Synthesis and X-ray Study of Hexahydro- and Tetrahydrophospholo-[2,3-*d*]isoxazoles, a New Class of Heterocycles of Potential Fungicidal Activity

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Hexahydro-, **5b-l** and **6a,f,l** and tetrahydrophospholo[2,3-*d*]isoxazoles **8**, **9** and **10** were synthesized by 1,3-dipolar cycloaddition of nitrones **3b-l** and benzonitrile oxide (**4**) to 2,3-dihydro-1-phenyl-1*H*-phosphole 1-oxide (**1**) and 2,3-dihydro-1-ethoxy-1*H*-phosphole 1-oxide (**2**). The structural assignment to the compounds was confirmed by an X-ray study of two compounds of the series **5a** and **5m**. The compounds show a good activity as fungicides against *Plasmopara viticola* on vines and against *Botrytis cinerea* on apples. Compounds **5a-d** showed weak to moderate activity as herbicides.

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Introduction.

In the course of the ongoing study on 1,3-dipolar cycloadditions to phosphinyl ethenes [1], novel oxaza-heterocylic structures containing a phosphorus atom became easily available in a highly stereoselective manner.

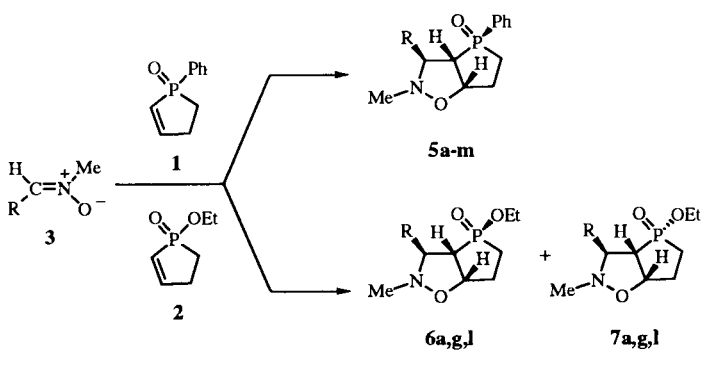
These compounds could be considered excellent candidates for testing of their fungicidal or herbicidal activity, as commonly such kind of heterocycles, containing one, or more than one, heteroatom like nitrogen, oxygen or sulfur, as well as phosphorylated compounds, are often found to show this activity [2]. In particular, of all the compounds submitted to test, the most active one was found to have the phospholo[2,3-*d*]isoxazolidine structure, obtained by cycloaddition of 2,3-dihydro-1-phenyl-1*H*-phosphole 1-oxide (**1**) to *N*-methyl-*C*-phenylnitrone (**3a**) [1d]. The high fungicidal activity showed by compound **5a** prompted us to synthesize structural analogues containing selected functionalities on the *C*-nitrone substituent, different substitution on the phosphorus atom and a different degree of saturation of the isoxazole ring. All these compounds were tested as fungicides and herbicides.

We now report about the synthesis of this new class of hexahydro-, **5a-m** and **6,7a,f,l** and tetrahydrophospholo[2,3-*d*]isoxazoles **8**, **9**, and **10** and their biological activity. The structural features of these rather novel heterocyclic systems incorporating phosphorus will also be detailed by two X-ray structures.

Results and Discussion.

In Table 1 are reported the results of the 1,3-dipolar cycloadditions of nitrones **3a-m** to 2,3-dihydro-1-phenyl-1*H*-phosphole 1-oxide (**1**) (Scheme 1). The cycloadditions of 2,3-dihydro-1-ethoxy-1*H*-phosphole 1-oxide (**2**) to nitrones **3a,f,l** (Scheme 1) and of both **1** and **2** to benzonitrile oxide (**4**) were also carried out (Table 1 and Scheme 2). All the cycloadditions needed a high temperature to take place due to the low reactivity of the dihy-

Scheme 1



a, R = Phenyl
b, R = 4-F_3C-Phenyl
c, R = 4-MeO-Phenyl
d, R = 2-Cl-Phenyl
e, R = 4-F-Phenyl
f, R = 2,4-Cl_2-Phenyl
g, R = 2-Pyridyl
h, R = 3-Pyridyl
i, R = 3-Quinolinyl
j, R = 2-Furyl
k, R = 2-(4-NO_2)-Furyl
l, R = EtOOC
m, R = MeOOC

Table 1

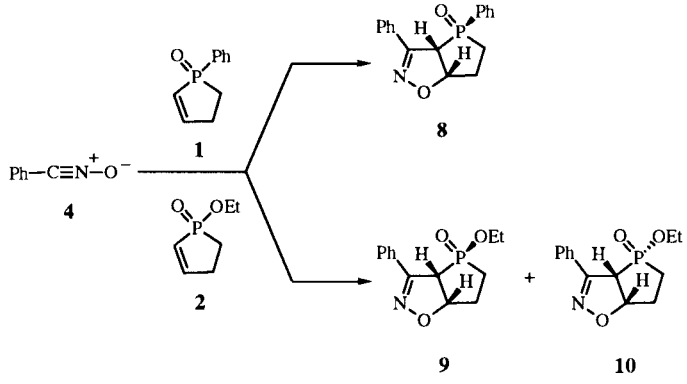
Cycloaddition of Nitrones **3a-m** to Dihydrophosphole **1**, of Nitrones **3a,f,l** to Dihydrophosphole **2** and of Dihydrophospholes **1** and **2** to Benzonitrile Oxide **4**.

Entry	Compound	Reactions conditions (refluxing solvent, time)	Yield, %	Diasterioisomer ratio [a]	^{31}p (ppm)
1	**5a** [b]	toluene, 2 h	72	—	58.00
2	**5b**	xylene, 20 h	30	—	59.35
3	**5c**	xylene, 4 h	85	—	58.11
4	**5d**	xylene, 5 h	84	—	55.58
5	**5e**	xylene, 6 h	50	—	59.33
6	**5f**	xylene, 7 h	66	—	55.36
7	**5g**	toluene, 3 h	55	—	54.27
8	**5h**	xylene, 23 h	49	—	59.07
9	**5i**	xylene, 8 h	84	—	59.10
10	**5j**	toluene, 3 h	46	—	58.60
11	**5k**	mesitylene, 24 h	12	—	58.02
12	**5l**	xylene, 2 h	64	—	57.94
13	**5m** [b]	toluene, 2 h	65	—	57.36
14	**6a, 7a**	toluene, 8 h	66	2:1	76.26[c], 70.49
15	**6g, 7g**	toluene, 3 h	47	5:1	70.84[c], 69.82
16	**6l, 7l**	toluene, 3 h	76	1.6:1	75.10[c], 71.29
17	**8**	benzene, 2 h	35	—	60.03
18	**9, 10**	benzene, 2 h	68	4:1	72.03[c], 71.48

[a] Calculated by integration of ^{1}H-nmr signals. [b] Ref 1d. [c] Resonances ofthe major and minor isomer are reported in sequence.

drophospholes. Nitrones were used in slight excess (1.2 equivalents) and the yields of the adducts were good to moderate, unless affected by the low stability of the nitrones (see entry 2 and 11, Table 1). Cycloadditions of the benzonitrile oxide (**4**) were carried out by slow addition of a solution of the benzohydroximic acid chloride to the refluxing reaction mixture containing triethylamine. In all the reactions the cycloaddition gave regioselectively adducts bearing the phosphorus substituent in the 4 position of the isoxazolidine ring. Dihydrophosphole **1** gave in all the reactions one single diastereoisomer with complete stereoselectivity. The structure assignment can be made in all cases on the basis of nmr data and their comparison with previous results [1]. The *trans* C3-C4 (isoxazolidine numberings) relationship in all the isoxazolidine compounds **5a-m** and **6a,g,l** is documented by diagnostic coupling constants of H3 and H4 protons (in the range 5-7 Hz, when observed) and confirmed by the high values of H3-P coupling constants (in the range 14-17 Hz, when observed) in accord with a *cis* relationship between the H3 proton and the phosphorus atom [1b]. It is worth noting that the preference for a *trans* C3-C4 relationship in these isoxazolidines containing substituents at C4 is steered by the bias to minimize the steric interactions at the transition state, independently of what the *Z* or *E* configuration of the nitrone is. At the high temperature conditions of the cycloaddition a fast equilibrium between the more stable *Z* and *E* configurations of the nitrone is likely [3].

Scheme 2



The assigned stereochemistry at the phosphorus atom, as derived from the approach of the nitrone on the face of the phosphole opposite to the phenyl group in compounds **5a-m**, has been proven by the observation of the chemical shifts of H3 and H4 isoxazolidine protons. Values for H4 protons (in the range 2.80-3.56 ppm) denote the presence of a shielding effect of the *cis* phenyl group and compare with those for H3 protons (4.07-4.84 ppm) which experience a deshielding effect of the proximate phosphinyl oxygen.

The structural assignment has been confirmed by a single crystal X-ray study of compounds **5a** and **5m**. Figure 1 shows perspective views of **5a** and **5m**.

A deformation typical for a phosphorus tetrahedron containing carbon and oxygen atoms is observed in the molecules. The most distorted angles are the intraring angles C1-P-C4, equal 95.8(1) and 96.3(1) for molecule **5a** and **5m**, respectively.

The five membered phospholane rings in molecule **5a** and **5m** exists in the conformation of a deformed envelope with C2 atom deviated from the plane of the four atoms, similarly as observed in precedent studies [4].

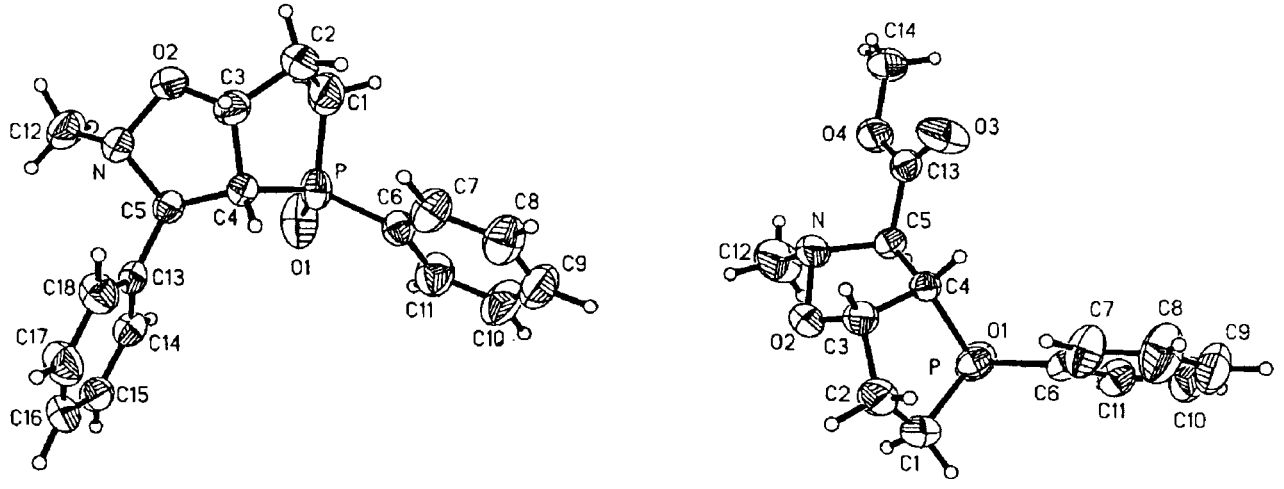


Figure 1. Ortep view of **5a** and **5m**.

Asymmetry parameters [5] of the rings in relation to the plane of symmetry are: ΔC_S (P-C4) = 6.8° and 6.4° for molecule **5a** and **5m**, respectively. The isoxazoline N-O2-C3-C4-C5 ring in **5a** exists in half-chair conformation with ΔC_S(N-O2) = 4.0°, contrary to envelope conformation in molecule **5m** (ΔC_S(C4-C5) = 1.0°). The planes P-C1-C3-C4 and N-C3-C4-C5 of the two condensed five-membered rings form the dihedral angle of 65.1(1)° in **5a**, and 60.0(1)° in **5m**. The decrease of this dihedral angle in **5m** is caused by the intramolecular attractive interaction C4-H41...03 (H41...03 = 2.41Å with the angle C4-H41...03 108°; distance C4...03 is 2.852(4)Å). Moreover, contrary to structure **5a**, in structure **5m** the molecules operated by the translations along the *x* and *z* axis are connected by the hydrogen bond C7-H71...01 (H71...01 = 2.30Å, C7...01 = 3.218(3)Å and angle C7-H71...01 = 160°). The positions of the P=O bonds in relation to the phospholane ring are similar in **5a** and **5m**, the torsion angles O1-P-C6-C11 being 7.1(2)° and 10.9(2)°, respectively. The conformation of -$COOCH_3$ group in **5m** along the C5-C13 bond in relation to N-C5 bond is -ac, +sc.

Dihydrophosphole **2** gave mixtures of diastereoisomers either in the cycloadditions of the nitrones **3a,f,l** or of the nitrile oxide **4**. The ^{31}P-nmr shows a regular trend for the minor isomers **7a,f,l** resonating upfield respect to the relative major isomers **6a,f,l** in both type of cycloadducts. Despite the assignment was only tentative from ^{1}H-nmr, because of the lack of a discriminating phenyl group on the molecule, by analogy, the major isomer was assigned

Table 2

Crystal Data end Experimental Parameters for **5a** and **5m**

	5a	**5m**
Molecular formula	$C_{18}H_{20}NO_2P$	$C_{14}H_{18}NO_4P$
M_r	313.34	295.27
Space group	$P2_1/n$	$P2_1/n$
a/Å	7.576(1)	6.453(1)
b/Å	22.132(2)	21.795(3)
c/Å	9.771(1)	11.021(1)
b/deg	95.26(1)	101.62(1)
β/Å^3	1631.4(4)	1518.3(4)
Z	4	4
F(000)	664	624
D_x /mg m^{-3}	1.276(3)	1.292(3)
D_m /mg m^{-3}	1.27(2)	1.28(2)
μ (Mo Kα) cm^{-1}	1.69	1.86
Transmission factor	0.97	0.98
Radiation	Mo Kα	Mo Kα
Scan mode	ω-2θ	ω-2θ
Crystal size/mm	0.40, 0.32, 0.24	0.42, 0.38, 0.08
2θ range (°)	2-60	2-60
Reflections with I>3σ(I)	2322	2199
R	0.045	0.046
R_w	0.045	0.045

Table 3

5a: Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 x 10^3)

	X	Y	Z	U(eq)
P	8500(1)	2426(1)	143(1)	45(1)
O	10176(3)	2562(1)	993(2)	73(1)
O	5757(2)	3647(1)	65(2)	47(1)
N	6982(3)	4038(1)	-597(2)	43(1)
C(1)	6547(4)	2378(1)	1062(3)	69(1)
C(2)	5026(4)	2600(1)	67(4)	67(1)
C(3)	5703(3)	3119(1)	-771(3)	44(1)
C(4)	7643(3)	3019(1)	-1053(2)	34(1)
C(5)	8526(3)	3633(1)	-698(2)	35(1)
C(6)	8674(3)	1736(1)	-821(2)	42(1)
C(7)	7351(4)	1515(1)	-1759(3)	55(1)
C(8)	7526(4)	954(1)	-2356(3)	64(1)
C(9)	9014(4)	613(1)	-2052(3)	67(1)
C(10)	10352(4)	839(2)	-1166(4)	76(1)
C(11)	10190(4)	1394(1)	-552(3)	63(1)
C(12)	7390(4)	4531(1)	358(3)	62(1)
C(13)	9699(3)	3886(1)	-1724(2)	35(1)
C(14)	11504(3)	3941(1)	-1414(3)	41(1)
C(15)	12575(3)	4174(1)	-2362(3)	49(1)
C(16)	11839(4)	4354(1)	-3628(3)	54(1)
C(17)	10046(4)	4307(1)	-3952(3)	59(1)
C(18)	8972(3)	4078(1)	-3011(3)	50(1)

as derived from the attack of the nitrone from the side of the phosphinoyl oxygen. The same argument applies for isoxazolines **9** and **10**. The low diastereofacial selectivity observed in these cycloadditions is clearly a consequence of the replacement of a sterically demanding phenyl group on phosphorus with an ethoxy group.

Results of Biological Tests.

The compounds have been tested for their activity as herbicides, both in pre-emergence tests as well as in post-emergence tests.

Compounds **5a**, **5c**, **5d**, showed only weak activity against *Sinapis* in the contact test (post emergence test) at test concentrations of 2 kg of active ingredient per hectare. At the same concentration **5b** showed moderate activity against *Sinapis* and against *Stellaria*. No remarkable activity against the other weed species has been observed. None of the compounds showed herbicidal activity in the pre-emergence test.

The compounds have also been tested for their activity as fungicides against *Plasmopara viticola* on vines and against *Botrytis cinerea* on apples. Compounds **5i** and **6a** showed good activity against *Plasmopara viticola* on vines at concentration of 200 ppm. At the same concentration a good activity against *Botrytis cinerea* on apples has been observed with **6g**.

Table 4

5a: Bond Lengths (Å)

P-O(1)	1.484 (3)	P-C(1)	1.803 (4)
P-C(4)	1.836 (3)	P-C(6)	1.805 (3)
O(2)-N	1.463 (3)	O(2)-C(3)	1.423 (3)
N-C(5)	1.484 (3)	N-C(12)	1.449 (4)
C(1)-C(2)	1.520 (5)	C(2)-C(3)	1.527 (4)
C(3)-C(4)	1.536 (4)	C(4)-C(5)	1.542 (3)
C(5)-C(13)	1.507 (4)	C(6)-C(7)	1.384 (4)
C(6)-C(11)	1.380 (4)	C(7)-C(8)	1.383 (4)
C(8)-C(9)	1.366 (5)	C(9)-C(10)	1.366 (5)
C(10)-C(11)	1.377 (5)	C(13)-C(14)	1.379 (4)
C(13)-C(18)	1.392 (4)	C(14)-C(15)	1.386 (4)
C(15)-C(16)	1.369 (4)	C(16)-C(17)	1.370 (4)
C(17)-C(18)	1.379 (4)		

Table 5

5a: Bond Angles (°)

O(1)-P-C(1)	115.6(1)	O(1)-P-C(4)	116.5(1)
C(1)-P-C(4)	95.8(1)	O(1)-P-C(6)	111.4(1)
C(1)-P-C(6)	108.3(1)	C(4)-P-C(6)	108.1(1)
N-O(2)-C(3)	102.6(2)	O(2)-N-C(5)	102.0(2)
O(2)-N-C(12)	105.5(2)	C(5)-N-C(12)	111.9(2)
P-C(1)-C(2)	105.7(2)	C(1)-C(2)-C(3)	108.3(2)
O(2)-C(3)-C(2)	107.7(2)	O(2)-C(3)-C(4)	104.1(2)
C(2)-C(3)-C(4)	111.2(2)	P-C(4)-C(3)	106.1(2)
P-C(4)-C(5)	111.5(2)	C(3)-C(4)-C(5)	103.6(2)
N-C(5)-C(4)	102.7(2)	N-C(5)-C(13)	109.7(2)
C(4)-C(5)-C(13)	116.6(2)	P-Cl(6)-C(7)	124.1(2)
P-C(6)-C(11)	117.6(2)	C(7)-C(6)-C(11)	118.2(2)
C(6)-C(7)-C(8)	120.3(3)	C(7)-C(8)-C(9)	120.9(3)
C(8)-C(9)-C(10)	119.0(3)	C(9)-C(10)-C(11)	120.8(3)
C(6)-C(11)-C(10)	120.7(3)	C(5)-C(13)-C(14)	121.4(2)
C(5)-C(13)-C(18)	120.4(2)	C(14)-C(13)-C(18)	118.3(2)
C(13)-C(14)-C(15)	121.1(2)	C(14)-C(15)-C(16)	119.8(3)
C(15)-C(16)-C(17)	120.0(2)	C(16)-C(17)-C(18)	120.4(3)
C(13)-C(18)-C(17)	120.4(2)		

Table 6

5m: Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 x 10^3)

	X	Y	Z	U(eq)
P	898(1)	2537(1)	2320(1)	39(1)
O(1)	-703(3)	2360(1)	1213(2)	56(1)
O(2)	3852(3)	1321(1)	2791(2)	52(1)
O(3)	-951(4)	1303(1)	4999(2)	72(1)
O(4)	-1668(3)	542(1)	3660(2)	59(1)
N	2200(4)	909(1)	3053(2)	51(1)
C(1)	3577(5)	2629(1)	2090(3)	56(1)
C(2)	5008(4)	2350(1)	3238(3)	56(1)
C(3)	3861(4)	1807(1)	3655(2)	43(1)
C(4)	1504(4)	1948(1)	3531(2)	34(1)
C(5)	428(4)	1335(1)	3130(2)	38(1)
C(6)	110(4)	3223(1)	3023(2)	41(1)
C(7)	1075(5)	3425(1)	4189(3)	65(1)
C(8)	363(7)	3950(2)	4670(3)	83(2)
C(9)	-1316(6)	4273(2)	4013(3)	77(2)
C(10)	-2298(6)	4070(2)	2862(3)	69(1)
C(11)	-1594(5)	3549(1)	2367(3)	52(1)
C(12)	1747(7)	506(2)	1982(4)	90(2)
C(13)	-791(4)	1072(1)	4052(3)	41(1)
C(14)	-2896(6)	254(2)	4476(4)	73(2)

Table 7

5m: Bond Lengths (Å)

P-O(1)	1.483(2)	P-C(1)	1.808(3)
P-C(4)	1.837(2)	P-C(6)	1.801(3)
O(2)-N	1.467(3)	O(2)-C(3)	1.423(3)
O(3)-C(13)	1.182(4)	O(4)-C(13)	1.320(3)
O(4)-C(14)	1.455(5)	N-C(5)	1.489(4)
N-C(12)	1.452(5)	C(1)-C(2)	1.533(4)
C(2)-C(3)	1.516(4)	C(3)-C(4)	1.531(3)
C(4)-C(5)	1.528(3)	C(5)-C(13)	1.517(4)
C(6)-C(7)	1.383(4)	C(6)-C(11)	1.385(4)
C(7)-C(8)	1.377(5)	C(8)-C(9)	1.371(5)
C(9)-C(10)	1.372(5)	C(10)-C(11)	1.376(5)

Table 8

5m: Bond Angles(°)

O(1)-P-C(1)	116.1(1)	O(1)-P-C(4)	115.2(1)
C(1)-P-C(4)	96.3(1)	O(1)-P-C(6)	111.1(1)
C(1)-P-C(6)	109.3(1)	C(4)-P-C(6)	107.8(8)
N-O(2)-C(3)	103.2(2)	C(13)-O(4)-C(14)	115.2(2)
O(2)-N-C(5)	103.0(2)	O(2)-N-C(12)	104.2(3)
C(5)-N-C(12)	113.1(2)	P-C(1)-C(2)	105.9(2)
C(1)-C(2)-C(3)	108.1(2)	O(2)-C(3)-C(2)	108.3(2)
O(2)-C(3)-C(4)	102.7(2)	C(2)-C(3)-C(4)	110.7(2)
P-C(4)-C(3)	105.5(2)	P-C(4)-C(5)	112.6(2)
C(3)-C(4)-C(5)	103.6(2)	N-C(5)-C(4)	104.6(2)
N-C(5)-C(13)	108.1(2)	C(4)-C(5)-C(13)	113.8(2)
P-C(6)-C(7)	123.4(2)	P-C(6)-C(11)	117.7(2)
C(7)-C(6)-C(11)	118.8(3)	C(6)-C(7)-C(8)	120.1(3)
C(7)-C(8)-C(9)	120.8(3)	C(8)-C(9)-C(10)	119.4(3)
C(9)-C(10)-C(11)	120.3(3)	C(6)-C(11)-C(10)	120.5(3)
O(3)-C(13)-O(4)	123.6(3)	O(3)-C(13)-C(5)	125.4(2)
O(4)-C(13)-C(5)	111.0(2)		

EXPERIMENTAL

All the reactions were carried out under inert atmosphere (nitrogen) and the solvents were appropriately dried before use. The R_f values refer to tlc on 0.25 mm silica gel plates obtained using the same eluent as in the column chromatographies. The ir data refers to spectra registered on chloroform solution of the samples. Only nmr resonances (deuteriochloroform solution) out of the aromatic region of the spectra were reported, unless otherwise stated. Chemical shifts values are reported in ppm from tetramethylsilane: notation s, d, t, q, m and b designate singlet, doublet, triplet, quartet, multiplet and broad, respectively; for ^{13}C-nmr multiplicity with phosphorus is reported. Dihydrophospholes **1** and **2** were synthesized according to references 6 and 7, respectively. Nitrones were synthesized according to published procedures by reaction of *N*-methylhydroxylamines with corresponding aldehydes [8].

Cycloadditions of Nitrones **3b-l** to 2,3-Dihydro-1-phenyl-1*H*-phosphole 1-Oxide (**1**).

A 2 *M* solution of 2,3-dihydro-1-phenyl-1*H*-phosphole 1-oxide (**1**) (5-10 mmoles) and nitrones **3b-l** (1.2 equivalents) in benzene (or toluene, or xylene) was heated at reflux for the appropriate time (see Table 1). The solvent was removed under vacuum and the crude product was purified either by flash column chromatography on silica gel or by recrystallization of the crude reaction mixture from diisopropyl ether.

(3*S**,3a*S**,4R_P*,6a*S**)-3,4-Diphenyl-2-methyl-3,3a,4s,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5a**).

See reference 1d.

(3*S**,3a*S**,4R_P*,6a*S**)-2-Methyl-4-phenyl-3-(4-trifluoromethyl)phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo-[2,3-*d*]isoxazole 4-Oxide (**5b**).

This compound was obtained as colorless needles (diisopropyl ether), mp 113-114°; ir: 3080, 2966, 1602, 1437, 1324, 1168, 1122 cm^{-1}; ^{1}H nmr: δ 4.96 (dm, 1H, J_{H-P} = 17 Hz), 4.36 (dd, 1H, J_{H-P} = 16 Hz, J = 8.1 Hz), 2.91 (td, 1H, J= 7.6, 3.3 Hz), 2.69 (s, 3H), 2.52-2.08 (m, 3H), 1.88-1.67 (m, 1H); ^{13}C nmr: δ 80.9 (d, J_{C-P} = 11 Hz), 73.0, 53.6 (d, J_{C-P} = 66.8 Hz), 42.8, 24.5 (d, J_{C-P} = 10 Hz), 24.4 (d, J_{C-P} = 66.8 Hz) (CF_3 not detected).

Anal. Calcd. for $C_{19}H_{19}NO_2PF_3$: C, 59.84; H, 5.02; N, 3.67. Found: C, 60.10; H, 5.23; N, 3.36.

(3*S**,3a*S**,4R_P*,6a*S**)-3-(4-Methoxy)phenyl-2-methyl-4-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5c**).

This compound was obtained as colorless needles (diisopropyl ether), mp 143-144°; ir: 3060, 2964, 2937, 1611, 1511, 1437, 1246, cm^{-1}; ^{1}H nmr: δ 4.93 (ddd, 1H, J_{H-P} = 21 Hz, J = 7.2, 4.6 Hz), 4.25 (dd, 1H, J_{H-P} = 16 Hz, J = 7.9 Hz), 3.77 (s, 3H), 2.95 (td, 1H, J = 7.0, 3.1 Hz), 2.68 (s, 3H), 2.52-2.07 (m, 3H), 1.89-1.73 (m, 1H); ^{13}C nmr: δ 80.8 (d, J_{C-P} = 11.4 Hz), 73.2, 55.2, 53.4 (d, J_{C-P} = 66.7 Hz), 42.6, 24.5 (d, J_{C-P} = 9.2 Hz), 24.4 (d, J_{C-P} = 66 Hz).

Anal. Calcd. for $C_{19}H_{22}NO_3P$: C, 66.46; H, 6.46; N, 4.08. Found: C, 66.32; H, 6.68; N, 3.99.

(3*S**,3a*S**,4R_P*,6a*S**)-3-(2-Chloro)phenyl-2-methyl-4-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5d**).

This compound was obtained as colorless needles (diisopropyl ether), mp 145-146°; ir: 3064, 2964, 2835, 1591, 1571, 1460, 1437, 1182 cm^{-1}; ^{1}H nmr: δ 4.96 (dm, 1H, J_{H-P} = 22 Hz), 4.84 (dd, 1H, J_{H-P} = 17 Hz, J = 5.1 Hz), 2.90 (td, 1H, J = 5.5, 2.9 Hz), 2.81 (s, 3H), 2.61-2.14 (m, 3H), 1.92-1.76 (m, 1H); ^{13}C nmr: δ 81.4 (d, J_{C-P} = 10 Hz), 69.3, 53.9 (d, J_{C-P} = 67 Hz), 43.4, 25.5 (d, J_{C-P} = 72 Hz), 24.9.

Anal. Calcd. for $C_{18}H_{19}NO_2PCl$: C, 62.16; H, 5.51; N, 4.03. Found: C, 62.17; H, 5.62; N, 3.92.

(3*S**,3a*S**,4R_P*,6a*S**)-3-(4-Fluoro)phenyl-2-methyl-4-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5e**)

This compound was obtained as colorless needles (diisopropyl ether), mp 89-90°; ir: 3080, 2926, 2855, 1603, 1506, 1435, 1222 cm^{-1}; ^{1}H nmr: δ 4.92 (dm, 1H, J_{H-P} = 21 Hz), 4.27 (dd, 1H, J_{H-P} = 15 Hz, J = 7.5 Hz), 2.91 (td, 1H, J = 10, 3.0 Hz), 2.67 (s, 3H), 2.51-2.07 (m, 3H), 1.90-1.71 (m, 1H); ^{13}C nmr: δ 80.8 (d, J_{C-P} = 11 Hz), 72.9, 53.5 (d, J_{C-P} = 67 Hz), 42.6, 24.3 (d, J_{C-P} = 66 Hz), 24.4 (d, J_{C-P} = 9.1 Hz).

Anal. Calcd. for $C_8H_{19}NO_2PF$: C, 65.25; H, 5.78; N, 4.23. Found: C, 65.15; H, 6.05; N, 4.23.

(3*S**,3a*S**,4R_P*,6a*S**)-3-(2,4-Dichloro)phenyl-2-methyl-4-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5f**).

This compound was obtained as colorless needles (diisopropyl ether), mp 216-217°; ir: 3040, 2963, 1588, 1466, 1437, 1186 cm^{-1}; ^{1}H nmr: δ 4.92 (dm, 1H, J_{H-P} = 23 Hz), 4.77 (dd, 1H, J_{H-P} = 16 Hz, J = 5.2 Hz), 2.80 (m, 1H), 2.78 (s, 3H), 2.62-2.11 (m, 3H), 1.95-1.74 (m, 1H); ^{13}C nmr: δ 81.4 (d, J_{C-P} = 9.8 Hz), 68.8, 54.1 (d, J_{C-P} = 67 Hz), 43.4, 25.6 (d, J_{C-P} = 67 Hz), 25.0 (d, J_{C-P} = 7.9 Hz).

Anal. Calcd. for $C_{18}H_{18}NO_2PCl_2$: C, 56.56; H, 4.75; N, 3.66. Found: C, 56.55; H, 4.92; N, 3.64.

(3*S**,3a*S**,4R_P*,6a*S**)-2-Methyl-4-phenyl-3-(2-pyridyl)-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5g**).

This compound was obtained as colorless needles (diisopropyl ether), mp 129-130°; ir: 3081, 2988, 1591, 1435, 1172, 1108 cm^{-1}; ^{1}H nmr: δ 5.07 (ddd, 1H, J_{H-P} = 22 Hz, J = 6.8, 4.4 Hz), 4.43 (dd, 1H, J_{H-P} = 16 Hz, J = 5.4 Hz), 3.58 (bt, 1H, J = 5.8 Hz), 2.77 (s, 3H), 2.57-2.10 (m, 3H), 1.93-1.72 (m, 1H); ^{13}C nmr: δ 81.4 (d, J_{C-P} = 11 Hz), 74.5, 52.0 (d, J_{C-P} = 66 Hz), 43.0, 24.8 (d, J_{C-P} = 66 Hz), 24.5 (d, J_{C-P} = 5 Hz).

Anal. Calcd. for $C_{17}H_{19}N_2O_2P$: C, 64.96; H, 6.09; N, 8.91. Found: C, 64.73; H, 6.23; N, 8.82.

(3*S**,3a*S**,4R_P*,6a*S**)-2-Methyl-4-phenyl-3-(3-pyridyl)-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5h**).

This compound was obtained as colorless needles (diisopropyl ether), mp 135-136°; ir: 3063, 2965, 2939, 1592, 1578, 1430, 1184 cm^{-1}; 1H nmr: δ 4.96 (dm, 1H, J_{H-P} = 21 Hz), 4.33 (dd, 1H, J_{H-P} = 16 Hz, J = 8.0 Hz), 2.94 (td, 1H, J = 7.0, 3.0 Hz), 2.70 (s, 3H), 2.58-2.08 (m, 3H), 1.90-1.68 (m, 1H); ^{13}C nmr: δ 80.9 (d, J_{C-P} = 11 Hz), 71.3, 53.5 (d, J_{C-P} = 68 Hz), 42.7, 24.5 (d, J_{C-P} = 8.3 Hz), 24.4 (d, J_{C-P} = 66 Hz).

Anal. Calcd. for $C_{17}H_{19}N_2O_2P$: C, 64.96; H, 6.09; N, 8.91. Found: C, 64.67; H, 6.20; N, 9.33.

(3*S**,3a*S**,4R_P*,6a*S**)-2-Methyl-4-phenyl-3-(3-quinolinyl)-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5i**).

This compound was obtained as colorless needles (diisopropyl ether), mp 175-176°; ir: 3065, 2964, 2881, 1570, 1495, 1437, 1184 cm^{-1}; ^1H nmr: δ 5.02 (dm, 1H, J_{H-P} = 21Hz), 4.52 (dd, 1H, J_{H-P} = 16 Hz, J = 7.7 Hz), 3.03 (td, 1H, J = 7.3, 3.3 Hz), 2.73 (s, 3H), 2.60-2.15 (m, 3H), 1.94-1.76 (m, 1H); ^{13}C nmr: δ 81.1 (d, J_{C-P} = 10 Hz), 71.7, 53.7 (d, J_{C-P} = 66 Hz), 42.8, 25.0 (d, J_{C-P} = 8 Hz), 24.9 (d, J_{C-P} = 64 Hz).

Anal. Calcd. for $C_{21}H_{21}N_2O_2P$: C, 69.22; H, 5.81; N, 7.69. Found: C, 69.30; H, 6.10; N, 7.31.

(3*S**,3a*S**,4R_P*,6a*S**)-3-(2-Furyl)-2-methyl-4-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5j**).

This compound was obtained as colorless needles (diisopropyl ether), mp 121-122°; ir: 3052, 2920, 2880, 1592, 1437, 1182 cm^{-1}; ^1H nmr: δ 7.35 (m, 1H), 6.36 (m, 1H), 6.27 (m, 1H), 4.96 (dm, 1H, J_{H-P} = 21 Hz), 4.38 (m, 1H), 3.27 (td, 1H, J = 14, 3.0 Hz), 2.75 (s, 3H), 2.52-2.08 (m, 3H), 1.95-1.70 (m, 1H); ^{13}C nmr: δ 149.9, 143.0, 110.4 and 109.4 (furan ring carbons), 81.1 (d, J_{C-P} = 16 Hz), 63.3, 44.6 (d, J_{C-P} = 66 Hz), 41.5 (b), 24.9 (d, J_{C-P} = 66 Hz), 22.2 (b).

Anal. Calcd. for $C_{16}H_{18}NO_3P$: C, 63.36; H, 5.98; N, 4.62. Found: C, 63.08; H, 6.04; N, 4.47.

(3*S**,3a*S**,4R_P*,6a*S**)-2-Methyl-3-(2-(4-nitro)furyl)-4-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5k**).

This compound was obtained as colorless needles (diisopropyl ether), mp 124-125°; ir: 3055, 2969, 1593, 1502, 1356, 1182 cm^{-1}; ^1H nmr: δ 7.23 (d, 1H, J = 3.7 Hz), 6.62 (d, 1H, J = 3.7 Hz), 5.03 (dm, 1H, J_{H-P} = 22 Hz), 4.63-4.38 (m, 1H), 3.37-3.22 (m, 1H), 2.80 (s, 3H), 2.61-2.14 (m, 4H); ^{13}C nmr: δ 113.3 and 112.7 (CH furan), 81.5 (d, J_{C-P} = 8.5 Hz), 66.2, 49.8 (d, J_{C-P} = 66 Hz), 43.2, 24.9 (d, J_{C-P} = 67 Hz), 24.7 (d, J_{C-P} = 8 Hz).

Anal. Calcd. for $C_{16}H_{17}N_2O_5P$: C, 55.18; H, 4.92; N, 8.04. Found: C, 55.20; H, 4.97; N, 7.70.

(3*S**,3a*S**,4R_P*,6a*S**)-3-Ethoxycarbonyl-2-methyl-4-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5l**).

This compound was purified by flash column chromatography (eluent EtOAc-MeOH 9:1, R_f= 0.53) and recrystallized from diisopropyl ether to obtain colorless needles, mp 64-65°; ir: 3063, 2984, 2939, 1731, 1437, 1187 cm^{-1}; ^1H nmr: δ 4.78 (dm, 1H, J_{H-P} = 21 Hz), 4.18 (q, 2H, J = 7 Hz), 4.07 (dd, 1H, J_{H-P} = 17 Hz, J = 6 Hz), 3.34 (td, 1H, J = 6.0, 3.6 Hz), 2.55-2.00 (m, 3H), 1.95-1.80 (m, 1H), 1.25 (t, 1H, J = 7 Hz); ^{13}C nmr: δ 169.4, 81.2 (d, J_{C-P} = 9.2 Hz), 69.9, 61.8, 48.3 (d, J_{C-P} = 70 Hz), 45.0, 24.7 (d, J_{C-P} = 24 Hz), 24.9.

Anal. Calcd. for $C_{15}H_{20}NO_4P$: C, 58.25; H, 6.52; N, 4.53. Found: C, 58.21; H, 6.50; N, 4.17.

(3*S**,3a*S**,4R_P*,6a*S**)-3-Methoxycarbonyl-2-methyl-4-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**5m**).

See reference 1d.

Cycloadditions of Nitrones **3a,g,l** to 2,3-Dihydro-1-ethoxy-1*H*-phosphole 1-Oxide (**2**).

A 3 *M* solution of 2,3-dihydro-1-ethoxy-1*H*-phosphole 1-oxide (**2**) (7-9 mmoles) and nitrones **3a,g,l** (1.2 equivalents) in toluene was heated at reflux for the appropriate time (see Table 1). The solvent was removed under vacuum and the products were isolated by flash column chromatography on silica gel as unseparable mixtures of diastereoisomers.

(3*S**,3a*S**,4R_P*,6a*S**)-4-Ethoxy-2-methyl-3-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**6a**) and (3*S**,3a*S**,4S_P*,6a*S**)-4-Ethoxy-2-methyl-3-phenyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**7a**).

These compounds were obtained as colorless oils, R_f = 0.35 (eluent dichloromethane-methanol 40:1); ir: 2984, 1641, 1465, 1381, 1267, 1214 cm^{-1}; ^1H nmr: δ (major isomer **6a**) 4.83 (ddd, 1H, J_{H-P} = 24 Hz, J = 7.4, 3.5 Hz), 4.05-3.90 (m, 2H), 4.00-3.85 (m, 1H), 2.68-2.50 (m, 1H), 2.60 (s, 3H), 2.35-1.60 (m, 4H), 1.23 (t, 3H, J = 7 Hz); (minor isomer **7a**, only discerned signals) 4.94 (dm, 1H, J_{H-P} = 24 Hz), 3.62-3.45 (m, 1H), 3.00-2.80 (m, 1H), 2.50 (s, 3H); ^{13}C nmr: δ (major isomer **6a**) 138.4, 128.6 (2C), 127.8, 127.5 (2C), 79.4 (d, J_{C-P} = 13.7 Hz), 74.6 (b), 61.0 (d, J_{C-P} = 6.5 Hz), 51.5 (d, J_{C-P} = 92.4 Hz), 42.5, 23.4 (d, J_{C-P} = 8.2 Hz), 20.3 (d, J_{C-P} = 88 Hz), 16.2 (d, J_{C-P} = 6.4 Hz).

Anal. Calcd. for $C_{14}H_{20}NO_3P$: C, 59.78; H, 7.17; N, 4.98. Found: C, 59.56; H, 7.45; N, 4.62.

(3*S**,3a*S**,4R_P*,6a*S**)-4-Ethoxy-2-methyl-3-(2-pyridyl)-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**6g**) and (3*S**,3a*S**,4R_P*,6a*S**)-4-Ethoxy-2-methyl-3-(2-pyridyl)-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**7g**).

These compounds were obtained as colorless oils, R_f = 0.45 (eluent dichloromethane methanol 10:1); ir: 3065, 2966, 2938, 1591, 1470, 1437, 1381, 1181 cm^{-1}; ^1H nmr: δ (major isomer **6g**) 5.01-4.81 (dm, 1H, J_{H-P} = 24 Hz), 4.15-3.92 (m, 1H), 3.99 (quintet, 2H, J = 7 Hz), 3.24-3.05 (m, 1H), 2.35-1.75 (m, 4H), 1.25 (t, 3H, J = 7 Hz); (minor isomer **7g**, only discerned signals) 5.08-4.90 (m, 1H), 2.59 (s, 3H); ^{13}C nmr: δ (major isomer **6g**) 79.9 (d, J_{C-P} = 13.4 Hz), 75.5 (d, J_{C-P} = 5.8 Hz), 60.7 (t, J_{C-P} = 6.5 Hz), 48.6 (d, J_{C-P} = 79.9 Hz), 42.7 (q), 23.5 (t, J_{C-P} = 9.3 Hz), 20.5 (t, J_{C-P} = 88.9 Hz), 16.3 (q, J_{C-P} = 6.1 Hz).

Anal. Calcd. for $C_{13}H_{19}N_2O_3P$: C, 55.32; H, 6.78; N, 9.92. Found: C, 55.29; H, 6.71; N, 9.75.

(3*S**,3a*S**,4R_P*,6a*S**)-4-Ethoxy-3-ethoxycarbonyl-2-methyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**6l**) and (3*S**,3a*S**,4R_P*,6a*S**)-4-Ethoxy-3-ethoxycarbonyl-2-methyl-3,3a,4,5,6,6a-hexahydro-2*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**7l**).

These compounds were obtained as a colorless oil, R_f = 0.45 (eluent dichloromethane-methanol 10:1); ir: 2984, 2941, 1736, 1440, 1226 cm^{-1}; ^1H nmr: δ (major isomer **6l**) 4.64 (dm, 1H, J_{H-P} = 25 Hz), 4.30-3.97 (m, 5H), 3.71 (dd, 1H, J = 18, 5 Hz), 2.84 (s, 3H), 2.30-1.70 (m, 4H), 1.40-1.18 (m, 6H); (minor isomer **7l**, only discerned signals) 4.77 (dm, 1H, J_{H-P} = 25 Hz), 3.12-2.90 (m, 2H), 3.38 (dd, 1H, J = 18, 7 Hz), 2.76 (s, 3H); ^{13}C nmr: δ (major isomer **6l**) 169.0, 79.8 (d, J_{C-P} = 13.4 Hz), 71.1, 61.7, 61.0 (d, J_{C-P} = 6.4 Hz), 45.5 (d, J_{C-P} = 93 Hz), 44.8, 23.3 (b), 20.7 (d, J_{C-P} = 90 Hz), 16.3 (d, J_{C-P} = 16 Hz), 13.9; (minor isomer **7l**, only discerned signals) 79.9 (d, J_{C-P} = 15.1 Hz), 71.8, 61.90 (d, J_{C-P} = 6.6 Hz), 21.6 (d, J_{C-P} = 115 Hz).

Anal. Calcd. for $C_{11}H_{20}NO_5P$: C, 47.63; H, 7.27; N, 5.05. Found: C, 47.68; H, 7.50; N, 4.90.

(3a*S**,4R_P*,6a*S**)-3,4-Diphenyl-3,6a,5,6-tetrahydro-4*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**8**).

A solution of 2,3-dihydro-1-phenyl-1*H*-phosphole 1-oxide (**1**) (1.9 g, 10.7 mmoles) and triethylamine (1.3 g, 1.8 ml, 12.9 mmoles) in 4 ml of benzene was heated at reflux and, under vigorous stirring, a solution of benzohydroximic acid chloride [9] (2 g, 12.9 mmoles) in 6 ml of benzene was added dropwise over two hours. After a further one hour at reflux, the solution was cooled, the solid formed filtered off, and the solution concentrated in vacuum. The crude mixture was purified by flash column chromatography (eluent ethyl acetate R_f = 0.31) to give 1.10 g (58%) of **8**, mp 176-177°; ir: 3065, 2941, 1591, 1437, 1344, 1196 cm^{-1}; ^1H nmr: δ 5.53 (dddd, 1H, J_{H-P} = 29 Hz, J = 9.2, 3.7, 1.8 Hz), 4.01 (dd, 1H, J = 9.2, 5.5 Hz), 2.84-2.10 (m, 4H); ^{13}C nmr: δ (C=N signal not discerned) 87.4 (d, J_{C-P} = 11 Hz), 57.8, 51.2 (d, J_{C-P} = 59 Hz), 27.3 (d, J_{C-P} = 11 Hz), 25.8 (d, J_{C-P} = 65 Hz).

Anal. Calcd. for $C_{17}H_{16}NO_2P$: C, 68.68; H, 5.42; N, 4.71. Found: C, 68.70; H, 5.30; N, 5.00.

(3a*S**,4R_P*,6a*S**)-3-Phenyl-4-ethoxy-4*H*-3,6a,5,6-tetrahydrophospholo[2,3-*d*]isoxazole 4-Oxide (**9**) and (3a*S**,4S_P*,6a*S**)-3-Phenyl-4-ethoxy-3,6a,5,6-tetrahydro-4*H*-phospholo[2,3-*d*]isoxazole 4-Oxide (**10**).

The reaction was carried out at the same manner as described before. 2,3-Dihydro-1-ethoxy-1*H*-phosphole-1-oxide (**2**) (1.57 g, 10.7 mmoles), triethylamine (1.3 g, 1.8 ml, 12.9 mmoles) in 4 ml of benzene; benzohydroximic acid chloride [9] (2 g, 12.9 mmoles) in 6 ml of benzene. Column chromatography gave 1.85 g (68%) of a mixture of diastereoisomers as a colorless oil (eluent dichloromethane-ethanol 10:1, R_f = 0.66); the major isomer **9** crystallized from diisopropyl ether, mp 73-74°; ir: 2985, 2940, 1600, 1444, 1345, 1267, 1223 cm^{-1}; ^1H nmr: δ (major isomer **9**) 5.43 (ddm, 1H, J_{H-P} = 35 Hz, J = 9 Hz), 4.21 (quintet, 2H, J = 7.2 Hz), 3.71 (dd, 1H, J = 15.7, 5.5 Hz), 2.67-2.25 (m, 1H), 2.15-1.85 (m, 3H), 1.40 (t, 3H, J = 7.2 Hz); (minor isomer **10**, only discerned signals) 4.00-3.75 (m, 2H), 0.88 (t, 3H, J = 7.2 Hz); ^{13}C nmr: δ (major isomer **9**) (C=N signal not discerned) 85.9 (d, J_{C-P} = 14.6 Hz), 61.4 (d, J_{C-P} = 6.8 Hz), 48.2 (d, J_{C-P} = 83 Hz), 25.4 (d, J_{C-P} = 12 Hz), 21.2 (d, J_{C-P} = 87.7 Hz), 16.5 (d, J_{C-P} = 6 Hz).

Anal. Calcd. for $C_{13}H_{16}NO_3P$: C, 58.87; H, 6.08; N, 5.28. Found: C, 58.51; H, 6.42; N, 5.23.

X-ray Analysis.

Crystals of **5a** and **5m** suitable for X-ray investigation were obtained by crystallization from ethyl acetate. The cell parameters and intensities were measured on a Enraf-Nonius CAD 4 diffractometer. Accurate cell parameters determined from a least-squares refinement of the $(\sin\theta/\lambda)^2$ values for 25 reflections. The intensity data were collected using graphite-monochromated MoKα radiation and the ω-2θ scan technique. The measured intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied [10]. The structure was solved by direct methods, using the SHELXS-86 program [11] and refined by the full-matrix least-squares method using the SHELXTL System [12]. During the refinement of the nonhydrogen atoms with anisotropic thermal parameters, the hydrogen atoms contributions (with exception of the methyl hydrogens) were included in the structure factors, after calculating their positions on the basis of idealized geometry, and refined isotropically in the riding mode. The positions of the methyl hydrogens were found from a difference map and refined with isotropic thermal parameters. The function $\Sigma w(|F_o|-|F_c|)^2$ was minimized, and in the final cycles of calculation a weighting based on counting statistics was used with $w=[\sigma^2(F_o) + 0.0002\ (F_o)^2]^{-1}$ for **5a** and $w=[\sigma^2(F_o) + 0.0002\ (F_o)^2]^{-1}$ for **5m**. Convergence was obtained at R = 0.045, R_w = 0.045 for **5a** and R = 0.046, R_w = 0.045 for **5m**. The final difference Fourier map did not show any peak higher than 0.21 eÅ^3 for **5a** and 0.23 eÅ^3 for **5m**.

Biological Assays: Weed Control.

Test for Pre-emergence Herbicidal Activity.

Monocotyledonous and *dicotyledonous* test species (Avena, Setaria, Sinapis, Stellaria) are seeded in plastic pots containing standard soil. Immediately after seeding the pots are sprayed with an aqueous suspension of the test compounds at rates of 2000 g of active ingredient per hectare (500 liters of water per hectare). The pots are then transferred to the greenhouse for germination/growth under optimal conditions. The evaluation takes place after 3 weeks.

Test for Post-emergence Herbicidal Activity.

Monocotyledonous and *dicotyledonous* tests species (Avena, Setaria, Sinapis, Stellaria) are raised in plastic pots containing standard soil. At the 4-6 leaf-stage the plants are sprayed with an aqueous suspension of the test compounds at rates of 2000 g of active ingredient per hectare (500 liters of water per hectare). The pots are then transferred to the greenhouse for further cultivation under optimal conditions. The evaluation takes place after 18 days.

Biological Assays: Disease Control.

Residual-preventive Action Against *Plasmopara viticola* on Vines.

Vine cuttings cv. "Chasselas" are grown in the greenhouse. When they have reached the 10-leaf stage 3 plants are sprayed with a solution containing 200 ppm of active ingredient. After the spray coating on the plants has dried the leaf underside is inoculated uniformly with a spore suspension of the fungus. The plants are subsequently kept in a humid chamber for 8 days. After this period the disease symptoms of the control plants are used to assess the activity of the test substance.

Residual-preventive Action Against *Botrytis Cinerea* on Apple Fruits.

Artificially wounded apples are treated by applying dropwise a solution containing 200 ppm of active ingredient to the wounds. The treated fruits are subsequently inoculated with a spore suspension of the fungus and incubated for one week at high atmospheric humidity at approximately 20°. The fungicidal action on the test substance is deduced from the number of wounds showing sign of rot.

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