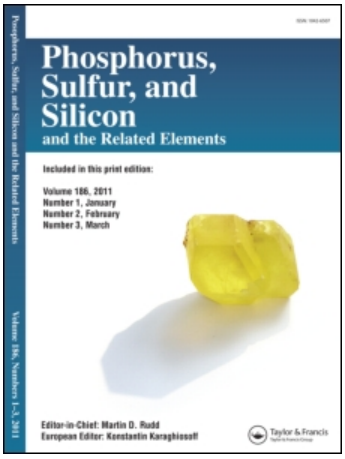

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF SUBSTITUTED N-[(PHOSPHONYL)METHYL]-2-IMIDAZOLIDINONES AND N-[(PHOSPHONYL)METHYL]-2-PYRROLIDINONE

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To cite this Article Mikroyannidis, John A.(1982) 'SYNTHESIS OF SUBSTITUTED N-[(PHOSPHONYL)METHYL]-2-IMIDAZOLIDINONES AND N-[(PHOSPHONYL)METHYL]-2-PYRROLIDINONE', Phosphorus, Sulfur, and Silicon and the Related Elements, 12: 2, 249 — 258
To link to this Article: DOI: 10.1080/03086648208077453
URL: http://dx.doi.org/10.1080/03086648208077453

Phosphorus and Sulfur, 1982, Vol. 12, pp. 249-258
0308-664X/82/1202-0249/$06.50/0

SYNTHESIS OF SUBSTITUTED N-[(PHOSPHONYL)METHYL]-2-IMIDAZOLIDINONES AND N-[(PHOSPHONYL)METHYL]-2-PYRROLIDINONE

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(*Received September 17, 1981; in final form October 16, 1981*)

2-Imidazolidinone or 2-imidazolidinethione reacts with aldehydes and phosphorous acid triesters to form substituted 1-[(phosphonyl)methyl]-2-imidazolidinones and 1,3-bis[(phosphonyl)methyl]-2-imidazolidinones or their thio-analogous compounds. 2-Pyrrolidinone reacts in the same way to form substituted 1-[(phosphonyl)methyl]-2-pyrrolidinone. Acid catalysis promotes these reactions in some cases. Triaryl phosphites are more reactive than trialkyl phosphites in this process. The substituted 1-[(phosphonyl)-methyl]-2-imidazolidinones undergo an acid-catalyzed hydrolysis of their phosphonyl ester groups more readily than the corresponding substituted 1,3-bis[(phosphonyl)methyl]-2-imidazolidinones.

Flammability has been recognized as an increasingly important social and scientific problem. The development of flame-retardant polymeric materials is mainly succeeded by using organophosphorus compounds which are either added in the polymers during their moulding or attached on them with chemical bonds.[1,2] Consequently, the synthesis of organophosphorus compounds, which may be used for reduction of polymers flammability, is very attractive.

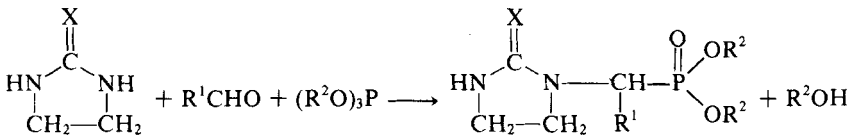
The present investigation deals with the synthesis of substituted N-[(phosphonyl)-methyl]-2-imidazolidinones. Previous attempts to prepare substituted N-phosphonyl-ureas have been reported.[3] The resulting compounds, which have N—P bond, present less than the desired degree of hydrolytic stability. Moreover, such compounds are prepared through the use of dangerously unstable N-chlorourea intermediate. For these reasons urea derivatives in which the phosphonyl group is attached to the nitrogen atoms of ureas through carbon atom have been suggested.[4-16]

Synthesis, structure identification and hydrolysis of substituted N-[(phosphonyl)-methyl]-2-imidazolidinones and N-[(phosphonyl)methyl]-2-pyrrolidinone are shown in this investigation. The phosphorus-containing compounds mentioned above may be used as flame-retardants for some polymers and also as biologically active materials.

RESULTS AND DISCUSSION

The synthesis of substituted 1-[(phosphonyl)methyl]-2-imidazolidinones (**1**) and 1,3-bis[(phosphonyl)methyl]-2-imidazolidinones (**2**) is carried out by reaction of 2-imidazolidinone with aldehydes and phosphorous acid triesters. When the employed mole ratio of the reactants 2-imidazolidinone/aldehyde/phosphorous acid triester is close to 1 : 1 : 1 respectively, the predominant reaction products are compounds **1**, while when the mole ratio of the reactants is close to 1 : 2 : 2 respectively, the predominant reaction products are compounds **2**. The thio-analogous com-

pounds are synthesized by reaction of 2-imidazolidinethione instead of 2-imidazolidinone. Substituted 1-[(phosphonyl)methyl]-2-pyrrolidinone (**3**) is synthesized in the same way. Synthesis reactions for these compounds are given in Scheme 1. The



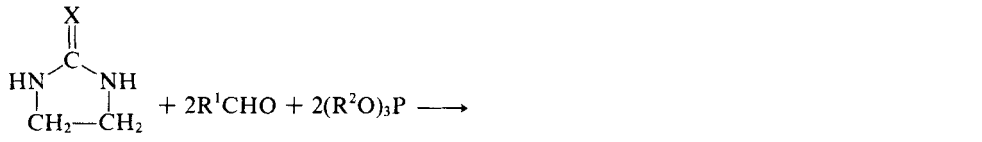
1

1a: R^1, R^2=C_6H_5, X=O

1b: R^1=O·CH:CH·CH:C, R^2=C_6H_5, X=O

1c: R^1=C_6H_5, R^2=$ClCH_2CH_2$, X=O

1d: R^1, R^2=C_6H_5, X=S



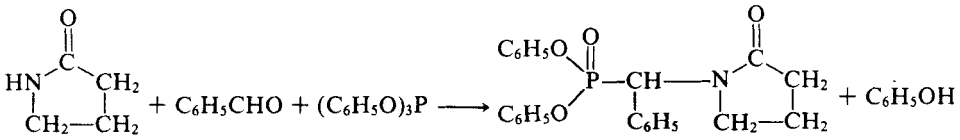
2

2a: R^1, R^2=C_6H_5, X=O

2b: R^1=O·CH:CH·CH:C, R^2=C_6H_5, X=O

2c: R^1=CH_3, R^2=C_6H_5, X=O

2d: R^1, R^2=C_6H_5, X=S



3

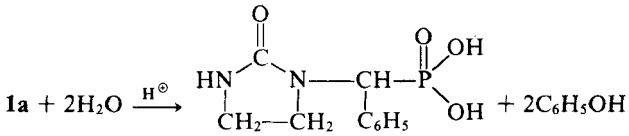
SCHEME 1

reactions are completed when the mixture of the three reactants is heated to about 90–110°C for 1–1.5 hours. If the reactions are exothermic, the gradual addition of aldehyde to the mixture of 2-imidazolidinone and phosphorous acid triester is preferred. Addition of an acid catalyst, such as boron trifluoride etherate or anhydrous acetic acid, promotes these reactions in some cases.

G. H. Birum[12–16] studied the reactions of acyclic ureas with aldehydes and phosphorous acid triesters. He reported that triaryl phosphites are more reactive than trialkyl phosphites in this process.[12] Our results are in agreement. Specifically, it is found that the reaction of 2-imidazolidinone with an aldehyde, such as acetaldehyde or benzaldehyde, and with a trialkyl phosphite, such as trimethyl phosphite,

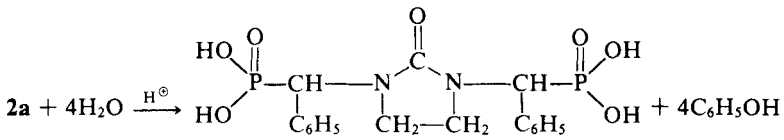
yields mainly a polymer product from the reaction of 2-imidazolidinone with aldehyde. On the other hand, the desired phosphonate is formed to a very small extent, even if an acid catalyst is used. Tris(2-chloroalkyl)phosphites are less reactive than triaryl phosphites but more reactive than unsubstituted trialkyl phosphites.

It is also found that the substituted 1-[(phosphonyl)methyl]-2-imidazolidinones (**1**) are hydrolyzed in the presence of acids more readily than the corresponding 1,3-bis[(phosphonyl)methyl]-2-imidazolidinones (**2**), which conformes with the findings of G. H. Birum.[12] Thus, 1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**1a**) is hydrolyzed to the corresponding phosphonic acid **4**, when a solution of **1a** is heated in the presence of hydrochloric acid.



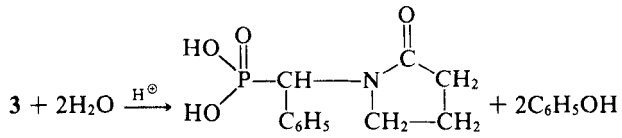
4

If a large excess of water is used, hydrolysis may be made essentially quantitative. 1,3-Bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**2a**) is not hydrolyzed to a considerable extent, when its solution is heated in the presence of hydrochloric acid. Compound **2a** may be hydrolyzed to the corresponding diphosphonic acid **5**, if stronger acids, such as perchloric acid, are used.



5

Furthermore, the hydrolysis of 1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-pyrrolidinone (**3**) to the corresponding phosphonic acid **6** is carried out readily, when a solution of **3** is heated in the presence of hydrochloric acid.



6

The structure of the synthesized compounds was confirmed by elemental analysis, by IR, ^{31}P nmr and by ^{1}H nmr. Specifically, the following characteristic absorption bands appear in the infrared spectra of substituted 1-[(phosphonyl)methyl]-2-imidazolidinones (**1**): NH (3.07–3.12μ) C = 0 (5.87–5.91μ), P = 0 (7.90–7.93μ), P—O—R (when R = C_6H_5 at 10.6μ and when R = CH_2CH_2Cl at 9.25–9.70μ). The same characteristic absorption bands appear in the infrared spectra of substituted 1,3-bis[(phosphonyl)methyl]-2-imidazolidinones (**2**), except for the absorption of NH group which is absent. A very broad absorption band of P—O—H is extented from 2.0 to 4.5μ in the infrared spectra of the compounds **4**, **5** and **6**, which contain free P—O—H groups.

^{31}P nmr measurements were used as a means for the determining the conditions

required for the reactions. The values of the chemical shifts both of the phosphorus-containing reactants and of the reaction products differ significantly.[17]

All the methylene protons of the imidazolidinone ring do not absorb in the same region of the ^1H nmr spectrum in the case of substituted 1,3-bis[phosphonyl)-methyl]-2-imidazolidinones (**2**), 1-[(phosphonyl)methyl]-2-imidazolidinones (**1**) and of their thio-analogous compounds, when R^1 is phenyl of furanyl group. Thus, two of the methylene protons of the imidazolidinone ring in the ^1H nmr spectrum of 1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**2a**) absorb at δ 3.50, while the other two methylene protons absorb at δ 2.72 (Figure 1). Similarly, one of the methylene protons of the imidazolidinone ring in the ^1H nmr spectrum of 1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**1a**) absorbs at δ 3.82 and the other three methylene protons absorb at δ 3.17 (Figure 2). This differentiation of the values of the chemical shifts of methylene protons can possibly be attributed to a deshielding effect caused by the neighboring aromatic nuclei of benzyl groups. It is known that the aromatic nuclei contain large closed loops of π electrons in which strong diamagnetic currents are induced by the magnetic field.[18] This effect causes in the molecule of 1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**2a**) the deshielding of the two methylene protons Ha and Hb. These atoms are sterilically oriented so that they are close to the plane of the benzene rings of benzyl groups (Figure 3). Space-filling models show that the benzene rings of benzyl groups can not be freely rotated. On the other hand, one of the four methylene protons of 1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**1a**) is sterically oriented so that it is approached by the plane of the benzene ring of neighborings benzyl group. As a consequence, it experiences the deshielding influence of the ring currents. In addition, the inequivalence if the methylene protons in the ^1H nmr spectrum can be possibly caused by the equatorial and axial position of these protons, as well as by the presence of two chiral

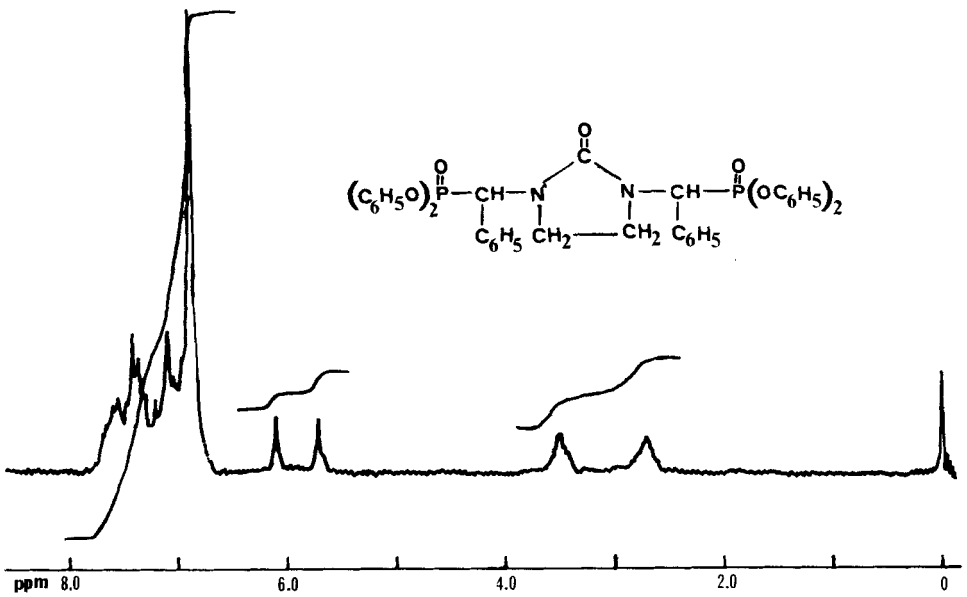


FIGURE 1 ^1H nmr spectrum of 1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone in $CDCl_3$ solution.

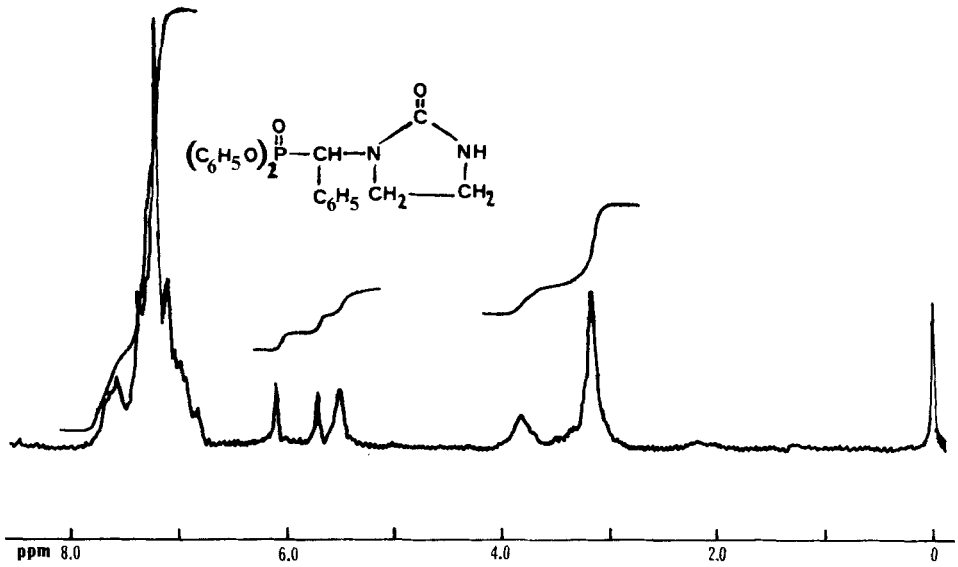


FIGURE 2 ^{1}H nmr spectrum of 1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone in $CDCl_3$ solution.

C-atoms.[19] In a similar way, the chemical shifts of the methylene protons differ 1.13 ppm in the ^{1}H nmr spectrum of 1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinethione (**2d**) and 0.70 ppm in the ^{1}H nmr spectrum of 1,3-bis[(1-furanyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**2b**).

EXPERIMENTAL

The melting points were determined with a Büchi apparatus and are uncorrected. Infrared spectra were determined in potassium bromide disks using a Perkin-Elmer Infracord Model 137 Spectrometer. Proton nuclear magnetic resonance (^{1}H nmr) spectra were obtained at 60.0 MHz on Varian T-60A spectrometer with tetramethylsilane as an internal standard. ^{31}P nmr spectra were obtained at 24.3 MHz on Varian T-60A spectrometer and are reported with respect to 85% H_3PO_4 contained in a capillary. Since the received signals of ^{31}P nmr spectra were very weak, a signal averager model V-2048 of Varian-Tracor was used. The nmr measurements were in general made on saturated solutions. Chemical shifts are given in ppm. Elemental analyses were determined by Microanalytical Laboratory of National Hellenic Research Foundation in Athens, Greece.

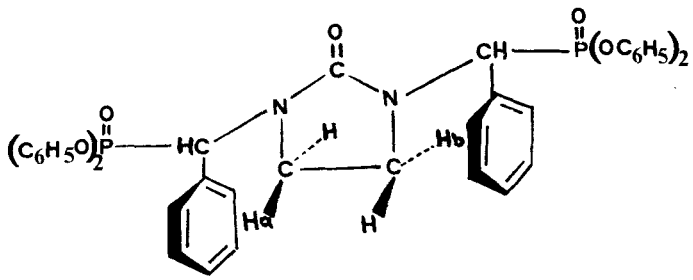


FIGURE 3 Conformation of methylene protons of imidazolidinone ring in the 1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone molecule.

1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**1a**)

8.61 g (0.10 mol) of powdered 2-imidazolidinone, 31.03 g (0.10 mol) of freshly distilled triphenyl phosphite, 10.61 g (0.10 mol) of benzaldehyde and 80 ml of toluene were placed in a flask equipped with a condenser. The mixture was stirred under nitrogen and heated at 80°C for 0.5 hr. Subsequently, it was boiled (110°C) for 1 hr. The solution obtained was filtered to remove a small amount of insoluble material and washed three times with 50 ml of 5% NaOH solution and finally three times with 50 ml of water. Next, the solution was dried (Na_2SO_4) and concentrated to give 19.6 g (48.0%) of a white solid having mp 162–170°C. Repeated recrystallizations from benzene gave an analytical sample: mp 169–172.5°C; ^{31}P nmr ($CDCl_3$) −12.4 ppm (d, J = 22 Hz); ^1H nmr ($CDCl_3$) δ 6.75–7.83 (m, 15, C_6H_5), 5.90 (d, 1, J = 23 Hz, PCH), 5.52 (broad, 1, NH), 3.82 (m, 1, NCH_2), 3.17 (m, 3, NCH_2); ir (KBr) 3.12 (m), 3.27 (w), 5.90 (vs), 6.27 (m), 6.69 (s), 7.02 (m), 7.90 (vs), 8.22 (s), 8.42 (s), 9.70 (m), 10.60 (vs).

Anal. Calcd for $C_{22}H_{21}N_2O_4P$: C 64.70, H 5.18, N 6.86.
Found: C 64.23, H 5.55, N 6.72.

1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**2a**)

4.30 g (0.05 mol) of powdered 2-imidazolidinone, 31.03 g (0.10 mol) of freshly distilled triphenyl phosphite, 10.61 g (0.10 mol) of benzaldehyde and 70 ml of toluene were placed in a flask equipped with a condenser. The procedure of **1a** was followed. A white solid of 15.5 g (42.5%) was obtained, having mp 162–172°C. Recrystallizations from acetonitrile gave an analytical sample: mp 178–182°C; ^{31}P nmr ($CDCl_3$) −11.6 ppm (d, J = 22 Hz); ^1H nmr ($CDCl_3$) δ 6.63–7.82 (m, 30, C_6H_5), 5.90 (d, 2, J = 23 Hz, PCH), 3.50 (m, 2, NCH_2), 2.72 (m, 2, NCH_2); ir (KBr) 3.30 (w), 5.87 (s), 6.27 (s), 6.70 (s), 7.07 (m), 7.93 (vs), 8.21 (s), 8.40 (s), 9.29 (m), 9.71 (m), 10.55 (vs), 13.17 (s).

Anal. Calcd for $C_{41}H_{36}N_2O_7P_2$: C 67.39, H 4.97, N 3.83.
Found: C 67.60, H 4.85, N 3.67.

1-[(1-furanyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**1b**)

4.30 g (0.05 mol) of powdered 2-imidazolidinone, 15.51 g (0.05 mol) of freshly distilled triphenyl phosphite and 30 ml of 1,1,2,2-tetrachloroethane were placed in a flask equipped with a condenser and a dropping funnel. Half the volume of the solution prepared by mixing 4.80 g (0.05 mol) of freshly distilled furfural and 10 ml of 1,1,2,2-tetrachloroethane was added dropwise to the above mixture while it was stirred under nitrogen and at room temperature. The addition of furfural solution lasted 0.5 hr during which an exothermic reaction was observed. The addition of the remaining furfural solution was made while the reaction mixture was heated at 50°C for 1 hr. Then, the obtained solution was stripped (115°C/0.5 mm Hg) to remove solvent and most of the by-product phenol. A dark solid (13.0 g, 65.3%, mp 127–137°C) was obtained by ether addition to the residue. A part of this was purified from the reaction by-products by column chromatography using neutral aluminum oxide of activity 1 as absorbent and chloroform as solvent. The reaction by-products were absorbed on the column top and formed a dark band. The fraction which had mp 147–153°C and $R_f = 0.33$ according to thin layer chromatography on aluminum oxide plates and chloroform solvent, was collected. This fraction constituted 43% of the chromatographed product. Repeated recrystallizations from benzene using charcoal for decolorization gave an analytical sample: mp 155–159°C; ^{31}P nmr ($CDCl_3$) −9.8 ppm (d, J = 22 Hz); ^1H nmr ($CDCl_3$) δ 6.77–7.47 (m, 10, C_6H_5), 6.40 (d of m, 3, J = 17 Hz, furanyl protons), 5.90 (d, 1, J = 23, PCH), 5.05 (broad, 1, NH), 3.73 (m, 1, NCH_2), 3.15 (m, 3, NCH_2); ir (KBr) 3.10 (m), 5.89 (vs), 6.27 (m), 6.69 (s), 7.00 (m), 7.89 (vs), 8.23 (s), 8.42 (s), 8.57 (m), 9.77 (m), 10.60 (vs).

Anal. Calcd for $C_{20}H_{19}N_2O_5P$: C 60.30, H 4.81, N 7.03.
Found: C 60.46, H 4.93, N 6.95.

1,3-bis[(1-furanyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**2b**)

4.30 g (0.05 mol) of powdered 2-imidazolidinone, 31.03 g (0.10 mol) of freshly distilled triphenyl phosphite and 30 ml of 1,1,2,2-tetrachloroethane were placed in a flask equipped with a condenser and a dropping funnel. The solution prepared by mixing 9.61 g (0.10 mol) of freshly distilled furfural and 10 ml of 1,1,2,2-tetrachloroethane was added to the above mixture according to the procedure of **1b**. A dark solid was obtained (24.30 g, 68.4%, mp 128–138°C). A part of this was purified from the reaction by-products by column chromatography, as in **1b**. The fraction with mp 152–163°C and $R_f = 0.32$ was collected. This fraction constituted 53% of the chromatographed product. Repeated recrystallizations from

benzene-petroleum ether (1 : 1.7 vol/vol), using charcoal for decolorization, gave an analytical sample: mp 168–171°C; ^{31}P nmr ($CDCl_3$) −9.2 ppm (d, J = 22 Hz); ^{1}H nmr ($CDCl_3$) δ 6.73–7.40 (m, 20, C_6H_5), 6.40 (d of m, 6, J = 17 Hz, furanyl protons), 5.95 (d, 2, J = 23 Hz, PCH), 3.50 (m, 2, NCH_2), 2.80 (m, 2, NCH_2); ir (KBr) 5.86 (s), 6.28 (m), 6.72 (s), 7.07 (m), 7.93 (vs), 8.29 (s), 8.47 (s), 8.59 (m), 9.77 (m), 10.62 (vs).

Anal. Calcd for $C_{37}H_{32}N_2O_9P_2$: C 62.54, H 4.54, N 3.94.
Found: C 62.38, H 4.61, N 3.64.

1-[[(1-phenyl-1-di(2-chloroethoxy)phosphonyl]methyl]-2-imidazolidinone (**1c**)

4.30 g (0.05 mol) of powdered 2-imidazolidinone, 13.47 g (0.05 mol) of tris (2-chloroethyl) phosphite, 5.31 g (0.05 mol) of benzaldehyde, 50 ml of toluene and a few drops of boron trifluoride etherate were placed in a flask equipped with a condenser. The mixture was stirred under nitrogen and heated at 90°C for 1.5 hr. The solution obtained was filtered and stripped (80°C/0.5 mm Hg) to give 13.22 g (85.2%) of a viscous liquid which solidified on standing. A part of this was purified from the reaction by-products by column chromatography using neutral aluminum oxide of activity III as absorbent and chloroform as solvent. The fraction with mp 104–120°C and R_f = 0.20 according to thin layer chromatography on aluminum oxide plates and chloroform solvent, was collected. This fraction constituted about 60% of the chromatographed product and after repeated recrystallizations from carbon tetrachloride-ether (1 : 2.5 vol/vol) an analytical sample was obtained: mp 116–120°C; ^{31}P nmr ($CDCl_3$) −21.2 ppm; ^{1}H nmr ($CDCl_3$) δ 7.10–7.67 (m, 5, C_6H_5), 5.53 (d, 1, J = 23 Hz, PCH), 5.25 (broad, 1, NH), 4.18 (m, 4, $POCH_2$), 3.98 (m, 1, NCH_2), 3.62 (m, 4, $ClCH_2$), 3.32 (m, 3, NCH_2); ir (KBr) 3.08 (m), 5.91 (vs), 6.72 (m), 7.03 (m), 7.68 (m), 7.92 (s), 8.20 (s), 9.27 (s), 9.70 (vs), 10.46 (s).

Anal. Calcd for $C_{14}H_{19}Cl_2N_2O_4P$: C 44.11, H 5.02, N 7.35.
Found: C 44.07, H 5.09, N 7.28.

1,3-bis[(1-methyl-1-diphenoxyphonyl)methyl]-2-imidazolinone (**2c**)

4.30 g (0.05 mol) of powdered 2-imidazolidinone, 31.03 g (0.10 mol) of freshly distilled triphenyl phosphite, 5.29 g (0.12 mol) of distilled acetaldehyde and 50 ml of toluene were placed in a flask equipped with a condenser. The condenser was cooled by isopropanol of temperature about −20°C. The mixture was stirred under nitrogen and heated at 90°C for 1 hr. During heating the solution was gradually colored orange. The solution obtained was filtered to remove a small amount of insoluble material and washed three times with 50 ml of 5% NaOH solution and finally three times with 50 ml of water. Subsequently, the solution was dried (Na_2SO_4) and concentrated to give 14.81 g (48.8%) of a viscous orange liquid, which solidified on standing overnight. A yellowish solid (8.75 g, 28.9%, mp 115–122°C) was obtained after treatment with ether. A part of this was purified from the reaction by-products by column chromatography using neutral aluminum oxide of activity I as absorbent and chloroform as solvent. The fraction with mp 121–127°C and R_f = 0.31 according to thin layer chromatography on aluminum oxide plates with chloroform solvent, was collected. This fraction constituted 34% of the chromatographed product and after recrystallizations from benzene-petroleum ether (1 : 1 vol/vol) using charcoal for decolorization an analytical sample was obtained: mp 139–142°C; ^{31}P nmr ($CDCl_3$) −16.2 ppm; ^{1}H nmr ($CDCl_3$) δ 6.73–7.50 (m, 20, C_6H_5), 4.78 (m, 2, PCH), 3.52 (m, 4, NCH_2), 1.43 (m, 6, CH_3); ir (KBr) 3.38 (w), 5.89 (s), 6.25 (m), 6.70 (s), 6.98 (m), 7.82 (s), 8.26 (s), 8.38 (s), 8.56 (s), 9.71 (m), 10.71 (vs), 12.90 (s).

Anal. Calcd for $C_{31}H_{32}N_2O_7P_2$: C 61.38, H 5.32, N 4.62.
Found: C 61.85, H 5.38, N 4.46.

1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinethione (**1d**)

5.11 g (0.05 mol) of powdered 2-imidazolidinethione, 15.51 g (0.05 mol) of freshly distilled triphenyl phosphite, 5.31 g (0.05 mol) of benzaldehyde, 50 ml of acetonitrile and a few drops of anhydrous acetic acid were placed in a flask equipped with a condenser. The mixture was stirred under nitrogen and boiled (80°C) for 2 hr. The solution obtained was filtered and concentrated. Toluene (~50 ml) was added to the residue and the resulting solution was washed three times with 50 ml of 5% NaOH solution and finally three times with 50 ml of water. Subsequently, the solution was dried (Na_2SO_4) and concentrated to give 8.0 g (38.0%) of a white solid with mp 165–172°C. Recrystallizations from acetonitrile gave an analytical sample: mp 170–174°C: ^{31}P nmr (DMSO-d_6) −12.5 ppm (d, J = 23 Hz); ^{1}H nmr (DMSO-d_6) δ 8.78 (broad, 1, NH), 6.83–7.87 (m, 15, C_6H_5), 6.95 (d, 1, J = 23 Hz, PCH), 4.0 (m, 1, NCH_2), 3.38 (m, 3,

NCH_2); ir (KBr) 3.10 (m), 6.26 (m), 6.72 (s), 6.97 (m), 7.58 (m), 7.82 (s), 8.03 (s), 8.22 (s), 8.42 (s), 9.72 (m), 10.53 (vs).

Anal. Calcd for $C_{22}H_{21}N_2O_3PS$: C 62.25, H 4.99, N 6.60.
Found: C 62.51, H 4.73, N 6.47.

1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinethione (**2d**)

5.11 g (0.05 mol) of powdered 2-imidazolidinethione, 31.03 g (0.10 mol) of freshly distilled triphenyl phosphite, 10.61 g (0.10 mol) of benzaldehyde, 60 ml of acetonitrile and a few drops of anhydrous acetic acid are placed in a flask equipped with a condenser. The procedure of **1d** was followed. A yellowish viscous liquid (35.3 g, 94.6%) was obtained, which solidified on standing. A white solid (12.1 g, 32.4%, mp 155–159°C) was obtained after treatment with ether. Recrystallizations from acetonitrile gave an analytical sample: mp 157–161°C; ^{31}P nmr ($CDCl_3$) −11.0 ppm (d, J = 23 Hz); ^1H nmr ($CDCl_3$) δ 6.40–7.97 (m, 32, C_6H_5 and PCH), 3.70 (m, 2, NCH_2), 2.57 (m, 2, NCH_2); ir (KBr) 6.27 (m), 6.72 (s), 7.07 (s), 7.54 (s), 7.95 (s), 8.27 (s), 8.43 (s), 8.60 (s), 9.73 (m), 10.62 (vs).

Anal. Calcd for $C_{41}H_{36}N_2O_6P_2S$: C 65.94, H 4.86, N 3.75.
Found: C 66.26, H 5.04, N 3.58.

Attempt for the preparation of 1-[(1-phenyl-1-dimethoxyphosphonyl)methyl]-2-imidazolidinone

4.30 g (0.05 mol) of powdered 2-imidazolidinone, 6.20 g (0.05 mol) of freshly distilled trimethyl phosphite, 5.31 g (0.05 mol) of benzaldehyde, 50 ml of toluene and a few drops of boron trifluoride etherate were placed in a flask equipped with a condenser. The mixture was stirred under nitrogen and heated at 90°C for 2 hr. The solution obtained was filtered and concentrated. The viscous concentrate obtained solidified upon standing. Treatment of the residue with ether gave 7.13 g (50.2%) of a white solid, having mp 232–238°C. The ir spectrum of this product had a very weak absorption band, in comparison to the other bands of the spectrum, at 9.63 μ assigned to P—O—CH_3 group. The ^1H nmr spectrum of this product had also a very weak doublet peak (J = 10.5 Hz), in comparison to the other peaks of the spectrum, at δ 3.55 assigned to P—O—CH_3 group, whereas the expected doublet peak (J ≃ 23 Hz) of PCH was entirely absent.

Attempt for the preparation of 1,3-bis[(1-methyl-1-dimethoxyphosphonyl)methyl]-2-imidazolidinone

2.58 g (0.03 mol) of powdered 2-imidazolidinone, 7.44 g (0.06 mol) of freshly distilled trimethyl phosphite, 2.64 g (0.06 mol) of acetaldehyde, 50 ml of toluene and a few drops of boron trifluoride etherate were placed in a flask equipped with a condenser. The condenser was cooled by isopropanol of temperature about −20°C. The mixture was stirred under nitrogen and heated at 90°C for 2 hr. The solution obtained was filtered and concentrated. The viscous concentrate obtained solidified upon standing. Treatment of the residue with ether gave 5.10 g (47.5%) of a solid product, having mp 130–132°C. The ir spectrum of this product had a very weak absorption band, in comparison to the other bands of the spectrum, at 9.57 μ assigned to P—O—CH_3 group. The ^1H nmr spectrum of this product had also a very weak doublet peak (J = 10.5 Hz), in comparison to the other peaks of the spectrum, at δ 3.73 assigned to P—O—CH_3 group, whereas the expected doublet peak (J ≃ 23 Hz) of PCH was entirely absent.

1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-pyrrolidinone (**3**)

4.26 g (0.05 mol) of 2-pyrrolidinone, 15.51 g (0.05 mol) of freshly distilled triphenyl phosphite, 5.31 g (0.05 mol) of benzaldehyde, 30 ml of toluene and a few drops of boron trifluoride etherate were placed in a flask equipped with a condenser. The mixture was stirred under nitrogen and heated at 90°C for 2 hr. The solution obtained was washed three times with 50 ml of 5% NaOH solution and finally three times with 50 ml of water. Subsequently, the solution was dried (Na_2SO_4) and stripped to 100°C/0.3 mm Hg. A viscous liquid of 10.45 g (51.3%) was obtained which solidified on standing overnight. Treatment with ether gave 9.76 g (47.9%) of a white solid, having mp 108–116°C. Recrystallizations from carbon tetrachloride-petroleum ether (1:3.5 vol/vol) gave an analytical sample: mp 113–116°C; ^{31}P nmr ($CDCl_3$) −11.5 ppm; ^1H nmr ($CDCl_3$) δ 6.47–7.67 (m, 15, C_6H_5), 6.10 (d, 1, J = 23 Hz, PCH), 3.73 (m, 1, NCH_2), 3.13 (m, 1, NCH_2), 1.83 (m, 4, $COCH_2CH_2$); ir (KBr) 3.40 (w), 5.92 (vs), 6.27 (m), 6.71 (s), 7.13 (m), 7.90 (s), 8.12 (s), 8.43 (s), 9.74 (m), 10.58 (vs).

Anal. Calcd for $C_{23}H_{22}NO_4P$: C 67.80, H 5.44, N 3.44.
Found: C 68.05, H 5.32, N 3.48.

1-[(1-phenyl-1-dihydroxyphosphonyl)methyl]-2-imidazolidinone (**4**)

5.00 g (12.24 mmol) of 1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**1a**), 1.00 g of 4N hydrochloric acid solution and 20 ml of acetonitrile were placed in a flask equipped with a condenser. The mixture was stirred and boiled for 1 hr. The hydrolysis product was precipitated while the mixture was heated. A white solid of 2.29 g (92.0%) was obtained after filtration, having mp 246–248°C (decomposition). Recrystallizations from methanol-ether (1:2 vol/vol) gave an analytical sample: mp 246–248°C (decomposition); ^{31}P nmr (DMSO-d_6) −16.4 ppm (d, J = 22 Hz); ^{1}H nmr (DMSO-d_6) δ 8.62 (broad, 3, POH and NH), 7.00–7.67 (m, 5, C_6H_5), 5.06 (d, 1, J = 23 Hz, PCH), 3.70 (m, 1, NCH_2), 3.15 (m, 3, NCH_2).

Anal. Calcd for $C_{10}H_{13}N_2O_4P$: C 46.88, H 5.11, N 10.94.
Found: C 47.03, H 5.26, N 11.08.

1,3-bis[(1-phenyl-1-dihydroxyphosphonyl)methyl]-2-imidazolidinone (**5**)

7.00 g (9.55 mol) of 1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**2a**), 3.00 g of 4N hydrochloric acid solution and 60 ml of acetonitrile were placed in a flask equipped with a condenser. The mixture was stirred and boiled for 2 hr. Precipitation of the hydrolysis product was not observed while the mixture was heated. Concentration of the solution led to the recovery of unchanged 1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**2a**).

3.24 g (4.42 mmol) of 1,3-bis[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-imidazolidinone (**2a**), 0.70 g of 60% perchloric acid solution and 20 ml of acetonitrile were placed in a flask equipped with a condenser. The solution was stirred and boiled for 1 hr. The hydrolysis product was precipitated during the course of the reaction. A white solid of 1.68 g (89.1%) was obtained after filtration having mp 237–239°C. Recrystallizations from water-acetonitrile (1:10 vol/vol) gave an analytical sample: mp 239–240°C (decomposition); ^{31}P nmr (DMSO-d_6) −15.8 ppm (d, J = 22 Hz); ^{1}H nmr (DMSO-d_6) δ 9.57 (broad, 4, POH), 7.10–7.67 (m, 10, C_6H_5), 5.13 (d, 2, J = 23 Hz, PCH), 3.70 (m, 2, NCH_2), 3.17 (m, 2, NCH_2).

Anal. Calcd for $C_{17}H_{20}N_2O_7P_2$: C 47.89, H 4.73, N 6.57.
Found: C 48.05, H 4.60, N 6.32.

Aniline-salt was formed by reaction of compound **5** with aniline. Thus, 1.00 g of **5**, was dissolved in 10 ml of anhydrous methanol and excess of aniline (0.87 g, 9.38 mmol) was added. The solution was stirred and heated on a steambath for about 5 min. The aniline-salt (1.14 g, 93.6%, mp 235–240°C) was precipitated upon cooling the solution in an icebath and was separated by filtration. Recrystallizations of this salt from N,N-dimethylformamide-ether (1:1 vol/vol) gave an analytical sample: mp 248–252°C.

Anal. Calcd for $C_{23}H_{27}N_3O_7P_2$: C 53.18, H 5.24, N 8.09.
Found: C 53.05, H 5.48, N 7.95.

1-[(1-phenyl-1-dihydroxyphosphonyl)methyl]-2-pyrrolidinone (**6**)

1.26 g (3.09 mmol) of 1-[(1-phenyl-1-diphenoxyphosphonyl)methyl]-2-pyrrolidinone (**3**), 0.30 g of 4N hydrochloric acid solution and 12 ml of acetonitrile were placed in a flask equipped with a condenser. The mixture was stirred and boiled for 1 hr. The hydrolysis product was precipitated while the mixture was heated. A white solid of 0.65 g (82.5%) was obtained by filtration, having mp 238–240°C. Recrystallizations from water-acetonitrile (1:10 vol/vol) gave an analytical sample: mp 241–243°C; ^{31}P nmr (DMSO-d_6) −15.9 ppm (d, J = 22 Hz); ^{1}H nmr (DMSO-d_6) δ 8.40 (broad, 2, POH), 6.96–7.73 (m, 5, C_6H_5), 5.33 (d, J = 23 Hz, PCH), 3.80 (m, 1, NCH_2), 3.23 (m, 1, NCH_2), 2.13 (m, 4, $COCH_2CH_2$).

Anal. Calcd for $C_{11}H_{14}NO_4P$: C 51.77, H 5.53, N 5.49.
Found: C 51.93, H 5.48, N 5.47.

ACKNOWLEDGMENT

The author expresses his thanks to Professor A. K. Tsolis, Director of Chemical Technology Laboratory in University of Patras, for his encouragement. He also thanks Dr. H. Mantzos, Director of Microanalytical Laboratory in National Hellenic Research Foundation, for the determination of elemental analyses.

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