SYNTHESIS OF 1,3-DITHIETANE-2,4-DIYLIDENEBIS-(CYANOMETHYLPHOSPHONATES) AND -PHENYL-PHOSPHINATES AND THEIR REACTION WITH CARBOXYLIC ACID HYDRAZIDES

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Abstract - 1,3-Dithietane-2,4-diylidenebis(cyanomethylphosphonates) and -phenylphosphinates react with carboxylic acid hydrazides to yield tautomeric derivatives of 1,3,4-oxadiazoles. One of the starting materials as well as one of the reaction products is examined by X-ray crystal structure analysis.

INTRODUCTION

Organophosphorus compounds have become remarkably important from a chemical as well as a pharmacological point of view. Some have been reported to possess antibiotic, antineoplastic, antiviral or herbicidal attributes.[1]

Therefore, the development of new phosphonato- and phosphinato-substituted compounds *via* simply prepared starting materials should be significant.

Desaurines (1,3-dithietanes with two exo-cyclic C,C-double bonds[2]) are potential synthetic components for the preparation of heterocyclic systems. For this group of compounds, which have been known for more than one hundred years, there are noted numerous synthetic methods.[2]

Some phosphonato-substituted desaurines were synthesized accidentially by Hartke and Günther[3] in 1974 and by Schaumann and Grabley[4] in 1979. In 1991 Neidlein and Eichinger[5] also synthesized a phosphonato-substituted desaurine; however, the synthetic potential has not yet been examined.

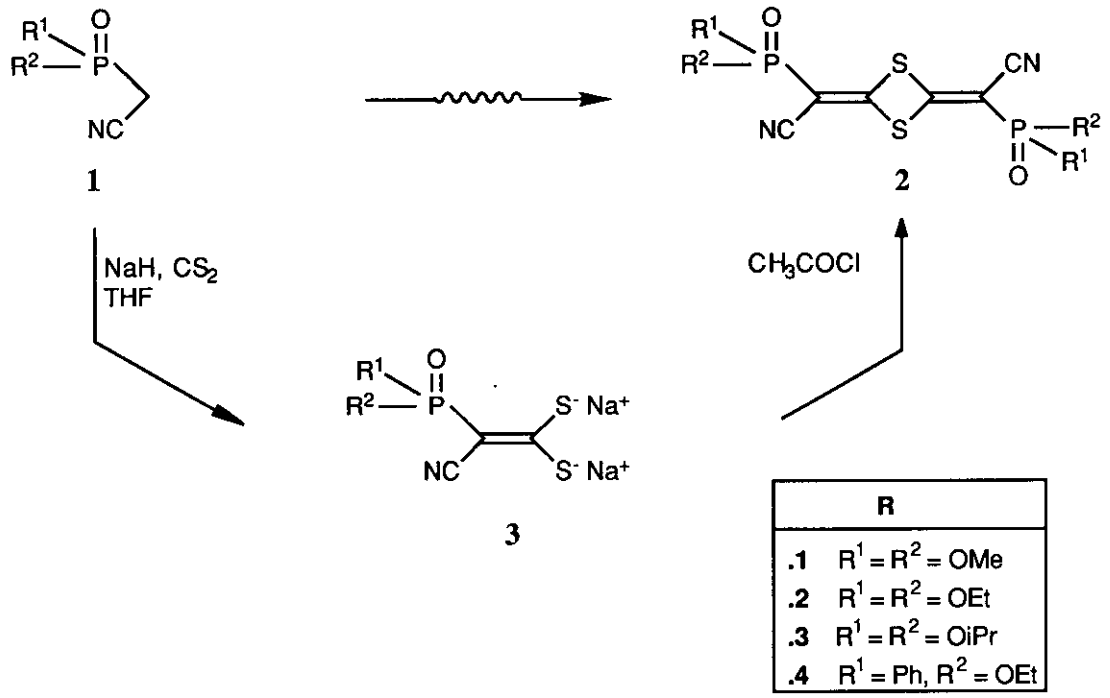
The present paper describes the results of our studies concerning the preparation of phosphonato- and phosphinato-substituted 1,3-dithietane compounds and their reaction with carboxylic acid hydrazides.

RESULTS AND DISCUSSION

Hartke and Günther[3] obtained the tetraethyl 1,3-dithietane-2,4-diylidene-bis(cyanomethylphosphonate) (**2.2**) as a decomposition product resulting from the elimination of alcohol in boiling dioxane from diethyl 2-mercapto-2-ethoxy-1-cyanoethylenephosphonate in poor yield. The *trans* configuration was supposed, but could not be proved.

Using methods developed by Eichinger[5b] and Schaumann and Grabley[4] the 1,3-dithietane-2,4-diylidenebis(cyanomethylphosphonates) (**2.1-3**) and -phenylphosphinate (**2.4**) were synthesized using cyanomethylphosphonates (**1.1-3**) as well as cyanomethylphenylphosphinate (**1.4**) in a three-stage process (Scheme 1). The starting materials (**1.1-4**) were obtained in good yields from the corresponding trialkylphosphite or dialkylphenylphosphonite by treatment of the preceeding with chloroacetonitrile[6] (4 h, reflux).

When reacted with sodium hydride (THF, room temperature) the methylene activated cyanomethylphosphonates (**1.1-3**) and -phenylphosphinate (**1.4**) led to the corresponding sodium salts, which underwent addition of carbon disulfide in the presence of a further equimolar amount of sodium hydride yielding dithiocarboxylates (**3**). The crude products (**3**) were directly treated with acetyl chloride (1 h, reflux) to give the 1,3-dithietanes (**2**) (yields: 10 - 54 %).



Scheme 1: Synthesis of 1,3-dithietanes (**2**)

Only one isomer was isolated. The configuration of the 1,3-dithietane (**2.2**) was examined by X-ray structure analysis and should be representative for this class of compounds (**2**).

By recrystallization from ether colorless crystals of **2.2** (monoclinic) with the space group $P2_1/n$ (# 14 Int. Tables) were obtained: $C_{14}H_{20}N_2O_6P_2S_2$, mol. weight = 438.40 g mol^{-1}. The unit cell parameters were: a = 8.649 (3) Å, b = 10.708 (3) Å, c = 23.652 (4) Å, β = 97.21 (2) °, V = 2173 (2) $Å^3$, Z = 4, D_x = 1.339 g cm^{-3}, μ = 4.077 cm^{-1} (Mo Kα), F_{000} = 912 e. (The atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms are given in Table 1.)

Intensity data were collected using a graphite-monochromated Mo-Kα (λ = 0.7107 Å) radiation (Enraf-Nonius CAD 4) and applying ω-2Θ scan technique. Up to $\sin\Theta/\lambda = 0.62$ $Å^{-1}$ 4252 symmetry independent reflections were measured out of which 2667 with $I \geq 3.0\ \sigma(I)$ were graded as observed. The structure was solved by the direct method (SIR) and refined by full-matrix least -

squares technique using anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms (R = 0.044, R_w = 0.050).

In crystalline form the molecule (**2.2**) possesses nearly perfect C_i-symmetry (Figures 1 and 2); thus the 1,3-dithietane ring must be planar and the phosphonato- and cyano-substituents lie in a *trans* relationship.

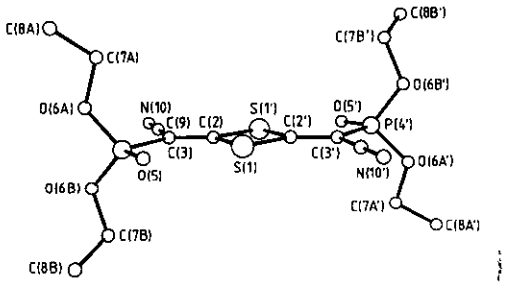


Figure 1: Molecular structure and atom numbering of **2.2** in the crystalline state

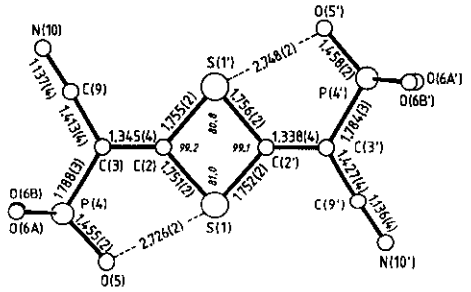
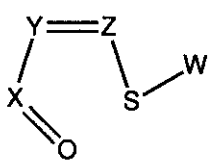
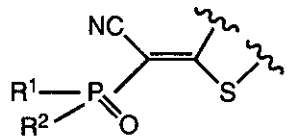


Figure 2: Bond distances (in Å) and some bond angles (in °) of **2.2**

The sulfur-carbon bond lengths of 1.751 (2) Å - 1.756 (2) Å are in accord with other sp^2-carbon sulfur bond distances reported.[9,13] The C2=C3- and C2′=C3′-bond distances, 1.345 (4) Å and 1.338 (4) Å respectively, are somewhat longer than the corresponding [Csp^2=Csp^2]-bonds[13] due to conjugation effects in the molecule. The P4-O5 (P4′-O5′)- as well as the C9-N10 (C9′-N10′)-bonds are coplanar with the ring; therefore all atoms, except the ones of the ethoxy groups of the phosphonato-substituents, lie in the plane of the 1,3-dithietane ring. Associated with the described planarity is the intramolecular S1...O5 (S1′...O5′)-distance of 2.726 (2) Å (2.748 (2) Å), which is considerably shorter than the sum of the van der Waals radii for sulfur and oxygen (3.25 Å[7]). This is in accordance with molecules containing a five-atom conjugated system linking sulfur to oxygen (Figure 3).[8-11]

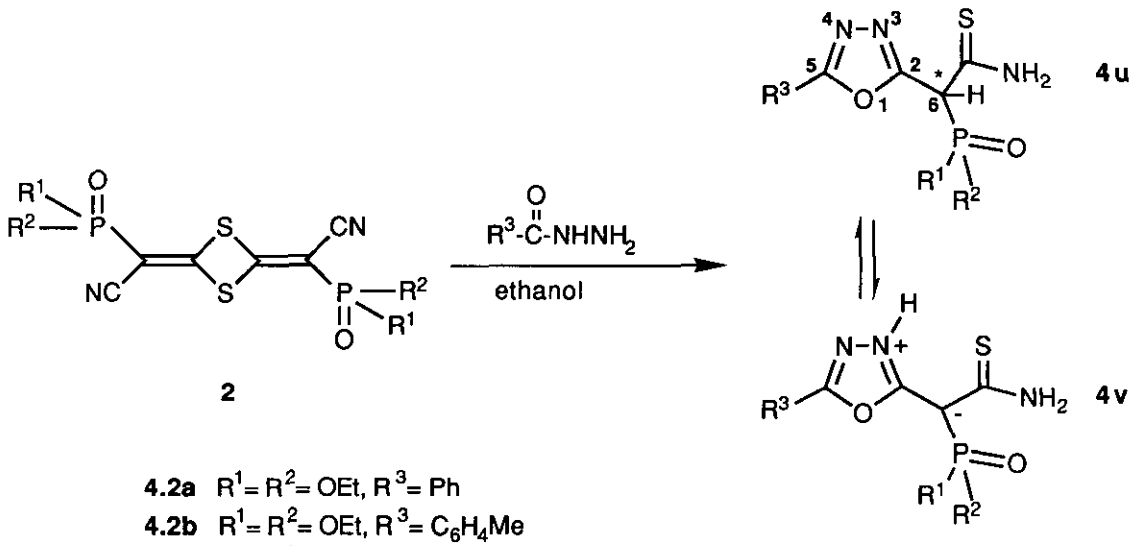
Figure 3:





The reaction of the phosphonato- as well as phosphinato-substituted 1,3-dithietanes (**2**) with carboxylic acid hydrazides (ethanol, 1-3 h, reflux) leads directly to the 1,3,4-oxadiazoles (**4**) (Scheme 2). However, in the reaction of phosphor free desaurines with carboxylic acid hydrazides pyrazolines[12] are obtained.

The substitution on the methine carbon atom in the 2-position with electron withdrawing thiocarbamoyl- and phosphonato- or phosphinato-groups respectively results in an increased acidity of the corresponding methine proton. Evidence for two different tautomeric structures (**4u**) and (**4v**) in solution was proved by nmr-spectroscopy.



4.2a $R^1 = R^2 = OEt$, $R^3 = Ph$
4.2b $R^1 = R^2 = OEt$, $R^3 = C_6H_4Me$
4.2c $R^1 = R^2 = OEt$, $R^3 = C_6H_4Cl$
4.3a $R^1 = R^2 = OiPr$, $R^3 = Ph$
4.3b $R^1 = R^2 = OiPr$, $R^3 = C_6H_4Me$
4.4a $R^1 = Ph$, $R^2 = OEt$, $R^3 = Ph$
4.4b $R^1 = Ph$, $R^2 = OEt$, $R^3 = C_6H_4Me$

Scheme 2: Synthesis of 1,3,4-oxadiazoles (**4**)

In the J-modulated spin-echo ^{13}C nmr spectrum of **4.2b** in DMSO-d_6 one set of signals and a negative phase of the C6-doublet at 51.2 ppm indicates that only tautomer (**4.2b u**) is present. In $CDCl_3$-solution however, two sets of signals are obtained, one for tautomer (**4.2b u**) with similiar chemical shifts as in DMSO-d_6 and another one, in which the C6-signal has the character of a downfield shifted quarternary carbon atom. The structure of the second tautomer was proved to be **4.2b v** by a series of heteronuclear $^{13}C\{^1H\}$-nOe experiments as follows:
The irradiation of each of the two NH_2-protons (9.33 ppm and 10.11 ppm) in DMSO-d_6 solution resulted in the enhancement of the CS-carbon signal in the ^{13}C nmr spectra. In $CDCl_3$-solution four signals for the NH_2-protons (two for each isomer) could be observed in the ^1H nmr spectrum (6.74 ppm, 8.04 ppm, 8.91 ppm, 10.00 ppm) and irradiation of each of them produced an nOe at the corresponding CS-carbon signal in the ^{13}C nmr spectra, too. Irradiation of the most deshielded proton at 15.02 ppm ($CDCl_3$-solution) however causes a strong signal enhancement of the C2-signal of the oxadiazole ring (165.4 ppm), indicating the protonation of N3.

To confirm the proposed cyclic structure of **4** and to obtain further structural information an X-ray crystal structure analysis of **4.2b** was performed.

Single crystals of **4.2b** (monoclinic) with the space group $P2_1/n$ (# 14 Int. Tables) were obtained from ethanol. The unit cell parameters were: a = 7.640 (1) Å, b = 28.906 (5) Å, c = 8.517 (1) Å, β = 110.93 (1) °, V = 1756.8 (9) Å^3, Z = 4, D_x = 1.396 g cm^{-3}, μ = 2.884 cm^{-1} (Mo Kα), F_{000} = 776 e. (The atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms are given in Table 2.)

Intensity data were collected using a graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) (Enraf-Nonius CAD 4) and applying ω-2Θ-scan technique. Up to sin Θ/λ = 0.62 Å^{-1} 3450 symmetry independent reflections were measured from which 1789 with $I \geq 3.0\ \sigma(I)$ were graded as observed. The structure was solved by the conventional direct method (SIR). Full-matrix least-squares refinement of the atomic coordinates using anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms led to a convergence at R = 0.046 (R_w = 0.050).

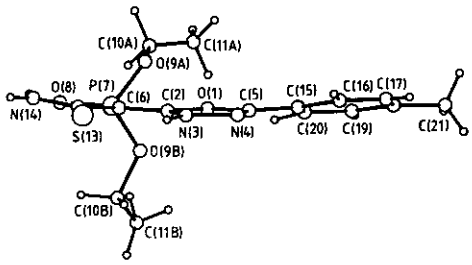


Figure 4: Molecular structure and atom numbering of **4.2b** in the crystalline state

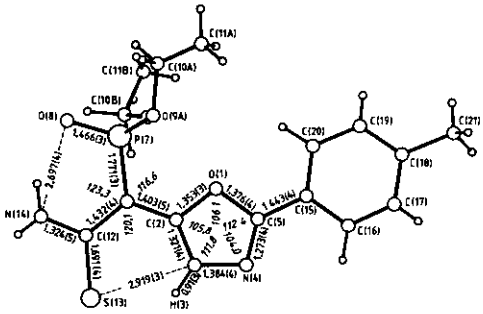


Figure 5: Bond distances (in Å) and some bond angles (in °) of **4.2b**

As seen from Figures 4 and 5, compound (**4.2b**) is nearly planar with the exception of the ethoxy groups of the phosphonato-substituents and the hydrogen atoms of the methyl group of the aryl substituent. In the oxadiazolering the maximum distance of the atoms from the least squares plane through the five ring atoms (O1, C2, N3, N4, C5) is 0.006 Å. The angle between the neighbouring phenyl ring and the heterocyclic plane is about 12 °. The thiocarbamoyl group and the P=O of the phosphonato group are both slightly twisted (about 4 °) out of the plane of the oxadiazole ring.

An intramolecular hydrogen bond was observed between N14-H...O8 (2.697 (4) Å; sum of the van der Waals radii for nitrogen and oxygen: 2.90 Å[7]); moreover the intramolecular S13...N3-distance (2.919 (3) Å) is visibly shorter than the sum of the van der Waals radii for sulfur and nitrogen (3.35 Å[7]).

Scheme 2 shows only one possible mesomeric derivative of **4v**. The bond lengths of the oxadiazole ring system are in accordance with the results of Ziyaev *et al.*[14] The delocalization of the π–electrons is reflected in the variations of the bond lengths. In the oxadiazole ring of **4.2b** the O1-C2- and O1-C5-distances (1.353 (3) Å and 1.376 (4) Å) show typical values for C-O single bonds.[13] The N4=C5 double bond (1.273 (4) Å) is shorter than comparable values described in the literature,[13] however the N3-N4-distance (1.384 (4) Å) is longer than expected for a N-N single bond.[13] The C2-N3 bond distance (1.321 (4) Å) corresponds to that of a C=N double bond in comparison with the ionic furoxan $^{+}N_2=C_3$-distance (1.316 Å),[13] while the C2-C6-bond (1.403 (5) Å) can be described with a bond order of about 1.5. The C6-C12- (1.432 (4) Å) and the

C5-C15-distances (1.443 (4) Å) are somewhat shorter than the corresponding [Csp^2-Csp^2]-bond (1.460 Å) earlier reported.[13]

The reaction mechanism can be described hypothetically in two different ways. One possibility could involve an initial nucleophilic attack on the 1,3-dithietane carbon by the β-N atom of the carboxylic acid hydrazide. Subsequent tautomerism, cyclization and transformation of the cyanogroup can lead directly to the observed 1,3,4-oxadiazole **4**. The initial nucleophilic attack is in accordance with the reaction of the 1,3-dithietane **2** with amines. These afford thiocarbamoyl-cyanomethylphoshonates and -phosphinates.[15] Another possibility involves nucleophilic attack by the β-N atom of the carboxylic acid hydrazide at the cyanogroup. This can also lead to the same product after tautomerism, cyclization and cleavage of the 1,3-dithietane ring system and corresponds to the observed addition of amines at the isocyano moiety of diethyl [(2,2-methylthio-1-isocyano)ethenyl]phosphonates.[16] Neither mechanism can be excluded at this time.

In some mass spectra of the 1,3,4-oxadiazoles (**4.2b**), (**4.2c**) and (**4.4b**) a mass peak of $M^+ + 28$ is determined, which probably can be explained by an intermolecular alkylation reaction, which takes place under the circumstances of the measurement.

In summary phosphonato- and phosphinato-substituted 1,3-dithietanes (**2**) are interesting starting materials for the synthesis of heterocyclic compounds.

EXPERIMENTAL

Melting points were determined on a Reichert hot stage microscope and are uncorrected. Infrared spectra were measured with a Perkin-Elmer ir-spectrophotometer 283 using potassium bromide and are given as cm^{-1}. ^1H- and ^{13}C Nmr spectra were recorded on either a Bruker WM-250 (^1H-Nmr: 250.13 MHz, ^{13}C-Nmr: 62.89 MHz) or a Varian XL 300 (^1H-Nmr: 299.95 MHz, ^{13}C-Nmr: 75.43 MHz) spectrometer in $CDCl_3$ or DMSO-d_6. In certain cases where the origin of splitting patterns can not unambigously be attributed to P,H-couplings or chemical shifts (diastereomeric effects), measurements at a higher field strength were performed (Bruker AMX 500, ^1H-Nmr: 500.14 MHz, ^{13}C-Nmr: 125.77 MHz). The chemical shifts are reported in parts per million (ppm) downfield from internal tetramethylsilane; coupling constants J are given in Hz.

^{31}P Nmr spectra were recorded with the Varian XL 300 (^{31}P-Nmr: 121.42 MHz) spectrometer using 85% H_3PO_4 as external standard. Ultraviolet spectra were measured with Perkin-Elmer 320 uv-spectrophotometer in acetonitrile and are given as λ_{max} (lg ϵ). Electron impact mass spectra were obtained on a Varian MAT 311A instrument. Element analyses were performed on a Heraeus Vario EL CHNS apparatus. P-analyses were conducted by the Department of Chemistry of the University of Heidelberg.

General procedure for the preparation of 1,3-dithietanes (**2**)

Either dialkyl cyanomethylphosphonate (**1.1-3**) or ethyl cyanomethylphenylphosphinate (**1.4**) (20 - 200 mmol) was slowly added at room temperature to a stirred suspension of sodium hydride (42 - 420 mmol, washed with n-pentane) in dry tetrahydrofuran (50 - 500 ml) under argon. Vigorous evolution of hydrogen and increasing reaction temperature (< 50 °C) were noted. After the addition was completed, the suspension was stirred for 1 h at room temperature. A solution of carbon disulfide (20 - 200 mmol) in dry tetrahydrofuran (5 - 50 ml) was added dropwise and the yellow suspension was vigorously stirred for 1.5 h at room temperature. A solution of acetyl chloride (40 - 400 mmol) in dry tetrahydrofuran (5 - 50 ml) was added and the suspension was refluxed for 1 h. The reaction mixture was cooled to room temperature and the excess of sodium hydride was quenched carefully with ice water (40 - 200 ml). The aqueous layer was acidified with 10 % HCl and extracted with three portions (20 - 100 ml) of chloroform. The combined organic layers were dried with anhydrous magnesium sulfate and filtered. The solvents were removed under reduced pressure and the product was either washed with ether or chromatographed on silica gel (*n*-hexane / ethyl acetate (2 : 1) as eluant).

Tetraethyl 1,3-dithietane-2,4-diylidenebis(cyanomethylphosphonate) (**2.2**):

Diethyl cyanomethylphosphonate (**1.2**) (35.4 g, 200 mmol) was treated in dry tetrahydrofuran (600 ml) under argon with sodium hydride (10.1 g, 420 mmol), carbon disulfide (15.2 g, 200 mmol) and acetyl chloride (31.4 g, 400 mmol).

- 23.8 g (54 %) **2.2** *were obtained as colorless crystals, mp* 137 °C *(ether).* ^1H*-Nmr (250.13 MHz,*

$CDCl_3$) δ = 1.37 (dt, $^4J_{PH}$ = 0.8 Hz, $^3J_{HH}$ = 7.1 Hz, 12H, $OCH_2C\underline{H}_3$), 4.07 - 4.34 (m, 8H, $OC\underline{H}_2CH_3$). ^{13}C-Nmr (62.89 MHz, $CDCl_3$, {^{1}H}) δ = 16.1 (d, $^3J_{PC}$ = 6 Hz, $OCH_2\underline{C}H_3$), 64.5 (d, $^2J_{PC}$ = 6 Hz, $O\underline{C}H_2CH_3$), 93.1 (d, $^1J_{PC}$ = 195 Hz, C-5, C-5'), 110.7 (d, $^2J_{PC}$ = 7 Hz, CN), 163.9 (d, $^2J_{PC}$ = 6 Hz, C-2, C-4). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 7.9 (s). Ir (KBr, tablet) ν = 3000(m), 2910(w), 2210(s), 1540(s), 1480(m), 1450(w), 1400(w), 1375(w), 1300(w), 1250(s), 1165(s), 1150(s), 1050(s), 1000(s), 955(s), 930(m), 910(w), 835(s), 750(s), 605(m), 595(m), 550(s). Uv (CH_3CN) λ_{max} (lg ε) = 214 (4.02), 309 (4.58), 323 (4.58). Anal. Calcd for $C_{14}H_{20}N_2O_6P_2S_2$: C, 38.36; H, 4.60; N, 6.39; P, 14.13; S, 14.63. Found: C, 38.46; H, 4.59; N, 6.42; P, 13.91; S, 14.45.-

Table 1: Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen-Atoms of **2.2**

Atom	x	y	z	$U_{eq} \cdot \frac{10^4}{Å^2}$
S(1)	0.57805(8)	0.32438(7)	0.29918(3)	633(2)
S(1')	0.40382(8)	0.38947(7)	0.20247(3)	628(2)
P(4)	0.30545(8)	0.41078(7)	0.38195(3)	647(2)
P(4')	0.67922(8)	0.30305(7)	0.12020(3)	666(2)
C(2)	0.3948(3)	0.3887(2)	0.2762(1)	574(6)
C(3)	0.2810(3)	0.4267(3)	0.3061(1)	612(6)
C(9)	0.1427(3)	0.4796(3)	0.2779(1)	740(8)
N(10)	0.0303(3)	0.5239(3)	0.2570(1)	1076(9)
O(5)	0.4575(2)	0.3552(2)	0.39938(7)	789(5)
O(6A)	0.2702(2)	0.5402(2)	0.40661(7)	738(5)
O(6B)	0.1594(2)	0.3399(2)	0.39757(8)	808(5)
C(7A)	0.3781(4)	0.6444(4)	0.4027(2)	980(9)
C(8A)	0.3650(5)	0.7312(4)	0.4474(2)	1380(10)
C(7B)	0.1468(4)	0.2033(3)	0.3896(1)	1055(10)
C(8B)	0.1622(6)	0.1434(5)	0.4444(2)	1591(18)
C(2')	0.5873(3)	0.3245(2)	0.2256(1)	555(6)
C(3')	0.6998(3)	0.2857(3)	0.1958(1)	611(6)
C(9')	0.8387(3)	0.2321(3)	0.2249(1)	767(8)
N(10')	0.9497(3)	0.1866(3)	0.2461(1)	1127(9)
O(5')	0.5240(2)	0.3524(2)	0.10163(8)	856(6)
O(6A')	0.7244(2)	0.1755(2)	0.09541(7)	741(5)
O(6B')	0.8221(2)	0.3802(2)	0.10610(8)	843(5)
C(7A')	0.6189(4)	0.0689(3)	0.0940(1)	955(9)
C(8A')	0.6721(4)	-0.0257(4)	0.0561(2)	982(9)
C(7B')	0.8300(5)	0.5151(4)	0.1165(2)	1183(12)
C(8B')	0.8287(9)	0.5822(5)	0.0686(2)	1945(28)

$U_{eq} = \frac{1}{3} \sum \sum U_{ij} a_i \cdot a_j a_i^* a_j^*$

Tetrakis(1-methylethyl) 1,3-dithietane-2,4-diylidenebis(cyanomethylphosphonate) (**2.3**):

Bis(1-methylethyl) cyanomethylphosphonate (**1.3**) (4.38 g, 20.0 mmol) was treated in dry tetrahydrofuran (100 ml) under argon with sodium hydride (1.00 g, 41.7 mmol), carbon disulfide (1.52 g, 20.0 mmol) and acetyl chloride (3.14 g, 40.0 mmol).

- 2.47 g (50 %) **2.3** were obtained as colorless crystals, mp 164 °C. ^{1}H-Nmr (299.95 MHz, $CDCl_3$) δ = 1.30, 1.41 (2 · d, $^3J_{HH}$ = 6.2 Hz, 24H, OCH(C<u>H</u>$_3$)$_2$), 4.72 (dseptett, $^3J_{HH}$ = 6.2 Hz, $^3J_{PH}$ = 7.7 Hz, 4H, OC<u>H</u>(CH$_3$)$_2$). ^{13}C-Nmr (75.43 MHz, $CDCl_3$, {1H}) δ= 23.7, 23.8 (2 · d, $^3J_{PC}$ = 5 Hz, OCH(<u>C</u>H$_3$)$_2$), 73.9 (d, $^2J_{PC}$ = 6 Hz, O<u>C</u>H(CH$_3$)$_2$), 94.1 (d, $^1J_{PC}$ = 194 Hz, C-5, C-5´), 110.9 (d, $^2J_{PC}$ = 7 Hz, CN), 163.0 (d, $^2J_{PC}$ = 6 Hz, C-2, C-4). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 5.7 (s). Ir (KBr, tablet) ν = 2990(m), 2940(w), 2200(s), 1540(s), 1470(w), 1455(w), 1385(m), 1380(w), 1375(w), 1245(s), 1180(w), 1150(m), 1140(w), 1095(w), 1000(s), 940(w), 890(m), 820(m), 750(m), 740(w), 605(m), 595(m), 555(s), 520(w). Uv (CH_3CN) λ_{max} (lg ε) = 214 (4.11), 309 (4.57), 323 (4.57). Anal. Calcd for $C_{18}H_{28}N_2O_6P_2S_2$: C, 43.72; H, 5.71; N, 5.67; P, 12.53; S, 12.97. Found: C, 43.81; H, 5.63; N, 5.68; P, 12.44; S, 12.76.-

Tetramethyl 1,3-dithietane-2,4-diylidenebis(cyanomethylphosphonate) (**2.1**):

Dimethyl cyanomethylphosphonate (**1.1**) (4.47 g, 30.0 mmol) was treated in dry tetrahydrofuran (150 ml) under argon with sodium hydride (1.50 g, 62.5 mmol), carbon disulfide (2.28 g, 30.0 mmol) and acetyl chloride (4.71 g, 60.0 mmol).

- 0.60 g (10 %) **2.1** were obtained as light yellow crystals, mp 187 °C. ^{1}H-Nmr (299.95 MHz, $CDCl_3$) δ = 3.88 (d, $^3J_{PH}$ = 11.7 Hz, 12H, OC<u>H</u>$_3$). ^{13}C-Nmr (75.43 MHz, $CDCl_3$, {1H}) δ = 54.3 (d, $^2J_{PC}$ = 6 Hz, O<u>C</u>H$_3$), 91.8 (d, $^1J_{PC}$ = 196 Hz, C-5, C-5´), 110.3 (d, $^2J_{PC}$ = 7 Hz, CN), 164.4 (d, $^2J_{PC}$ = 6 Hz, C-2, C-4). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 10.7 (s). Ir (KBr, tablet) ν = 2970(w), 2210(s), 1545(s), 1460(m), 1255(s), 1190(s), 1160(s), 1020(s), 935(w), 910(w), 850 (s), 840(s), 765(s), 600(m), 595(m), 555(s). Uv (CH_3CN) λ_{max} (lg ε) = 214 (4.05), 309 (4.55), 323 (4.56). Anal. Calcd for $C_{10}H_{12}N_2O_6P_2S_2$: C, 31.42; H, 3.16; N, 7.33; P, 16.20; S, 16.78. Found: C, 31.57; H, 3.28; N, 7.37; P, 16.01; S, 16.54.-

Diethyl 1,3-dithietane-2,4-diylidenebis(cyanomethylphenylphosphinate) (**2.4**):

Ethyl cyanomethylphenylphosphinate (**1.4**) (9.78 g, 47 mmol) was treated in dry tetrahydrofuran (250 ml) under argon with sodium hydride (2.40 g, 100 mmol), carbon disulfide (3.58 g, 47 mmol) and acetyl chloride (7.38 g, 94 mmol).

- 4.10 g (35 %) **2.4** were obtained as colorless crystals, mp 165-166 °C. ^{1}H-Nmr (299.95 MHz, $CDCl_3$) δ = 1.44 - 1.51 (m, 6H, $OCH_2C\underline{H}_3$), 4.21 - 4.32 (m, 4H, $OC\underline{H}_2CH_3$), 7.52 - 7.92 (m, 10H, H_{ar}). ^{13}C-Nmr (75.43 MHz, $CDCl_3$, {1H}) δ = 16.4 (d, $^3J_{PC}$ = 6 Hz, $OCH_2\underline{C}H_3$), 63.1 (d, $^2J_{PC}$ = 7 Hz, $O\underline{C}H_2CH_3$), 94.9 (d, $^1J_{PC}$ = 130 Hz, C-5, C-5´), 111.2 (d, $^2J_{PC}$ = 10 Hz, CN), 127.4 (d, $^1J_{PC}$ = 154 Hz, C-1´), 128.8 - 133.8 (m, C2´-6´). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 25.8 (m). Ir (KBr, tablet) ν = 2990(w), 2200(m), 1530(s), 1485(w), 1440(m), 1395(w), 1320(w), 1290(w), 1230(s), 1160(w), 1145(m), 1125(m), 1100(w), 1030(s), 1020(s), 995(w), 960(m), 815(m), 805(w), 770(w), 745(m), 715(m), 690(m), 600(m), 595(w), 530(s), 505(w). Uv (CH_3CN) λ_{max} (lg ε) = 219 (4.35), 320 (4.63), 334 (4.69). Anal. Calcd for $C_{22}H_{20}N_2O_4P_2S_2$: C, 52.59; H, 4.01; N, 5.58; P, 12.33; S, 12.76. Found: C, 52.49; H, 4.11; N, 5.58; P, 12.16; S, 12.82.-

General procedure for the preparation of tautomeric derivatives of Dialkyl 1,3,4-oxadiazole-2-yl-thiocarbamoylmethylphosphonates (**4.2-3**) and Alkyl 1,3,4-oxadiazole-2-yl-thiocarbamoylmethyl-phenylphosphinates (**4.4**):

A mixture of either tetraalkyl 1,3-dithietane-2,4-diylidenebis(cyanomethylphosphonates) (**2.2-3**) or diethyl 1,3-dithietane-2,4-diylidenebis(cyanomethylphenylphosphinate) (**2.4**) (2.0 mmol) and the corresponding carboxylic acid hydrazide (4.0 mmol) was refluxed in ethanol (10 ml) for 1-3 h (tlc-control). The reaction mixture was cooled to room temperature and either the colorless precipitate was isolated by filtration or the solution was concentrated to about 5 ml and then filtered.

Diethyl 5-phenyl-1,3,4-oxadiazole-2-yl-thiocarbamoylmethylphosphonate (**4.2a**):

- 1.14 g (80 %) **4.2a**, colorless crystals, mp 167 °C (ethanol). ^{1}H-Nmr (250.13 MHz, DMSO-d_6) δ = 1.25, 1.28 (2 • t, $^3J_{HH}$ = 7.0 Hz, 6H, $OCH_2C\underline{H}_3$), 4.14 - 4.26 (m, 4H, $OC\underline{H}_2CH_3$), 5.53 (d, $^2J_{PH}$ = 25.1 Hz, 1H, CH), 7.61 - 7.67 (m, 3H, H-3´, H-4´, H-5´), 7.97 - 8.01 (m, 2H, H-2´, H-6´), 9.32 (broad, 1H, NH), 10.11 (broad, 1H, NH). ^{13}C-Nmr (62.89 MHz, DMSO-d_6, {1H}) δ = 16.0 (2 • d, $^3J_{PC}$ = 6 Hz, $OCH_2\underline{C}H_3$), 51.1 (d, $^1J_{PC}$= 130 Hz, CH), 63.5, 63.8 (2 •d, $^2J_{PC}$ = 7 Hz, $O\underline{C}H_2CH_3$), 123.0 (s, C-1´), 126.4 (s, C-2´, C-6´), 129.5 (s, C-3´, C-5´), 132.1 (s, C-4´), 160.3 (d, $^2J_{PC}$ = 6 Hz, C-2), 164.6 (s, C-5), 193.6 (d, $^2J_{PC}$ = 5 Hz, CS). ^{31}P-Nmr (121.42 MHz, DMSO-d_6) δ = 13.9 (s). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 13.3 (s), 19.2 (s). Ir (KBr, tablet) ν = 3290(m), 3140(m), 2980(w), 2930(w), 2890(w), 1645(m), 1640(m), 1610(w), 1560(m), 1550(m), 1485(m), 1460(m), 1450(s), 1395(w), 1370(m), 1285(m), 1270(m), 1245(s), 1210(w), 1165(w), 1145(w), 1060(s), 1025(s), 980(m), 960(m), 775(m), 765(m), 735(m), 705(s), 685(m), 660(w), 605(m), 595(m), 535(w). Uv (CH_3CN) λ_{max} (lg ε) = 260 (4.36), 323 (3.73). Anal. Calcd for $C_{14}H_{18}N_3O_4PS$: C, 47.32; H, 5.11; N, 11.82; P, 8.72; S, 9.02. Found: C, 47.35; H, 5.01; N, 11.81; P, 8.63; S, 9.12.-

Diethyl 5-(4-methylphenyl)-1,3,4-oxadiazole-2-yl-thiocarbamoylmethylphosphonate (**4.2b**):

- 1.05 g (71 %) **4.2b**, colorless crystals, mp 151 °C (ethanol). ^{1}H-Nmr (250.13 MHz, DMSO-d_6) δ = 1.25, 1.28 (2 • dt, $^4J_{PH}$ = 0.7 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, $OCH_2C\underline{H}_3$), 2.40 (s, 3H, CH_3), 4.13 - 4.30 (m, 4H, $OC\underline{H}_2CH_3$), 5.52 (d, $^2J_{PH}$ = 25.0 Hz, 1H, CH), AA´BB´-signal ($\delta_A = \delta_{A'}$ = 7.45, 2H, H-3´, H-5´.- $\delta_B = \delta_{B'}$ = 7.89, 2H, H-2´, H-6´), 9.33 (broad, 1H, NH), 10.11 (broad, 1H, NH). ^{13}C-Nmr (75.43 MHz, DMSO-d_6, {1H}) δ = 16.1 (2 • d, $^3J_{PC}$ = 6 Hz, $OCH_2\underline{C}H_3$), 21.1 (s, $C_6H_4\underline{C}H_3$), 51.2 (d, $^1J_{PC}$ = 130 Hz, CH), 63.6, 63.8 (2 •d, $^2J_{PC}$ = 7 Hz, $O\underline{C}H_2CH_3$), 120.4 (s, C-1´), 126.4 (s, C-2´, C-6´), 130.1 (s, C-3´, C-5´), 142.4 (s, C-4´), 160.1 (d, $^2J_{PC}$= 7 Hz, C-2), 164.8 (s, C-5), 193.8 (d, $^2J_{PC}$ = 4 Hz, CS). ^{31}P-Nmr (121.42 MHz, DMSO-d_6) δ = 13.9 (s). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 13.3 (s), 19.3 (s). Ir (KBr, tablet) ν = 3410(m), 3260(m), 3180(m), 2980(m), 2910(w), 1620(s), 1605(s), 1575(s), 1560(s), 1540(s), 1505(m), 1480(w), 1440(w), 1395(s), 1320(m), 1300(m), 1200(s), 1180(m), 1115(w), 1050(s), 1020(s) 965(s), 895(m), 820(m), 800(m), 750(w), 730(m), 710(m), 685(m), 630(m), 600(w), 570(s), 530(w), 505(w). Uv (CH_3CN) λ_{max} (lg ε) = 262 (4.37), 323 (3.62). Anal. Calcd for $C_{15}H_{20}N_3O_4PS$: C, 48.77; H, 5.46; N, 11.38; P, 8.39; S, 8.68.

Found: C, 48.94; H, 5.49; N, 11.58; P, 8.33; S, 8.57.-

Table 2: Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen-Atoms of **4.2b**

Atom	x	y	z	$U_{eq} \cdot \frac{10^4}{Å^2}$
O(1)	0.8925(3)	0.07872(7)	0.6525(3)	417(6)
C(2)	1.0101(5)	0.0934(1)	0.8043(4)	419(9)
N(3)	1.0595(4)	0.0560(1)	0.8988(3)	509(9)
N(4)	0.9779(4)	0.0166(1)	0.8111(4)	532(9)
C(5)	0.8809(5)	0.0314(1)	0.6651(4)	429(9)
C(6)	1.0611(5)	0.1401(1)	0.8353(4)	415(9)
P(7)	0.9481(2)	0.17964(4)	0.6715(1)	569(3)
O(8)	1.0097(4)	0.22754(8)	0.7143(3)	728(9)
O(9*A*)	0.9864(5)	0.15996(9)	0.5156(3)	787(9)
C(10*A*)	0.921(1)	0.1818(2)	0.3551(7)	1500(30)
C(11*A*)	0.8245(9)	0.1578(3)	0.2260(8)	1350(20)
O(9B)	*0.7331(4)*	*0.1732(1)*	*0.6174(4)*	*880(10)*
C(10*B*)	0.6243(8)	0.1973(2)	0.6976(7)	1030(20)
C(11*B*)	0.4361(7)	0.2076(2)	0.5764(8)	1130(20)
C(12)	1.1968(5)	0.1538(1)	0.9936(4)	471(9)
S(13)	1.2888(2)	0.11843(4)	1.1612(1)	634(3)
N(14)	1.2563(5)	0.1972(1)	1.0100(4)	710(10)
C(15)	0.7678(5)	0.0056(1)	0.5189(4)	413(9)
C(16)	0.7798(5)	-0.0426(1)	0.5197(4)	541(9)
C(17)	0.6684(6)	-0.0669(1)	0.3844(5)	591(9)
C(18)	0.5398(5)	-0.0462(1)	0.2456(4)	483(9)
C(19)	0.5318(5)	0.0015(1)	0.2454(5)	534(9)
C(20)	0.6437(5)	0.0273(1)	0.3799(4)	478(9)
C(21)	0.4150(6)	-0.0745(2)	0.1015(5)	712(9)

$U_{eq} = \frac{1}{3} \sum \sum U_{ij} \, a_i \cdot a_j \, a_i^* \, a_j^*$

Diethyl 5-(4-chlorphenyl)-1,3,4-oxadiazole-2-yl-thiocarbamoylmethylphosphonate (**4.2c**):

- 1.42 g (91 %) **4.2c**, colorless crystals, mp 148 °C (ethanol). ^{1}H-Nmr (299.95 MHz, DMSO-d_6) δ = 1.27, 1.29 (2 • t, $^3J_{HH}$ = 6 Hz, 6H, $OCH_2C\underline{H}_3$), 4.05 - 4.31 (m, 4H, $OC\underline{H}_2CH_3$), 5.58 (d, $^2J_{PH}$ = 25.0 Hz, 1H, CH), AA'BB'-signal ($\delta_A = \delta_{A'}$ = 7.71, 2H, H-3', H-5'.- $\delta_B = \delta_{B'}$ = 8.00, 2H, H-2', H-6'), 9.38 (broad, 1H, NH), 10.17 (broad, 1H, NH). ^{13}C-Nmr (62.89 MHz, DMSO-d_6, {1H}) δ = 16.0 (2 • d, $^3J_{PC}$ = 6 Hz, $OCH_2\underline{C}H_3$), 51.1 (d, $^1J_{PC}$ = 130 Hz, CH), 63.6, 63.9 (2 • d, $^2J_{PC}$ = 6 Hz, $O\underline{C}H_2CH_3$), 121.9 (s, C-1'), 128.2 (s, C-2', C-6'), 129.7 (s, C-3', C-5'), 136.9 (s, C-4'), 160.5 (d, $^2J_{PC}$ = 6 Hz, C-2), 163.9 (s, C-5), 193.6 (d, $^2J_{PC}$ = 4 Hz, CS). ^{31}P-Nmr (121.42 MHz, DMSO-d_6) δ = 13.8 (s). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 13.2 (s), 19.0 (s). Ir (KBr, tablet) ν = 3400(w), 3250(w), 3170(w), 2970(w), 2910(w), 1620(m), 1595(m), 1550(s), 1485(m), 1380(m), 1315(m), 1290(m), 1195(s), 1170(m), 1105(w), 1090(m), 1040(s), 1010(s), 965(s), 945(m), 895(m), 895(m), 830(m), 810(w), 790(m), 750(w), 725(w), 715(w), 685(w), 650(w), 630(w), 625(w), 570(s), 540(m), 500(w). Uv (CH_3CN) λ_{max} (lg ε) = 265 (4.43), 326(3.54). Anal. Calcd for $C_{14}H_{17}N_3O_4ClPS$: C, 43.14; H, 4.40; N, 10.78; Cl, 9.10; P, 7.95; S, 8.23. Found: C, 43.28, H,4.44; N, 10.77; Cl, 9.34; P, 7.88; S, 8.07.-

Bis(1-methylethyl) 5-phenyl-1,3,4-oxadiazole-2-yl-thiocarbamoylmethylphosphonate (**4.3a**):

- 1.11 g (97 %) **4.3a**, colorless crystals, mp 175 °C (ethanol). ^{1}H-Nmr (299.95 MHz, DMSO-d_6) δ = 1.25, 1.27, 1.31, 1.32 (4 • d, $^3J_{HH}$ = 6.2 Hz, 12H, $OCH(C\underline{H}_3)_2$), 4.78 (dseptett, $^3J_{PH}$ = 7.3 Hz, $^3J_{HH}$ = 6.2 Hz, 2H, $OC\underline{H}(CH_3)_2$), 5.51 (d, $^2J_{PH}$ = 25.1 Hz, 1H, CH), 7.62 - 7.67 (m, 3H, H-3', H-4', H-5'), 7.99 - 8.02 (m, 2H, H-2', H-6'), 9.30 (broad, 1H, NH), 10.14 (broad, 1H, NH). ^{13}C-Nmr (75.43 MHz, DMSO-d_6, {1H}) δ = [23.2, 23.3 (2 • d, $^3J_{PC}$ = 6 Hz), 23.7, 23.8 (2 • d, $^3J_{PC}$ = 3 Hz); $OCH(\underline{C}H_3)_2$], 51.7 (d, $^1J_{PC}$ = 131 Hz, CH), 72.5, 72.8 (2 • d, $^2J_{PC}$ = 7 Hz, $O\underline{C}H(CH_3)_2$), 122.9 (s, C-1'), 126.2 (s, C-2', C-6'), 129.4 (s, C-3', C-5'), 132.0 (s, C-4'), 160.3 (d, $^2J_{PC}$ = 8 Hz, C-2), 164.4 (s, C-5), 193.6 (d, $^2J_{PC}$ = 4 Hz, CS). ^{31}P-Nmr (121.42 MHz, DMSO-d_6) δ = 12.1 (s). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 11.6 (s), 16.7 (s). Ir (KBr, tablet) ν =3320(m), 3080(s), 2980(s), 2940(m), 1645(s), 1605(m), 1545(s), 1480(s), 1440(s), 1385(s), 1370(s), 1315(w), 1250(s), 1210(m), 1180(s), 1140(m), 1105(s), 1065(m), 1000(s), 960(s), 900(m), 890(s), 820(m), 780(s), 765(s), 750(s), 705(s), 690(s), 650(s), 610(s), 595(m), 535(m). Uv (CH_3CN) λ_{max} (lg ε) = 260 (4.33), 324 (3.45).

Anal. Calcd for $C_{16}H_{22}N_3O_4PS$: C, 50.12; H, 5.78; N, 10.96; P, 8.08; S, 8.36. Found: C, 50.24; H, 5.74; N, 10.99; P, 8.04; S, 8.44.-

Bis(1-methylethyl) 5-(4-methylphenyl)-1,3,4-oxadiazole-2-yl-thiocarbamoylmethylphosphonate (**4.3b**):

- 0.99 g (83 %) **4.3b**, colorless crystals, mp 162 °C (ethanol). ^{1}H-Nmr (299.95 MHz, DMSO-d_6) δ = 1.25, 1.26, 1.30, 1.31 (4 • d, $^3J_{HH}$ = 6.0 Hz, 12H, OCH(C$\underline{H}_3$)$_2$), 2.41 (s, 3H, $C_6H_4C\underline{H}_3$), 4.78 (dseptett, $^3J_{PH}$ = 6.9 Hz, $^3J_{HH}$ = 6.3 Hz, 2H, OC$\underline{H}$(CH$_3$)$_2$), 5.49 (d, $^2J_{PH}$ = 25.1 Hz, 1H, CH), AA´BB´-signal ($\delta_A = \delta_{A'}$= 7.44, 2H, H-3´, H-5´.- $\delta_B = \delta_{B'}$= 7.89, 2H, H-2´, H-6´), 9.30 (broad, 1H, NH), 10.14 (broad, 1H, NH). ^{13}C-Nmr (75.43 MHz, DMSO-d_6, {1H}) δ = 21.1 (s, $C_6H_4\underline{C}H_3$), [23.2, 23.3 (2 • d, $^3J_{PC}$ = 6 Hz), 23.7, 23.8 (2 • d, $^3J_{PC}$ = 3 Hz); OCH(C$\underline{H}_3$)$_2$], 51.7 (d, $^1J_{PC}$ = 130 Hz, CH), 72.3, 72.7 (2 • d, $^2J_{PC}$ = 7 Hz, O$\underline{C}$H(CH$_3$)$_2$), 120.3 (s, C-1´), 126.2 (s, C-2´, C-6´), 129.9 (s, C-3´, C-5´), 142.2 (s, C-4´), 160.0 (d, $^2J_{PC}$ = 8 Hz, C-2), 164.5 (s, C-5), 193.6 (d, $^2J_{PC}$ = 4 Hz, CS). ^{31}P-Nmr (121.42 MHz, DMSO-d_6) δ = 12.3 (s). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 11.6 (s), 16.7 (s). Ir (KBr, tablet) ν = 3310(m), 3100(s), 2980(s), 2940(m), 1645(s), 1615(m), 1585(w), 1550(s), 1500(s), 1450(s), 1385(s), 1325(s), 1310(w), 1285(m), 1250(s), 1210(m), 1180(s), 1145(m), 1105(s), 1085(m), 1000(s), 960(s), 940(m), 890(m), 825(s), 750(m), 735(s), 720(s), 695(m), 660(m), 610(s), 595(m), 540(m). Uv (CH_3CN) λ_{max} (lg ε) = 263 (4.43), 323 (3.54). Anal. Calcd for $C_{17}H_{24}N_3O_4PS$: C, 51.38; H, 6.09; N, 10.57; P, 7.79; S, 8.07. Found: C, 51.31; H, 6.06; N, 10.45; P, 7.65; S, 8.01.-

Ethyl 5-phenyl-1,3,4-oxadiazole-2-yl-thiocarbamoylmethylphenylphosphinate (**4.4a**)

- 1.19 g (85 %) **4.4a**, colorless crystals, mp 180 °C (ethanol). ^{1}H-Nmr (299.95 MHz, DMSO-d_6) δ = 1.27, 1.31 (2 • t, $^3J_{HH}$ = 7.0 Hz, 3H, OCH$_2$C$\underline{H}_3$), 4.14 - 4.20 (m, 2H, OC$\underline{H}_2$CH$_3$), [5.73 (d, $^2J_{PH}$ = 19.8 Hz), 5.76 (d, $^2J_{PH}$ = 20.8 Hz); 1H, CH], 7.51 - 7.96 (m, 10H, H_{ar}), 9.33 (broad (2 signals), 1H, NH), 10.13 (broad (2 signals), 1H, NH). ^{13}C-Nmr (75.43 MHz, DMSO-d_6, {1H}) δ = 16.4 (2 • d, $^3J_{PC}$ = 6 Hz, OCH$_2$$\underline{C}H_3$), [54.3 (d, $^1J_{PC}$ = 82 Hz), 54.5 (d, $^1J_{PC}$ = 81 Hz); CH], 62.4, 62.6 (2 • d, $^2J_{PC}$ = 7 Hz, O$\underline{C}$H$_2$CH$_3$), 122.8, 123.0 (2 • s, C-1´), 128.1, 128.3 (2 • d, $^1J_{PC}$ = 139 Hz, C-1´´), 126.3 - 133.1 (m, C-2´-6´; C-2´´-6´´), [159.9 (d, $^2J_{PC}$ = 4 Hz), 160.0 (d, $^2J_{PC}$ = 5 Hz); C-2], 164.4,

164.5 (2 • s, C-5), 193.4, 193.6 (2 • d, $^2J_{PC}$ = 3 Hz, CS). ^{31}P-Nmr (121.42 MHz, DMSO-d_6) δ = 30.8 (s), 31.4(s). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 31.4 (s), 32.0(s), 32.4(s). Ir (KBr, tablet) ν = 3280(m), 3100(m), 2990(w), 1640(w), 1610(w), 1585(w), 1565(m), 1550(m), 1485(m), 1450(s), 1370(w), 1270(w), 1230(s), 1205(w), 1160(w), 1125(m), 1070(w), 1030(s), 995(w), 960(m), 780(m), 755(w), 705(s), 690(s), 665(w), 605(s), 595(s), 540(w). Uv (CH_3CN) λ_{max} (lg ε) = 261 (4.33), 319 (3.53). Anal. Calcd for $C_{18}H_{18}N_3O_3PS$: C, 55.81; H, 4.68; N, 10.85; P, 8.00; S, 8.28. Found: C, 56.04; H, 4.80; N, 10.90; P, 8.07; S, 8.43.-

Ethyl 5-(4-methylphenyl)-1,3,4-oxadiazole-2-yl-thiocarbamoylmethylphenylphosphinate (**4.4b**):

-1.39 g (87 %) **4.4b**, colorless crystals, mp 157 °C (ethanol). ^{1}H-Nmr (299.95 MHz, DMSO-d_6) δ = 1.26, 1.30 (2 • t, $^3J_{HH}$ = 7.0 Hz, 3H, $OCH_2C\underline{H}_3$), 2.39, 2.40 (s, 3H, CH_3), 4.09 - 4.38 (m, 2H, $OC\underline{H}_2CH_3$), [5.71 (d, $^2J_{PH}$ = 19.8 Hz), 5.74 (d, $^2J_{PH}$ = 20.8 Hz); 1H, CH], 7.35 - 8.00 (m, 9H, H_{ar}), 9.38 (broad (2 signals), 1H, NH), 10.18 (broad (2 signals), 1H, NH). ^{13}C-Nmr (75.43 MHz, DMSO-d_6, {1H}) δ = 16.3 (2 • d, $^3J_{PC}$ = 6 Hz, $OCH_2\underline{C}H_3$), 21.1 (s, $C_6H_4\underline{C}H_3$), [54.2 (d, $^2J_{PC}$ = 82 Hz), 54.5 (d, $^2J_{PC}$ = 81 Hz); CH], 62.2, 62.5 (2 • d, $^2J_{PC}$ = 7 Hz, $O\underline{C}H_2CH_3$), 120.0, 120.2 (2 • s, C-1´), 128.1, 128.2 (2 • d, $^1J_{PC}$ = 139 Hz, C-1´´), 126.2 - 133.0 (m, C-2´,3´,5´,6´,C-2´´-6´´), 142.2 (s, C-4´), [159.6 (d, $^2J_{PC}$ = 4 Hz), 159.7 (d, $^2J_{PC}$ = 5 Hz); C-2], 164.4, 164.5 (2 • s, C-5), 193.3, 193.5 (2 • d, $^2J_{PC}$ = 3 Hz, CS). ^{31}P-Nmr (121.42 MHz, DMSO-d_6) δ = 30.8 (s), 31.5 (s). ^{31}P-Nmr (121.42 MHz, $CDCl_3$) δ = 31.4 (s), 32.0 (s), 32.4 (s). Ir (KBr, tablet) ν = 3360(m), 3230(w), 3255(m), 2980(w), 1620(m), 1605(m), 1560(s), 1505(m), 1440(m), 1390(s), 1315(s), 1300(m), 1175(s), 1120(s), 1055(m), 1040(s), 1020(m), 995(m), 970(m), 890(m), 820(m), 780(m), 760(m), 730(m), 710(m), 695(m), 650(w), 630(w). Uv (CH_3CN) λ_{max} (lg ε) = 265 (4.41), 320 (3.61). Anal. Calcd for $C_{19}H_{20}N_3O_3PS$: C, 56.85; H, 5.02; N, 10.47; P, 7.72; S, 7.99. Found: C, 56.97; H, 5.07; N, 10.52; P, 7.71; S, 8.07.-

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Dedicated on 70th birthday of Arnold B r o s s i, Scientist Emeritus NIH, Bethesda / Washington / USA.

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