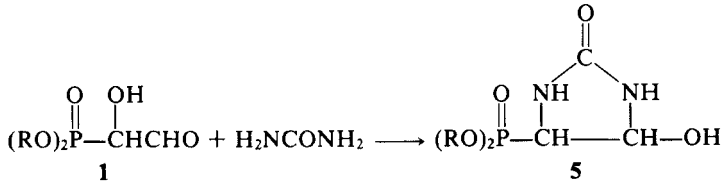


It has been previously observed that α-hydroxyaldehydes exist in equilibrium with their dimer cyclic structures **4**.[26]



The observed IR absorption bands do not indicate the presence of structures such as **4** in the reaction mixture.

The formation of the ethanals **1** was demonstrated by their reaction with urea.



The corresponding 4-hydroxy-5-phosphonyl-2-imidazolidinones **5** were isolated in good overall yields as shown in Table I and were identified.[1]

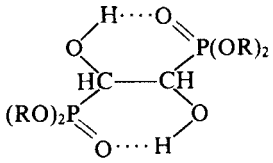
The 2-hydroxy-2-(dialkoxyphosphonyl)ethanals **1** were obtained in much higher yields than the 1,2-dihydroxy-1,2-bis(dialkoxyphosphonyl)ethanes **2**, even in the presence of excess sec. phosphites. This observation leads to the conclusion that the initial addition of one sec. phosphite to the strongly electrophilic carbonyl of the glyoxal occurs more readily than the subsequent addition of a second molecule of diester to the carbonyl of the phosphonylethanal **1** produced in the first step.

It was also observed that more vigorous conditions led to partial isomerization of the ethanal **1** to formylmethyl phosphate **3** discussed above and to some other side reactions. These reactions consumed the ethanal in competition to the formation of the bisphosphonyl product **2**.

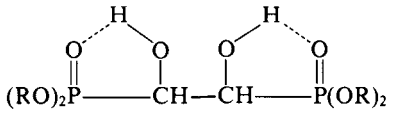
Substituted 1,2-dihydroxy-1,2-bisphosphonylethanes **2**

The 1,2-dihydroxy-1,2-bis(dialkoxyphosphonyl)ethanes **2** were obtained in somewhat higher yields when the reactions of glyoxal trimer dihydrate with sec. phosphites were carried out under a mol ratio 0.33:2.1 respectively. The bisphosphonyl products **2** were isolated and identified (Tables II, III and IV).

The infrared stretching frequencies of the hydroxyls and of the P=O groups of **2** shown in Table III are found in the region 2.98–3.13μ and in the region 8.07–8.31μ respectively, while the free hydroxyl and P=O group absorb at somewhat lower wavelengths.[27] The higher absorption wavelengths of **2** are attributed to intramolecular hydrogen bonding between the hydroxyl and the P=O group. Examination of models of **2** indicated that intramolecular hydrogen bonding between the hydroxyl and the P=O group β to each other results to less strained structures and less steric hindrance. Such hydrogen bonding would lead to two locked six-membered rings (structure **6**) and would be favored than the intramolecular H-bonding between vicinal hydroxyl and P=O groups (structure **7**).



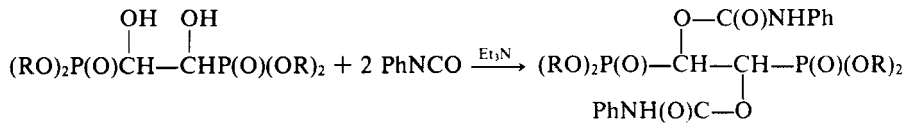
6



7

It should be noted that **2** contain two identical asymmetric centers and therefore they should be formed as a mixture of D, L racemic and meso stereoisomers.

The structures of some of **2** were further confirmed by the preparation[28] and identification of their 1,2-bisoxycarbanilino derivatives **8**.



8

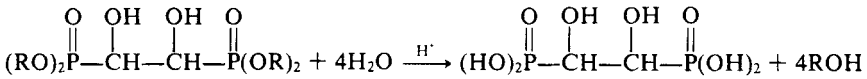
It was observed that in comparison to the esters **1a–1h** the tetraesters **2a–2h** are relatively more stable towards heating and towards Et_3N and they are not isomerized. Analogous thermal stability has been observed in the case of [1-(diethoxyphosphonyl)-1-hydroxyethyl]ethyl (or methyl) phosphonic acid esters.[29]

From the reaction of glyoxal trimer dihydrate with O-(*n*-butyl)phenylphosphonite the bisphosphinylethane **2i** was isolated and identified and the ethanal **1i** formed was converted to its 2-imidazolidinone by reaction with urea after previous separation of **2i**. From the reaction of aqueous glyoxal with diethyl- and diphenylphosphineoxide only the bisoxophosphino products **2k** and **2l** were isolated in high yields and they were identified spectroscopically. The 1,2-bisoxycarbanilino derivative of **2k** was also prepared. Reactions of certain dialdehydes with primary phosphine oxides leading to addition to both carbonyls have been reported[30] as well as some addition reaction of secondary phosphine oxides to single carbonyl compounds[31,32] and to glyoxal.[33] It appears from the results that the yields of the bisphosphonylethane products **2** increase following the trend of increasing nucleophilicity of the phosphorus reactants in the order hydrogen phosphites, hydrogenphosphonites, secondary phosphine oxides.

The products **2k** and **2l** were found to be relatively stable towards triethylamine in agreement to the stability of **2a–2h** presumably due to their locked conformations of type **6**.

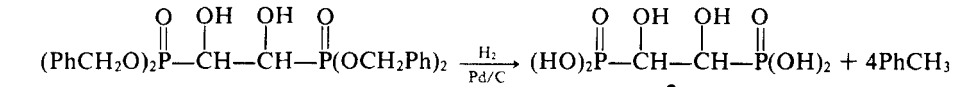
1,2-Dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane **2m**

1,2-Dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane **2m** was obtained in a nearly quantitative yield by acid catalyzed hydrolysis of 1,2-dihydroxy-1,2-bis(dialkoxyphosphonyl)ethanes.



2m

Alternatively **2m** was prepared by hydrogenation under atmospheric pressure of 1,2-dihydroxy-1,2-bis(dibenzyloxyphosphonyl)ethane **2f** in the presence of 10% palladium on carbon at 20°C.



2m

The kinetics of the hydrogenation was found to be zero order. No differentiation was observed between the rate constants of the possible hydrogenation steps.

EXPERIMENTAL

Melting points were measured on a Büchi apparatus and are uncorrected. Infrared spectra were determined on a Perkin–Elmer Model 137 Infracord Spectrophotometer. ^{1}H NMR spectra were obtained at 60.0 MHz with a Varian T-60A spectrometer. Tetramethylsilane was used as an internal standard in $CDCl_3$ and DMSO-d_6 solutions and 3-trimethylsilylpropane sulfonate as an internal standard in D_2O solutions. ^{31}P NMR spectra were obtained at 24.3 MHz with a Varian T-60A spectrometer connected to a V-2048 Signal Averager of Varian-Tracor. Some ^{31}P NMR spectra were obtained at 40.5 MHz with a Varian XL-100 spectrometer. All NMR spectra were recorded on saturated solutions and at 30°C, normal probe temperature. ^{31}P chemical shifts are reported in ppm (δ) with respect to 85% H_3PO_4. Elemental analyses were carried out by Dr. H. Mantzos of the Microanalytical Laboratory of the National Hellenic Research Foundation in Athens, Greece.

General procedure for the synthesis of 2-hydroxy-2-(dialkoxyphosphonyl)ethanals **1a–1h**

Glyoxal trimer dihydrate and phosphorous acid diester under a mol ratio 0.33:1.1 respectively together with 750 ml of dioxane per mol of glyoxal trimer dihydrate were introduced in a flask equipped with a side condenser. The reaction mixture was boiled under stirring and the water released was distilled together with dioxane at atmospheric pressure in a slow rate. The reaction time for the various phosphorous acid diesters is given in Table 1. At the end of the reaction time the solution obtained was cooled to 40°C and the volatile components were removed by a rotary evaporator at 40°C under 12 mm Hg. The IR and ^{31}P NMR spectra of the reaction mixture and of the viscous liquid product were recorded. The IR spectrum for example of the mixture of the reaction of glyoxal trimer dihydrate with diethyl phosphite revealed the decrease of the concentration of the phosphite (decrease of the intensity of the P—H bond at 4.12μ) and the appearance of a new band at 6.11μ assigned to the carbonyl of 2-hydroxy-2-(diethoxyphosphonyl)ethanal **1b** hydrogen bonded to the hydroxyl (3.13μ) and the characteristic bands of P=O (8.22μ) and P—O—C (9.25–9.75μ). The ^{31}P NMR spectrum of the viscous reaction product with decoupling from the hydrogens in addition to other phosphorus nuclei in minor amounts consisted of the peaks: −0.9 $(EtO)_2P(O)OCH_2CHO$, 4.7 $P(OH)_3$, 6.1 $(EtO)P(O)(H)OH$, 7.9 $(EtO)_2P(O)H$[24a], 11.9 $(EtO)_2$-

P(O)CH(OH)CHO, 16.3 unassigned, 23.7 $(EtO)_2P(O)CH(OH)CH(OH)P(O)(OEt)_2$. The ^{31}P NMR spectrum of the same reaction product recorded after treatment with a few drops of $(Et)_3N$ for 10 min at 50°C showed the absence of the resonance peak at 11.9 ppm $(EtO)_2P(O)CH(OH)CHO$ and the increase of the intensity of the resonance peak at −0.9 ppm $(EtO)_2P(O)OCH_2CHO$.

The viscous liquid products were caused to react with urea to afford the corresponding 4-hydroxy-5-phosphonyl-2-imidazolidinones **5** which were isolated and identified.[1] Their overall yields are shown in Table I.

General procedure for the synthesis of 1,2-dihydroxy-1,2-bis(dialkoxyphosphonyl)ethanes **2a–2h**

Glyoxal trimer dihydrate and phosphorous acid diester under a mol ratio 0.33:2.1 respectively together with 750 ml of dioxane per mol of glyoxal trimer dihydrate were introduced in a flask equipped with a side condenser. The mixture was boiled for a time period, during which dioxane was distilled at a slow rate together with the released water. The solution obtained was cooled to 40°C and the volatile components were removed by a rotary evaporator at 40°C and under 12 mm Hg. A dilution solvent was added to the remaining liquid and upon cooling at 2°C for 12 hours the esters **2a–2h** precipitated as white solids. The reaction times, the dilution solvents, and the yields of 1,2-dihydroxy-1,2-bis(dialkoxyphosphonyl)ethanes **2a–2h** are given in Table II. The crystallization solvents, the melting points of the analytical samples as well as the elemental analyses of **2a–2h** are given in Table III. Their ^1H NMR and ^{31}P NMR spectral data as well as their characteristic infrared absorption bands are given in Table IV. A solution of **2b** in chloroform refluxed for 5 hours in the presence of Et_3N did not show any change in its ^{31}P NMR spectrum and **2b** was recovered unchanged.

2-Hydroxy-2-(diethoxyphosphonyl)ethanal and 1,2-dihydroxy-1,2-bis(diethoxyphosphonyl)ethane from gaseous glyoxal

Gaseous glyoxal was prepared by heating at about 120°C a mixture of phosphorus pentoxide and glyoxal trimer dihydrate in a mol ratio 1:1.2 respectively. The gaseous glyoxal was passed into 41.5 g (0.30 mol) of diethyl phosphite at 60°C stirred in a reaction flask until 4.0 g (69.0 mmol) of glyoxal were absorbed. The reaction was exothermic and the temperature of the reaction mixture increased to 75°C. Most of the unreacted diethyl phosphite (28.5 g, 0.21 mol) was removed under vacuum and the remaining viscous liquid was diluted with ether. 1,2-Dihydroxy-1,2-bis(diethoxyphosphonyl)ethane precipitated (1.45 g) as a white solid upon cooling at 2°C for 12 hours. The residue after the removal of the ether was treated with 4.14 g of urea in 20 ml of water at 50°C for 1 hour to give 4.0 g (25.0%) of 4-hydroxy-5-diethoxyphosphonyl-2-imidazolidinone.

2-Hydroxy-2-(diethoxyphosphonyl)ethanal from aqueous solution of glyoxal

The water was removed from a 30% aqueous solution of glyoxal by a rotary evaporator at 50°C. The remaining viscous liquid was diluted with 250 ml of dioxane per mol of glyoxal and 1.1 mol of diethylphosphite per mol of glyoxal was added to the solution. The reaction mixture was boiled for 35 min in a reaction flask equipped with a side condenser during which time the remaining water was distilled together with a part of the dioxane at atmospheric pressure. The reaction mixture was cooled at 40°C and the volatile components were removed by a rotary evaporator at 40°C and 12 mm Hg. The 2-hydroxy-2-(diethoxyphosphonyl)ethanal **2b** contained in the residue gave 4-hydroxy-5-diethoxyphosphonyl-2-imidazolidinone in a 40% overall yield by reaction with equimolar quantity of urea in water at 50°C for 1 hour.

TABLE I

Reaction times of glyoxal trimer dihydrate with $(RO)_2P(O)H$ for preparation of 2-hydroxy-2-(dialkoxyphosphonyl)ethanals **1a–1h** and overall yields of the corresponding 4-hydroxy-5-(dialkoxyphosphonyl)-2-imidazolidinones **5**

R	CH_3	C_2H_5	i-C_3H_7	n-C_4H_9	CH_2CH_2Cl	$CH_2C_6H_5$
Reaction time (min)	25	35	55	60	25	30
Overall yield in % of 4-hydroxy-5-(dialkoxyphosphonyl)-2-imidazolidinones **5**	20	52	45	21	46	15

TABLE II

Conditions and results of the reactions of glyoxal trimer dihydrate with phosphorous acid diesters for the synthesis of $(RO)_2P(O)CH(OH)CH(OH)P(O)(OR)_2$

R	CH_3	C_2H_5	*i*-C_3H_7	*n*-C_4H_9	CH_2CH_2Cl	C_6H_5	$CH_2C_6H_5$	C_6H_{11}
Reaction time (min)	40	50	60	60	55	15	25	90
Dilution solvent	Acetonitrile	Ether	Ether	Ether	Acetonitrile	Acetone	Ether	Ether
Yield of 1,2-dihydroxy-1,2-bisphosphonylethanes (%)	4.0	6.3	4.2	13.4	6.7	2.8	3.1	2.3

TABLE III

Melting points and analysis data of $(RO)_2P(O)CH(OH)CH(OH)P(O)(OR)_2$

R	Formula	Recrystallization solvent	MP (°C)	Analysis % Calculated C	Calculated H	Found C	Found H
CH_3	$C_6H_{16}O_8P_2$	N,N-Dimethylformamide	190–192 (decomp.)	25.91	5.80	26.03	5.84
C_2H_5	$C_{10}H_{24}O_8P_2$	Dioxane	175–177	35.93	7.24	35.64	7.03
i-C_3H_7	$C_{14}H_{32}O_8P_2$	Acetonitrile/chloroform 6:1 vol/vol	186–188	43.07	8.26	42.98	8.32
n-C_4H_9	$C_{18}H_{40}O_8P_2$	Acetonitrile	170–172	48.42	9.03	48.26	8.82
CH_2CH_2Cl	$C_{10}H_{20}Cl_4O_8P_2$	Dimethylsulfoxide	195–197	25.44	4.27	25.76	4.29
C_6H_5	$C_{26}H_{24}O_8P_2$	Dioxane	208–209	59.32	4.60	59.12	4.50
$CH_2C_6H_5$	$C_{30}H_{32}O_8P_2$	Chloroform	190–192	61.85	5.54	61.75	5.70
C_6H_{11}	$C_{26}H_{48}O_8P_2$	N,N-Dimethylformamide	209–210 (decomp.)	56.71	8.79	56.84	8.33

2-Hydroxy-2-[(n-*butoxy*)*phenylphosphinyl*]*ethanal* **1i**
and 1,2-dihydroxy-1,2-bis[(n-*butoxy*)*phenylphosphinyl*]*ethane* **2i**

4.20 g (20 mmol) of glyoxal trimer dihydrate, 11.89 g (60 mmol) of O-*n*-butylphenylphosphonite and 40 ml of dioxane were introduced in a flask equipped with a side condenser. The mixture was boiled under stirring for 20 min, during which time the water released was distilled with dioxane at atmospheric pressure in a slow rate. The remaining solution was cooled to 40°C and its volatile components were removed by a rotary evaporator at 40°C and 12 mm Hg. The viscous liquid obtained was diluted with ether and upon cooling at 2°C for 12 hours, 1,2-dihydroxy-1,2-bis[(*n*-butoxy)phenylphosphinyl]ethane **2i** precipitated as a white solid (1,2 g, 9.0% based on the phosphonite, mp 180–184°C). Recrystallizations from chloroform acetonitrile (3:1 vol/vol) gave an analytical sample: mp 190–192°C.

Anal. Calcd for $C_{22}H_{32}O_6P_2$: C 58.14, H 7.09.
Found: C 58.10, H 7.07.

The remaining liquid product (14.2 g) after the removal of ether contained 2-hydroxy-2-[(*n*-butoxy) phenylphosphinyl]ethanal **1i**; reaction with urea gave 4-hydroxy-5-[(*n*-butoxy)phenylphosphinyl]-2-imidazolidinone in a 28% overall yield.

The reaction of glyoxal trimer dihydrate with O-*n*-butylphenylphosphonite repeated under a mol ratio 1:6 respectively and under the same other conditions gave 1,2-dihydroxy-1,2-bis[(*n*-butoxy)phenylphosphinyl]ethane **2i** in a 16.0% yield.

1,2-Dihydroxy-1,2-bis(*diethyloxophosphino*)*ethane* **2k**

2.1 g of 30% aqueous glyoxal solution (15 mmols glyoxal), 3.18 g (30 mmols) of diethylphosphineoxide and 10 ml of water were introduced in a flask. The initial pH of the reaction mixture was 2. Evolution of heat was observed. The mixture was heated for 30 min at 50°C. A white solid precipitated upon cooling at 2°C and it was separated by filtration (2.5 g, 62.0%, mp 178–179°C). Recrystallizations from acetonitrile/chloroform (2:1 vol/vol) gave an analytical sample:mp 181–183°C; ^{31}P nmr ($CDCl_3$) 61.2 ppm; ^1H nmr ($CDCl_3$) δ 5.76 (d, 2, J = 20, PCH), 4.33 (broad, 2, OH), 1.90 (m, 8, PCH_2), 1.30 (m, 12, CH_3); IR (KBr) 3.28 (vs), 3.59 (m), 3.78 (w), 6.87 (s), 7.13 (s), 7.94 (m), 8.16 (w), 8.76 (vs), 9.49 (vs), 9.68 (s), 12.57 (s), 13.03 (s), 13.52 (m), 14.42 (w).

Anal. Calcd for $C_{10}H_{24}O_4P_2$: C 44.44, H 8.95.
Found: C 44.53, H 8.95.

1,2-Dihydroxy-1,2-bis(*diphenyloxophosphino*)*ethane* **2l**

7.73 g of 30% aqueous glyoxal solution (40 mmols glyoxal), 16.17 g (80 mmols) of diphenyl phosphineoxide and 40 ml of acetonitrile were introduced in a flask. The initial pH of the reaction mixture was 2. The mixture was heated under stirring for 30 min at 40°C. The precipitated solid was separated by filtra-

TABLE IV

^{1}H NMR, ^{31}P NMR and IR data for $(RO)_2P(O)CH(OH)CH(OH)P(O)(OR)_2$

R	^{1}H chemical shift δ, ppm	Multiplicity of peak	Number of protons	Coupling constant (cps)	Assignments	Solvent	^{31}P chemical shift δ, ppm	IR absorption bands (μ)		
								OH	P=O	P—O—C
CH_3	6.02	broad	2		OH	DMSO-d6	26.6	3.06	8.10	9.10–9.58
	3.97	m	2		PCH					
	3.60	m	12		OCH_3					
C_2H_5	4.93	broad	2		OH	$CDCl_3$	22.6	3.13	8.22	9.25–9.75
	4.23	m	10		PCH and OCH_2					
	1.35	t	12	7.5	CH_3					
i-C_3H_7	4.75	m	4		OCH	$CDCl_3$	22.3	2.98	8.07	9.24–10.12
	4.33	d of m	2	11.5	PCH					
	4.10	broad	2		OH					
	1.37	d	24	6.0	CH_3					
n-C_4H_9	4.91	broad	2		OH	$CDCl_3$	22.6	3.13	8.23	9.32–10.15
	4.17	m	10		PCH and OCH_2					
	1.58	m	16		CH_2					
	0.93	t	12	6.0	CH_3					
$ClCH_2CH_2$	6.25	broad	2		OH	DMSO-d6	25.5	3.12	8.13	9.00–9.88
	4.15	m	10		PCH and OCH_2					
	3.75	t	8	5.0	CH_2Cl					
$CH_2C_6H_5$	7.30	m	20		C_6H_5	DMSO-d6	25.1	3.13	8.24	9.35–10.18
	6.33	broad	2		OH					
	4.93	m	8		OCH_2					
	4.18	m	2		PCH					

tion (16.64 g, 90.0%, mp 211–214°C). Recrystallizations from dimethylsulfoxide/acetonitrile (3:2 vol/vol) gave an analytical sample: mp 216–217°C; ^{31}P NMR (CF_3COOH) 44.5; ^{1}H NMR (CF_3COOH) δ 7.37–6.50 (m, 20, C_6H_5), 4.70 (m, 2, PCH); IR (KBr) 3.03 (s), 3.53 (w), 6.71 (w), 6.91 (s), 8.53 (vs), 9.00 (s), 9.35 (s), 9.52 (m), 13.47 (s), 13.91 (s), 14.35 (s).

Anal. Calcd for $C_{26}H_{24}O_4P_2$: C 67.53 H 5.23
Found: C 67.42 H 5.34

1,2-Bis(oxycarbanilino)-1,2-bis(diethoxyphosphonyl)ethane **8**, (R = Et)

0.56 g (1.7 mmol) of 1,2-dihydroxy-1,2-bis(diethoxyphosphonyl)ethane, 0.44 g (3.7 mmol) of phenylisocyanate, 30 ml of anhydrous acetonitrile and a few drops of triethylamine as catalyst were refluxed under stirring for 40 min. A white solid precipitated upon cooling which was separated by filtration (0.62 g, 64.5%, mp 235–236°C). Recrystallizations from acetonitrile/chloroform (6:1 vol/vol) gave an analytical sample: mp 236–237°C; IR (KBr) 3.03 (m), 5.67 (vs), 6.17 (s), 6.40 (s), 6.59 (w), 6.87 (s), 7.53 (m), 7.97 (vs), 8.20 (vs), 9.20 (s), 9.60 (s), 10.07 (m), 10.36 (m), 12.10 (w), 13.08 (s), 14.32 (w).

Anal. Calcd for $C_{24}H_{34}N_2O_{10}$: C 50.35, H 5.16, N 4.89.
Found: C 49.91, H 5.31, N 4.72.

1,2-Bis(oxycarbanilino)-1,2-bis(diethyloxophosphino)ethane

0.76 g (2.8 mmol) of 1,2-dihydroxy-1,2-bis(diethyloxophosphino)ethane, 0.73 g (6.2 mmol) of phenylisocyanate, 15 ml of anhydrous chloroform and a few drops of triethylamine as catalyst were refluxed under stirring for 40 min. A white solid precipitated upon cooling, which was separated by filtration (0.98 g, 68.4%, mp 204–208°C). Recrystallizations from N,N-dimethylformamide gave an analytical sample: mp 206–208°C (decomposition); IR (KBr) 3.25 (s), 5.72 (s), 6.17 (s), 6.55 (m), 6.87 (s), 7.50 (w), 7.63 (w), 8.15 (s), 8.43 (s), 8.68 (s), 9.35 (s), 9.60 (m), 10.33 (w), 10.84 (w), 13.00 (s).

Anal. Calcd for $C_{24}H_{34}N_2O_6$: C 56.69, H 6.74, N 5.51.
Found: C 56.34, H 6.87, N 5.40.

1,2-Dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane **2m** *by acid-catalyzed hydrolysis of 1,2-dihydroxy-1,2-bis(diethoxyphosphonyl)ethane* **2b**

A 0.18 molar solution of 1,2-dihydroxy-1,2-bis(diethoxyphosphinyl)ethane in 10% hydrochloric acid was refluxed for two hours. After removal of the volatile components of the mixture under vacuum a white solid was obtained (0.57 g, 95.0%, mp 204–206°C decomposition). Recrystallizations from methanol/ether (8:2 vol/vol) gave an analytical sample: mp 209–211°C (decomposition), ^{31}P NMR (D_2O) 20.3 ppm; ^{1}H NMR (D_2O) δ 4.16 (d, 2, J = 4, PCH); IR (KBr) 3.00–3.80 (s), 4.20 (w), 7.07 (w), 7.70 (w), 8.07 (m), 8.57 (s), 8.87 (w), 9.32 (vs), 9.53 (w), 9.87 (m), 10.51 (s), 10.66 (s), 12.81 (w), 13.60 (m). $pK_{a1,2} = 5.94$, $pK_{a3} = 8.86$ and $pK_{a4} = 11.96$.

Anal. Calcd for $C_2H_8O_8P_2$: C 10.82, H 3.63.
Found: C 10.77, H 3.85.

1,2-Dihydroxy-1,2-bis(dihydroxyphosphonyl)ethane **2m** *by hydrogenation of 1,2-dihydroxy-1,2-bis(dibenzyloxyphosphonyl)ethane* **2f**

202 mg of recrystallized 1,2-dihydroxy-1,2-bis(dibenzyloxyphosphonyl)ethane, 20 ml of methanol and a small quantity of catalyst, 10% palladium on carbon, were introduced in a hydrogenation flask. The hydrogenation was carried out under atmospheric pressure at room temperature and under stirring of the dispersion until no more hydrogen was taken up. The volume of hydrogen consumed was 94% of theoretical. The initially heterogeneous reaction mixture became a homogeneous solution. After the filtration of the catalyst and the removal of the volatile components under vacuum a white solid was obtained (66.5 mg, 86.4%), having mp 204–206°C (decomposition). Recrystallizations from methanol/ether gave an analytical sample (mp 209–211°C, decomposition) with values correctly for $C_2H_8O_8P_2$. The hydrogenation rate constant K calculated on the basis of the kinetic equation: $dV_{H_2}/dt = K$ is 1.358 10^{-4} mol min^{-1} at 20°C.

An aqueous solution of an analytical sample of **2m** was titrated with 1 N aqueous solution of potassium hydroxide. Since the first inflection point was found to correspond to two mols of potassium hy-

droxide to one mol of **2m** this point is taken to correspond to the neutralization of two hydroxphosphonyl protons. The pKa values thus determined at 20°C are: $pK_{a1,2} = 5.94$, $pK_{a3} = 8.86$ and $pK_{a4} = 11.96$.

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