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The Regioselectivity of Nitrone Cycloadditions to Vinyl Phosphorus Compounds

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Abstract: The 1,3-dipolar cycloadditions of nitrones **1-5** to diphenylvinylphosphine oxide (**6**), sulfide (**7**) and selenide (**8**) were carried out. The cycloadditions of the nitrone **3**, as a model, to substituted vinylphosphorus derivatives **28-36** were also carried out with satisfactory results with the exception of the sulfoxide **33**. Nuclear Magnetic Resonance spectroscopy (^{31}P, ^{1}H and ^{13}C) allowed the complete, unambiguous identification and assignment of the regiochemistry to all the products, as well as their relative quantitative determination. The relative stereochemistry of isoxazolidine stereocenters was also assigned to compounds **9-23** and **37-46** on the basis of ^{1}H and ^{13}C NMR data.

Introduction

Isoxazolidines readily available from cycloaddition reactions of nitrones to alkenes are very useful intermediates in synthesis.[1] Reductive cleavage of the heterocyclic ring provides the γ-amino alcohol functionality with the stereochemistry of the carbon backbone fully preserved. The utility of the cycloaddition strategy is further enhanced by the possibility of preparation of isoxazolidines in optically active form. This can be achieved either by the use of an optically active nitrone[2] or, applied less frequently, use of an optically active dipolarophile.[3] Recent access to homochiral vinyl phosphine oxides[4] prompted us to evaluate such compounds in the latter approach. Our preliminary studies with a model compound methylphenylvinylphosphine oxide, have shown that the corresponding phosphinyl isoxazolidines can indeed be obtained in a stereoselective manner.[5] The presence of the versatile phosphinyl functionality on the isoxazolidine ring opens novel attractive possibilities for synthetic transformations.

Another factor of practical importance in the cycloaddition of nitrones to vinyl phosphorus compounds is regioselectivity. In principle, in such reactions two regioisomeric products A and B can be formed.

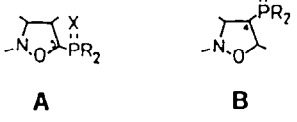
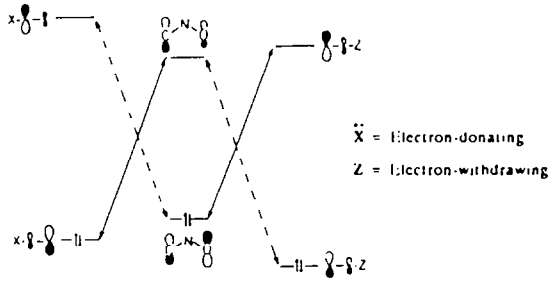


FIGURE 1: Frontier Molecular Orbitals Interactions of a Nitrone and Monosubstituted Dipolarophiles.



Nitrones, according to Sustmann's classification,[6,7] are Type II dipoles for which a $LUMO_{dipole}$-$HOMO_{dipolarophile}$ interaction would lead preferentially to products A and a $HOMO_{dipole}$-$LUMO_{dipolarophile}$ interaction would lead preferentially to products B (Figure 1). Thus, when the dipolarophile bears a strong

electron-withdrawing substituent as in the case of vinyl phosphine oxides the latter interaction should typically prevail[8] and the adducts of type B can be expected to predominate in the product mixtures. A survey of the literature on dipolarophilic reactivity of vinyl phosphine oxides[9] did not provide sufficient data to clearly corroborate these predictions, and our own preliminary results revealed additionally that the regiochemical outcome of cycloadditions of nitrones to vinyl phosphine oxides was strongly dependent on the nitrone structure.[10] We chose therefore to study the regiochemistry of the cycloaddition of nitrones to vinyl phosphine oxides and related compounds in greater detail in order to explore the effects resulting from substituent changes in the nitrones as well as in the vinyl phosphorus partner.

Results and discussion

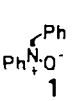
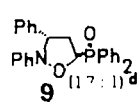
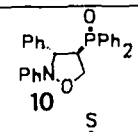
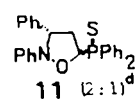
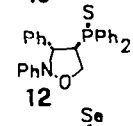
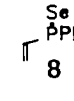
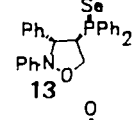
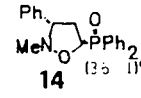
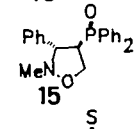
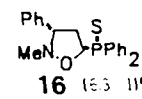
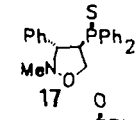
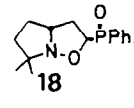
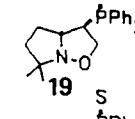
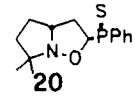
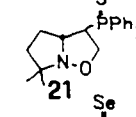
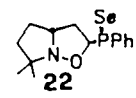
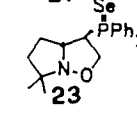
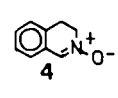
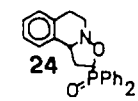
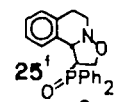
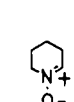
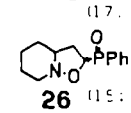
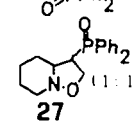
The cycloaddition reactions of five representative nitrones **1-5** with diphenylvinylphosphine oxide (**6**) diphenylvinylphosphine sulfide (**7**) and diphenylvinylphosphine selenide (**8**) are reported in Table 1. These cycloadditions were carried out under conditions favouring kinetic control. In Table 2 the results of reactions run under thermodynamic control are also reported. The reactions of nitrone **3** with nine structurally more diverse vinyl phosphorus derivatives **28-36** are listed in Table 3.

The cycloadditions involving dipolarophiles **6**, **7** and **8** and acyclic nitrones were best effected by heating benzene solutions of the two substrates at reflux, whereas those with cyclic nitrones proceeded with satisfactory rates already at ambient temperature. The high reactivity of dipolarophiles **6-8** in these reactions has to be ascribed to the electron-withdrawing behaviour of the phosphinyl group in an interaction with a dipole of Type II.[7] Interestingly, sulfide **7** appeared to be slightly more reactive than oxide **6**. A competition experiment with nitrone **3** provided k_{rel}(**7**/**6**) of only 1.5, compatible with a notion that interactions of the phosphorus substituents with the vinylic π-systems are mostly polar in nature.[11]

The structures of cycloadducts **9-27** of Table 1 were assigned by spectroscopic methods. Assignment of regiochemistry, troublesome in 1,3 dipolar cycloaddition on some occasions,[12] was straightforward in the case of phosphinyl isoxazolidines. In the ^{13}C NMR spectra the chemical shifts of easily discernible doublets corresponding to the isoxazolidine ring carbon bonded directly to phosphorus ($^1J_{PC}$ of 50-73 Hz) were especially diagnostic with respect to regiochemical assignment.[10] These carbon atoms, in 4-phosphinyl isoxazolidines, were found uniformly at least 20 ppm more upfield than in the corresponding 5-phosphinyl isoxazolidines, providing prompt and unambiguous distinction between the two regioisomers. Most of the other ^{13}C NMR parameters for the two regioisomeric products were not diagnostic and, generally, conformed to the previously known trends.[15] $^3J_{PC}$ coupling constants were found to be consistently larger than the corresponding $^2J_{PC}$ coupling constants. Replacing phosphinyl oxygen with sulfur or selenium resulted in considerable decreases in $^1J_{PC}$ coupling constants (by ca. 15 Hz for sulfides and ca. 20 Hz for selenides) and, at the same time, led to relative increases in the corresponding $^2J_{PC}$ coupling constants. Interestingly however, compounds **18** and **20** exhibited unique long range phosphorus-carbon coupling over five bonds, unprecedented, to our knowledge, in saturated organo-phosphorus systems. This was manifested by $^5J_{PC}$ of ca. 0.8 Hz of the more downfield methyl group in both compounds. The "extended W" pathway has been already recognized as responsible for transmission of coupling between nuclei separated by five single bonds in rigid molecules.[16]

^1H NMR spectra listed in Tables 4 and 5 provided in turn some insight into the stereochemistry of the adducts **9-27**. With the exceptions of 5-phosphinyl adducts (isoxazolidine numbering) derived from nitrone **3**, all other 5-substituted regioisomers were formed as mixtures of stereoisomers in ratios ranging from 1.5:1 to 6.3:1. In some cases the assignment of particular stereoisomers could be made directly, in others only based on analogy. For example, the major 5-phosphinyl isoxazolidine **9a** (entry 1, Table 1) showed two well separated signals for the C4 methylene protons, one at 3.08 δ ($^3J_{PH}$ = 15.6 Hz), and the other at 2.59 δ ($^3J_{PH}$ = 7.8 Hz). As the $^3J_{PH}$ for *cis* nuclei are typically larger than for *trans*,[17] the more shielded of the two protons could be readily assigned as trans to the phosphinyl group. Consequently, a reasonable assumption that shielding of this proton is caused by the anisotropy of the *cis* C-3 phenyl ring enabled straightforward assignment of the trans stereochemistry to the major adduct **9a**. By a similar reasoning, isoxazolidines of type A derived from nitrone **3** were assigned the same relative stereochemistry as found in **9a**. In **20** and **22** for example, the shielded protons of the C4-methylene group (isoxazolidine numbering) at 2.15 δ were coupled

TABLE 1: Cycloadditions of Nitrones 1-5 to Diphenylvinylphosphine Oxide (6), Sulfide (7), and Selenide (8).

entry	nitrone	vinyl phosphine derivative	reaction conditions	yield %[a]	adducts (diastereomeric ratio)[b] A	adducts (diastereomeric ratio)[b] B	A B regioisomer ratio[b]
1[c]	 1	 6	36h, 80°C C_6H_6	82	 9 (1.7 : 1)[d]	 10	40 : 60
2[c]	1	 7	24h, 80°C C_6H_6	90	 11 (2 : 1)[d]	 12	10 : 90
3	1	 8	3d, 80°C C_6H_6	58	(e)	 13	<10 : 90
4[c]	 2	6	2d, 80°C C_6H_6	88	 14 (3.5 : 1)[d]	 15	70 : 30
5	2	7	30h, 80°C C_6H_6	78	 16 (6.3 : 1)[d]	 17	82 : 18
6	 3	6	7d, r.t. $CHCl_3$	90	 18	 19	86 : 14
7	3	7	4d, r.t. C_6H_6	84	 20	 21	86 : 14
8	3	8	4d, r.t. C_6H_6	86	 22	 23	88 : 12
9	 4	6	18d, r.t. $CHCl_3$	83	 24 (1.7 : 1)[f]	 25[f]	89 : 11
10	 5	6	2d, 40°C CH_2Cl_2	93	 26 (1.5 : 1)[f]	 (1 : 1)[f] 27	76 : 24

Notes : a) Yield of isolated compounds; b) Determined from ^{31}P NMR spectra; c) ref. 10; d) *Trans* : *cis* ratio; e) From ^{31}P NMR spectrum other signals can be detected, but the concentration is too low for detection in ^{13}C NMR; f) Stereochemical assignment uncertain.

to phosphorus with $^3J_{PH}$ of ca. 18 Hz. Of the two protons in this group the one in the concave face of the cis-fused bicyclic system is deshielded by steric compression. It follows therefore, that in these compounds the phosphinyl group resides on the same side as the more shielded proton, i.e., on the convex side of the molecule. In turn, for 4-phosphinyl isoxazolidines which were normally obtained in the form of a single diastereoisomer, vicinal coupling constants $J_{P,H3}$ of 14-17 Hz and $J_{H3,H4}$ of 5-8 Hz suggested the assignment of trans configurations to all compounds of this type. The validity of this assignment has already been verified in the case of **10** by a single crystal X-ray diffraction analysis.[18]

TABLE 2. Cycloadditions of Nitrones 3-5 to 6 at 110 °C for one day.

entry	nitrone	products (diastereomeric ratio)		5/4 regioisomer ratio
1	3	**18a + 18b** (3.5: 1)	**19**	58 : 42
2	4	**24a + 24b** (1 : 1)[a]	**25**	74 : 26[a]
3	5	**26a + 26b** (1.2: 1)	**27a + 27b** (1.4: 1)	60 : 40

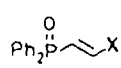
a. The mixture already contained appreciable amounts of decomposition products.

The regioselectivity of the cycloaddition of nitrones, particularly the cyclic ones, with electron-deficient dipolarophiles, has already been observed to be influenced by the temperature.[19] The change of regioisomeric composition affected by the temperature has been ascribed to a cycloreversion-cycloaddition process which eventually leads to a thermodynamic mixture of regioisomers. Table 2 reports our experiments with the cyclic dipoles **3-5** and the phosphine oxide **6**. An increased amount of 4-substituted regioisomers is generally observed, accompanied by an increase of endo products, in agreement with the literature.[19] The cycloreversion process seems to be limited to cyclic nitrones, as shown by the stability of isoxazolidine **16a** when subjected to the same conditions (110 °C, 2 days). Extensive formation of decomposition products resulted by prolonged reaction times in the cases studied (already observed after 1 day for nitrone **4**). This drawback reduces the synthetic utility of the cycloaddition under thermodynamic control to selectively produce Type B isoxazolidines.

Table 3 collects cycloadditions of a model nitrone **3** to dipolarophiles **28-36**, bearing additional substituents on the vinyl group.

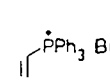
28 Z X = O
29 Z X = S
30 E X = O

31



32 X = SO_2Ph
33 X = SOPh
34 X = SPh

35

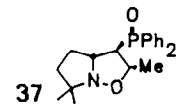
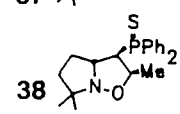
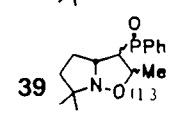
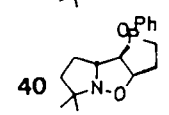
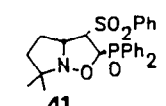
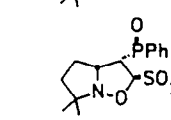
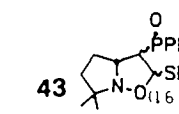
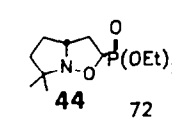
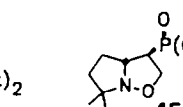
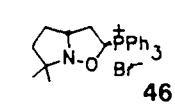


36

In general, reactivity of the dipolarophiles of this group was somewhat smaller than that of unsubstituted ones. The least reactive were the trans substituted isomers. Even introduction of a phenylsulfonyl group as the second electron-withdrawing substituent in **32** had relatively little activating effect. In order to obtain satisfactory conversion rates with **32** the reactants had to be heated at 110 °C in toluene for several hours. Interestingly, under these forcing conditions the closely related phenylsulfinyl derivative **33** was found completely unreactive[20,21] whereas sulfide **34** gave only low yields of the expected adduct **43**. In the latter reaction extensive decomposition of the nitrone was noted.

Most of the products in the reactions listed in Table 3 were regiochemically homogeneous. Their regiochemistry was assigned again from the ^{13}C NMR spectra by the chemical shifts of the ring carbons bonded directly to

TABLE 3: Cycloadditions of Nitrone 3 to Substituted Vinyl Phosphorus Derivatives 28-36.

entry	vinyl phosphine derivative	reaction conditions	yield %[a]	adducts A B (diastereomeric ratio)[b] A	regioisomer ratio[b] B
1	28	30h, 80°C C_6H_6	70		 37
2	29	30h, 60°C $CHCl_3$	86		 38
3	30	16h, 110°C C_7H_8	80		 39 (13 : 1)[c]
4	31	5h, 60°C $CHCl_3$	65		 40
5	32	5h, 110°C C_7H_8	67	 41	58 : 42  42
6	33	24h, 110°C C_7H_8	nr		
7	34	24h, 110°C C_7H_8	37		 43 (16 : 1)[d]
8	35	14h, r.t. $CHCl_3$	84	 44	72 : 28  45
9	35	3d, 110°C C_7H_8	75	44	28 : 72 45
10	36	6h, r.t. $CHCl_3$	63	 46	

Notes : a) Yield of isolated compounds; b) Determined from ^{31}P NMR spectra;
c) Major isomer is the endo product (relative to the phosphinyl group);
d) Major isomer is the exo product (relative to the phosphinyl group).

phosphorus. Also diagnostic was the coupling ($^3J_{PC}$ = 3-7 Hz) between phosphorus and C4 of these bicyclic systems which could be seen only in one of the two possible regioisomers, i.e. Type B.

The stereoisomers detected in entries 3 and 7 (Table 3) could also be distinguished spectrally and the structure possessing the phosphinyl group in the concave face of the fused ring system was assigned to the major isomer in entry 3 and to the minor isomer in entry 7. Evidence for this assignment came from chemical shifts of C4 (ca. 26 ppm, $^3J_{PC}$ = 4 Hz) found shielded in these isomers relatively to their opposite isomers. This shielding is likely to have steric origin due to interactions of CH with the bulky phosphinyl group residing in the more crowded concave face of the molecule. To compare, chemical shifts of C4 in the relative minor (entry 3) and major (entry 7) isomers (ca. 34 ppm, $^3J_{PC}$ = 7-8 Hz) resembled closely those found previously in the related non crowded systems **19**, **37**, **38**, **40**, as well as **45**. Although somewhat smaller for the sulfone group the upfield shift of C4 recurred also in regioisomers **41** and **42** aiding analogous assignment of the *cis* C3-C3a stereochemistry in both compounds.

Included in Table 3 are the reactions of the nitrone **3** with diethyl vinylphosphonate (**35**) and triphenylvinylphosphonium bromide (**36**) representing two other classes of vinyl phosphorus dipolarophiles. As expected for these monosubstituted derivatives, these cycloadditions were facile and highly selective. Again, spectral analysis provided firm evidence for the proposed structures (see Tables 4 and 5). Unfortunately, under the reaction conditions the phosphonium isoxazolidine **46** was quickly evolving into other, yet unidentified, products and the structural assignment for **46** had to be made by monitoring of the reaction using different NMR techniques. Again, in the cycloaddition to dipolarophile **35**, the relative amount of the 4-substituted regioisomer could be significantly increased by running the reactions under thermodynamic conditions (cf. entries 8 and 9). In this case a complete reversal of the regioisomeric ratio was indeed observed, accompanied by the detection of small quantities of the 5-substituted endo derivative.

Examples of cycloadditions of nitrones to vinyl phosphorus derivatives collected in Tables 1-3 provide an insight into regiochemistry of the studied process. With the monosubstituted dipolarophiles **6-8** the expected (vide supra) predominant formation of type B isoxazolidine was observed only for a single nitrone, i.e., C,N-diphenyl nitrone (**1**). As mentioned previously, formation of these regioisomers originates from the $HOMO_{dipole}$- $LUMO_{dipolarophile}$ interaction and is only weakly favored.[8] The delicate nature of this preference becomes indeed readily apparent from examination of regiochemical results in the first five entries in Table I. Thus, replacement of the N-phenyl substituent in **1** by the N-methyl group in **2** was already sufficient to make significant the contribute of the $LUMO_{dipole}$-$HOMO_{dipolarophile}$ interaction and, in consequence, to cause the reversal of the regioselectivity. Similar exchange in **6** of one P-phenyl group for P-methyl was also found sufficient to cause the reversal.[5] Most interestingly however, replacement of the phosphinyl oxygen with sulfur and selenium, as in **7** and **8**, led, in reactions with nitrones **1** and **2**, to overall enhancement of selectivity, but surprisingly, in each case towards formation of the already favored regioisomer. A comparison of entries 2 and 5 in Table 1 provides thus a spectacular example of the crossover in regioselectivity of the two closely related acyclic nitrones (10:90 vs 82:18). The cyclic nitrones, provided that kinetic control is secured, favored consistent formation of adducts of type A as did N-Me nitrone **2**. Selectivity in these reactions was relatively high and typically exceeded 6:1 ratio, securing practical access to a variety of phosphinyl isoxazolidines of Type A. Although that ratio could be considerably lowered under conditions of cycloreversion, according with the literature, access to phosphinyl isoxazolidines of type B was achieved effectively only with the doubly substituted dipolarophiles **28-31** and **34**. As shown in Table 3, all these dipolarophiles gave adducts of Type B exclusively. The directive influence of the phosphinyl group found in the monosubstituted series was now completely overridden by the effect of an added substituent such as electron-donating thiophenyl or methyl group. On the other hand, adding of the electron-withdrawing phenylsulfonyl substituent on the vinyl as in **32** resulted in competition of the two groups of the same nature, which was won by the $PhSO_2$ group, being more powerful an electron-withdrawing group than Ph_2PO. Indirect comparison of the two groups via reaction of C-Ph,N-Me nitrone with phenylvinylsulfone[8] and diphenylvinylphosphine oxide (entry 4, Table 1) corroborates this conclusion further.

Finally, as seen in entries 8 and 10 in table 3, a major change in the nature of the phosphorus derivative affects the regioselectivity only slightly. Both the phosphonate **35** and the phosphonium salt **36** gave, with nitrone **3**, type A adducts with great preference, as expected for the monosubstituted dipolarophiles and a cyclic nitrone under kinetic

control.[22] In addition, similar behaviour of diphenylvinylphosphine has already been recorded.[23]

It can thus be concluded that cycloadditions of nitrones to monosubstituted vinyl phosphorus dipolarophiles favor considerably formation of adducts of Type A under conditions that avoid cycloreversion. The selectivity in favor of this regioisomer is more pronounced for the cyclic nitrones than for acyclic ones and, as follows for example from comparison of reactions of nitrone 3, decreases with an increase in the electron-withdrawing ability of the substituent according to the sequence:

$$Ph_2\ddot{P} > PhMe\overset{\ddot{O}}{\ddot{P}} > Ph_2\overset{\ddot{S}}{\ddot{P}} \geq Ph_2\overset{\ddot{O}}{\ddot{P}} > (EtO)_2\overset{\ddot{O}}{\ddot{P}}$$

The divergent behaviour of C,N-diphenyl nitrone (1) favoring with monosubstituted dipolarophiles 6-8 formation of adducts of type B can be associated with the relatively high energy HOMO of this nitrone[24] suitable for interaction with the dipolarophile LUMO and may probably be occasionally observed for other aryl substituted nitrones as well.[7,8,16]

The stereoselectivity found in the two series of regioisomeric adducts indicates that the studied cycloadditions prefer considerably, for both regiochemical orientations, *exo* transition states for *E* dipoles and *endo* transition states for *Z* dipoles. The predominant formation of the 5-exo products in cycloadditions involving *E*-dipolarophiles (entries 3 and 5, Table 3) suggests additionally that this preference is considerably stronger for large substituents destined for position 5 (isoxazolidine numbering) in the product than for those directed to position 4 and is being enforced even at the expense of placing bulky groups at C4 (isoxazolidine numbering) in the highly crowded position (cf. Table 3).[25] Non-conflicting orientation of substituents in the exo transition states of reactions involving *Z*-dipolarophiles **28**, **29** and **31** leads, on the other hand, to the clean formation of single cycloadducts possessing three consecutive, highly functionalized stereogenic carbon atoms of predictable stereochemistry. Application of isoxazolidines of this type as synthetic intermediates will be the subject of future reports from our laboratories.

Experimental section

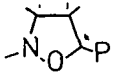
All reactions were carried out under nitrogen. Rf values refer to TLC, carried out on 0.25 mm silica gel plates (Merck F254), with the same eluent as indicated for the column cromatography separation. Melting points (uncorrected) were measured with a Kofler apparatus (unless otherwise stated). Microanalyses were carried out with a Perkin-Elmer 240 C elemental analyzer. IR spectra were recorded on Perkin-Elmer 283 and 881 spectrophotometers, and NMR spectra ($CDCl_3$ solutions) on Varian FT-80 A (^{13}C, 20MHz; ^{31}P, 32.203 MHz) and on Varian VXR 300 (^1H NMR, 300 MHz) spectrometers: the chemical shifts for ^1H and ^{13}C NMR spectra are given in ppm from TMS; for ^{31}P NMR spectra in ppm from H_3PO_4 85%. Coupling costants J are reported in Hz. Regioisomeric ratios were calculated from ^{31}P spectra, unless otherwise stated. ^1H and ^{13}C NMR signals of aromatic substituents are not reported. N-(Phenylmethylene)benzeneamine N-oxide (**1**), N-(phenylmethylene)methaneamine N-oxide (**2**), 2,2-dimethyl-3,4-dihydro-2*H*-pyrrole 1-oxide (**3**), 3,4-dihydroisoquinoline 2-oxide (**4**), and 2,3,4,5,-tetrahydropyridine 1-oxide (**5**) were synthesized by standard procedures according to the literature.[1] Diphenylvinylphosphine oxide (**6**), sulfide (**7**), and selenide (**8**) were synthesized from the phosphine[24] by treatment with H_2O_2, sulfur or selenium, respectively. Diphenylpropenylphosphine oxide *Z* (**28**) and *E* (**30**) and sulfide *Z* (**29**) were synthesized from the respective *Z* and *E* propenyl phosphines.[25] Phospholine oxide **31** was synthesized according to ref. 26. Thiosubstituted vinylphosphine oxides **32-34** were synthesized according to ref. 27. Diethylvinylphosphonate (**35**) and triphenylvinylphosphonium bromide (**36**) were purchased from Aldrich, and were used without purification.

General procedure for cycloaddition of nitrones to vinylphosphorus derivatives. Vinyl phosphorus derivative (1 mmol) was added to 1.2 to 2 equivalents of nitrone and the reaction carried out under the conditions reported in Tables 1 and 3. The reaction mixture was purified as specified.

Cycloaddition of 1 to 6: 2,3-Diphenyl-5-diphenylphosphinyltetrahydroisoxazole (9a and 9b) and 2,3-Diphenyl-4-diphenylphosphinyltetrahydroisoxazole (10). See ref. 10. In Table 2 in this paper however, numbers in columns headed "1cis" and "1trans" should be interchanged.

Cycloaddition of 1 to 7: 2,3-Diphenyl-5-diphenylthiophosphinyltetrahydroisoxazole (11a and 11b) and 2,3-Diphenyl-4-diphenylthiophosphinyltetrahydroisoxazole (12). The reaction mixture was purified by chromatography on a short pad of silica gel (eluent petroleum ether-diethyl ether 5:1).

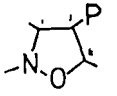
TABLE 4: ^{31}P, ^{1}H, ^{13}C NMR Data of 5-Substituted Phosphinoisoxazolidines.



	^{31}P	^{1}H								^{13}C						
		H_i	J_{HH} Hz	H_j	$^{3}J_{PH}$ Hz	$^{3}J_{HH}$ Hz	H_k	$^{2}J_{PH}$ Hz	J_{HH} Hz	Others [a]	C_i	$^{3}J_{PC}$ Hz	C_j	$^{2}J_{PC}$ Hz	C_k	$^{1}J_{PC}$ Hz	Others [a]
9a	28.09	4.28 dd	5.7, 8.4	2.59 ddt 3.78 ddt	7.9 11.4	5.7, 7.5, 13.5 14.5, 8.8, 8.8	5.08 dt	7.7	8.6, 7.7		67.38	5.1	40.25		74.57	85.0	
9b	27.76	4.72 t	7.8	2.65 m 3.17 m			4.99 ddd	5.9	10.4, 2.7		69.84	6.8	41.80	-	75.80	84.5	
11a	43.58	(b)		(b)			(b)			(b)	(b)		(b)		(b)		
11b	41.78	(b)		(b)			(b)			(b)	(b)		(b)		(b)		
14a	28.83	3.25 m		2.95 m			> 3.00 m			2.54(s,3H)	72.33	(c)	39.76	-	74.20	84.8	53.2(q)
14b	29.15	(b)		(b)			(b)			2.49(s,3H)	(b)		40.35	2.1	(b)		42.86(q)
16a	44.51	3.35 m		3.04-2.65 m 2.23-2.52 m			5.12 dt	6.1, 7.9	7.9 [d]	2.50(s,3H)	71.90	4.0	41.07	-	76.82	67.4	43.43(q)
16b	43.5	3.52 m		3.07-2.92 m 2.74-2.41 m			5.13 dt	6.5, 7.9	7.9 [d]	2.46(s,3H)	72.51	3.0	42.00	4.0	78.02	65.9	42.95(q)
18a	28.60	3.81 m		2.66-2.36 m			4.61 ddd	4.9, 6.1, 10.7	[d]	2.18(s,3H) 1.33(s,3H),1.03(s,3H)	61.95	7.1	38.67	-	75.16	88.5	69.44(q, $^{2}J_{PC}$ 22.1), 68.1(t) 27.10(q, $^{3}J_{PC}$ 9.9), 24.0(q)
18b	30.01	3.80 m		(b)			4.67 dt	8.9, 8.8	6.3, 5 [d]	(b)	61.63	6.5	38.53	-	73.51	86.8	67.82(d), 67.13(t), 31.6(t), 26.22(q), 23.91(q)
20	42.23	3.83 m		2.70-2.55 m 2.15 ddd 18.3, 9.3, 13.0			4.85 dt	10.2, 6.4, 4.10	[d]	2.45-2.47(m,1H), 1.83-1.50 (m,3H), 1.31(s,3H), 1.01(s,3H)	61.56	7.3	38.48	1.5	78.67	73.1	69.52(d), 26.57(t), 30.05(t) 26.85(q, $^{3}J_{PC}$ 10.7), 24.06(q)
22	35.54	3.80 m		2.68-2.53 m 2.15 ddd 18.1, 9.1, 13.2			4.96 m			2.65-2.53(m,2H), 1.85-1.50 (m,3H), 1.55(s,3H), 1.33(s,3H)	61.27	7.3	39.65	2.0	78.40	59.1	69.28(d), 26.25(t), 34.1(t) 26.55(q), 23.80(q)
24a	28.94	3.92 t	8.8	3.32 m			5.18 dt	5.2, 7.3, 11.3	[d]	1.15-2.40(m,8H)	63.18	4.5	47.98	-	75.37	87.8	37.99(t), 25.65(t)
24b	28.61	4.63 dd	6.3, 10.3	(b)			4.94 dt	11.1, 7.4, 11.1	[d]	(a)	62.58	4.0	49.46	-	77.47	82.3	37.09(t), 25.05(t)
26a	29.34	(b)		(b)			4.88 dtd	6.6, 6.4, 5.10	8 [d]	1.40-1.66(m,8H)	65.96	(c)	35.38	1.4	72.42	88.4	54.95(t), 28.34(t), 24.68(t), 23.71(t)
26b	29.31	(c)		(b)			5.11 dt	4.3, 4.1, 10.5	[d]	(b)	(b)		(b)		74.33	88.6	(b)
41	27.86		6.2, 4.2	m			5.03 t	6.5		2.47-1.92(m,14H), 1.35-1.15 (m,3H), 1.08(s,3H), 0.99(s,3H)	68.44	1.4	34.76	-	75.02	82.4	69.33(t), 35.60(t), 30.15(t) 26.85(q), 23.91(q)
44a	44.6	3.61 t		2.98 ddd 17.4, 12.2, 10.2, 7.8 2.26 ddt 6.5, 12.2, 6.4			4.59-4.45 m			2.08(dq, 13.3, 7.1), 1.94-1.72 m, 1.54 (m,3H), 1.35(s,3H), 1.07(s,3H)	61.80	12.0	38.89	-	71.74	69.1	69.14(t), 36.31(t), 30.72(t) 27.02(q, $^{3}J_{PC}$ 13.3), 20.1(q)
44b	45.42	(b)		(b)			(b)			(b)	(b)		(b)		(b)		(b)
46	21.88	> 6.5 m		3.42-3.22 m 2.85-2.68 m			6.35 -			2.12-1.95(m,3H), 1.66-1.46 (m,3H), 1.39(s,3H), 0.81(s,9H)	64.83	2.9	38.64	2.4	72.35	56.9	68.16(t), 34.73(t), 29.42(t) 26.15(q), 23.92(q)

Notes to Table: a) aromatic signals not reported; b) not detectable; c) broad; d) J_{PH} not identified

TABLE 5: ^{31}P, ^{1}H, ^{13}C NMR Data of 4-Substituted Phosphinoisoxazolidines.



	^{31}P	^{1}H										^{13}C					
		H_i	$^{3}J_{PH}$ Hz	J_{HH} Hz	H_j	$^{2}J_{PH}$ Hz	J_{HH} Hz	H_k	$^{3}J_{PH}$ Hz	J_{HH} Hz	Others (a)	C_i	$^{2}J_{PC}$ Hz	C_j	$^{1}J_{PC}$ Hz	C_k	$^{2}J_{PC}$ Hz	Others (a)
10	27.27	4.90 dd	14.4	7.2	3.66 dq	1.8	8.0,8.0	4.31 t	8.7	8.7		70.12	5.8	53.71	71.2	67.39	-	
12	43.27	4.98 dd	17.1	7.1	4.01 dtt	2.8	7.5,7.5, 8.5	4.37 dt 4.20 q	12.9 8.1	8.6,8.6 8.1,8.1		71.09	4.1	54.18	56.3	68.35	3.8	
11	39.01	4.98 dd	17.7	7.1	4.09 ddt	4.0	7.3,8.3	4.39 dt 4.31 q	13.4 8.0	8.5,8.5 8.0,8.0		72.04	5.2	53.57	49.2	69.25	4.9	
15	29.18	3.86 dd	14.0	8.5	3.52 ddt	0.8	6.1,9.0 9.0	4.36 ddd 4.27 dt	15.8 12.7	6.1,8.6 8.6,8.6	2.59 (s, 3H)	72.47	-	51.65	73.0	65.91	-	42.50
17	45.79	(b)			3.91 m			4.45-4.25 m			2.59 (s, 3H)	73.47	3.6	51.60	58.0	66.95	1.6	42.37(q)
19	28.97	4.16-4.04 m			3.09 dddd	3.1	5.0,8.5 9.8	4.01 dt 3.93 dt	3.9 10.4	9.1,9.1 9.1,9.1	1.28 (s, 3H), 0.96 (s, 3H)	64.53	-	51.76	73.2	66.13	1.8	67.10(s),33.01(t,J=5.7) 34.99(t),26.07(q),23.40(q)
21	43.53	(b)			(b)			(b)				65.53	2.0	52.45	57.9	66.96	3.6	67.05(s),34.94(t),32.90(t,J=6.0) 25.76(q),23.30(q)
23	38.12	(b)			(b)			(b)				65.71	3.0	51.17	50.3	67.51	5.0	66.74(s),34.72(t),32.47(t,J=5.5) 25.48(q),23.04(q)
25	30.77	5.04 dd	14.5	5.6	(b)			4.20 q 4.08 dt	9.6 15.6	9.6,9.6 7.8,7.8	(b)	61.93	-	49.86	71.7	66.51	1.7	67.72(t),25.18(t)
27a	28.67	(b)			(b)			4.82-4.73 m/4		8-3.95 m	(b)	(b)		(b)		(b)		
27b	27.84	(b)			(b)			4.82-4.73 m/4		8-3.95 m		(b)		(b)		(b)		
27	24.87	4.30 m			2.97 dt	2.1	7.1,7.1	4.46 m			1.83-1.67(m,3H),1.50-1.38(m,2H), 1.32 (d,J=6.4,3H),1.24(s,3H),0.99(s,3H)	63.35	-	54.83	72.2	75.70	-	66.37(s),35.38(t),32.03(t,J=2.9) 26.18(q),23.36(q),18.20(q,J=1.6)
38	40.15	(b)			3.31 dt	5	7.0,7.0	4.52-4.35 m			1.78-1.40(m,4H),1.2eld,J=6.6,3H) 1.24(s,3H),1.02(s,3H)	64.78	4.1	54.78	55.8	76.05	1.2	66.28(s),35.36(t),31.89(t,J=3.2) 26.23(q),23.19(q),17.66(q,J=1.8)
39a	22.64	3.84 dt	8.8	6.1	3.31 ddd	2.1	6.0,9.6	4.53 m			2.58(m,1H),1.88-1.72(m,1H), 1.60-1.47(m,2H),1.27(s,3H) 0.94(s,3H),0.91(d,J=5.9,3H)	67.24	0.8	52.64	74.3	72.75	2.1	68.09(s),37.04(t),27.12(q) 26.32(t,J=3.7),23.75(q),20.08(q)
39b	28.97	4.04 ddt	16.2	8.6 4.6 4.6	2.60 dt		8.9,4.2	4.29 tq	6.0	9.0,6.0	1.30(s,3H),0.93(s,3H),0.91 (d,J=5.9,3H)	66.59	-	58.29	72.3	73.43	1.7	67.42(s),35.15(t),34.12(t,J=7.2) 26.01(q),25.72(q),18.48(q)
40	56.61	4.77 m			2.79 m			4.42 m			2.47-1.93(m,4H),1.84(m,2H), 1.63(m,2H0,1.29(s,3H),1.09(s,3H)	64.95	2.2	52.10	68.3	80.39	12.8	68.42(s),36.24(t),32.02(t,J=9.11, 28.23 (t,J=9.11),27.56(q),25.00(t,J=65),23.95(q)
42	26.16	3.99 q	7.8	7.8 7.8	4.57 ddd	2.2	5.2,7.3	5.32 dd	12.9	5.1	2.58(m,1H),1.87-1.75(m,1H), 1.68-1.17(m,2H),1.03(s,3H),0.91(s,3H)	67.11	-	46.98	71.1	91.31	1.2	67.77(s),35.95(t),27.26(q) 26.00(t,J=4.3),23.68(q)
43a	26.86	4.07 m			2.59 dt	3.1	3.1,8.3	5.40 dd	11.5	8.3	2.07-1.20(m,4H),1.39(s,3H),0.97(s,3H)	65.83	-	55.42	70.8	82.37	(c)	68.43(s),35.77(t),33.4(t,J=8.3) 26.06(q),23.96(q)
43b	25.22	3.91 q	7.3	7.3 7.3	3.72 dt	3.1	6.5,6.5	5.89 dd	12.7	6.2	2.75(m,1H),2.05-1.40(m,3H) 1.35(s,3H),1.03(m,1H)	66.68	-	53.58	71.9	84.58	1.4	67.49(s),36.58(t),27.29(q), 25.52(t,J=4.3),24.08(q)
45	26.76	4.05-3.90 m			2.52 dddd	13.9	9.9,9.8,5.5	4.20-4.05 m 3.77 dd		11.3,9.9,8.8 (d)	2.33(ddt,J=13.6,6.12.2,1H), 2.15 (ddd,J=9.1,13 2,17.6,1H), 2.04-1.44 (m,2H),1.33(s,3H),1.06(s,3H)	64.79	-	48.70	147.2	66.23	-	66.85(s),34.58(t),32.31(t,J=7.3) 25.89(q),23.16(q)

Notes to Table: a) aromatic signals not reported, b) not detectable, c) broad, d) J_{PH} not identified

12: mp 164-166 °C (diethyl ether); Anal. Calcd. for $C_{27}H_{24}NOPS$: C, 73.45; H, 5.48; N, 3.17. Found: C, 72.97; H, 5.56; N, 3.57%. IR ($CDCl_3$): 3070, 2900, 1600, 1490, 1440, 1100 (vs) cm^{-1}.

Cycloaddition of 1 to 8: 2,3-Diphenyl-4-diphenylselenophosphinyltetrahydroisoxazole (13). The reaction mixture was purified by chromatography on a short pad of silica gel (eluent diethyl ether).

13: mp 158-160 °C (from ligroin (75-120 °C)). Anal. Calcd. for $C_{27}H_{24}NOPSe$: C, 66.39; H, 4.95; N, 2.87. Found: C, 66.27; H, 5.16; N, 2.94%. IR (CCl_4): 3061, 3036, 2932, 2870, 1598, 1437, 1214, 1176, 1096 (vs) cm^{-1}.

Cycloaddition of 2 to 6: 5-Diphenylphosphinyl-2-methyl-3-phenyltetrahydroisoxazole (14a and 14b) and 4-Diphenylphosphinyl-2-methyl-3-phenyltetrahydroisoxazole (15). The reaction mixture was purified by flash column chromatography (eluent dichloromethane-ethyl acetate 1:1).

14a + 14b: oil, R_f = 0.5. Anal. Calcd. for $C_{22}H_{22}NO_2P$: C, 72.71; H, 6.18; N, 3.85. Found: C, 72.96; H, 6.10; N, 3.50%. IR ($CDCl_3$): 3063, 2960, 2880, 1590, 1438, 1180 (vs), 1120 cm^{-1}.

15: R_f = 0.4; mp 139-141 °C (from CCl_4). Anal. Calcd. for $C_{22}H_{22}NO_2P$: C, 72.71; H, 6.10; N, 3.85. Found: C, 72.50; H, 6.20; N, 3.70%. IR ($CDCl_3$): 3070, 1590, 1440, 1200 (vs), 1110 cm^{-1}.

Cycloaddition of 2 to 7: 5-Diphenylthiophosphinyl-2-methyl-3-phenyltetrahydroisoxazole (16a and 16b) and 4-Diphenylthiophosphinyl-2-methyl-3-phenyltetrahydroisoxazole (17). The reaction mixture was purified by flash column chromatography (eluent ethyl acetate-petroleum ether 1:1). Anal. (of the mixture) Calcd. for $C_{22}H_{22}NOPS$: C, 69.64; H, 5.84; N, 3.69. Found: C, 69.65; H, 5.97; N, 3.69%.

16a: R_f = 0.3; mp 123-124 °C (from ligroin (75-120 °C)). IR ($CDCl_3$) 3064, 3033, 2955, 2876, 1603, 1437, 1100 (vs) cm^{-1}.

16b: oil, R_f = 0.4. IR ($CDCl_3$): 3063, 2922, 2851, 1603, 1437, 1100 cm^{-1}.

17: oil, R_f = 0.05. IR ($CDCl_3$): 3063, 3037, 1598, 1487, 1438, 1098 cm^{-1}.

Cycloaddition of 3 to 6: 6,6-Dimethyl-2-diphenylphosphinylhexahydropyrrolo[1,2-b]isoxazole (18) and 6,6-Dimethyl-3-diphenylphosphinylhexahydropyrrolo[1,2-b]isoxazole (19). The reaction mixture was purified by flash column chromatography (eluent chloroform-methanol 15:1).

18: R_f = 0.55; mp 67-68 °C (from CCl_4). Anal. Calcd. for $C_{20}H_{24}NO_2P$: C, 70.36; H, 7.08; N, 4.10. Found: C, 70.49; H, 7.21; N, 3.79%. IR (CCl_4): 3064, 2980, 1590, 1478, 1438, 1190 (vs), 1115 cm^{-1}.

Cycloaddition of 3 to 7: 6,6-Dimethyl-2-diphenylthiophosphinylhexahydropyrrolo[1,2-b]isoxazole (20) and 6,6-Dimethyl-3-diphenylthiophosphinylhexahydropyrrolo[1,2-b]isoxazole (21). The reaction mixture was purified by crystallization from ligroin (75-120 °C).

20: mp 127-128 °C. Anal. Calcd. for $C_{20}H_{24}NOPS$: C, 67.20; H, 6.77; N, 3.92. Found: C, 67.88; H, 6.91; N, 3.87%. IR (CCl_4): 3062, 2971, 2873, 1591, 1437, 1382, 1366, 1100 (vs) cm^{-1}.

Cycloaddition of 3 to 8: 6,6-Dimethyl-2-diphenylselenophosphinylhexahydropyrrolo[1,2-b]isoxazole (22) and 6,6-Dimethyl-3-diphenylselenophosphinylhexahydropyrrolo[1,2-b]isoxazole (23). The reaction mixture was purified by crystallization from ligroin (75-120 °C).

22: mp 129-131 °C. Anal. Calcd. for $C_{20}H_{24}NOPSe$: C, 59.41; H, 5.98; N, 3.46. Found: C, 59.25; H, 5.88; N, 3.40%. IR (CCl_4): 3062, 2971, 2870, 1544, 1437, 1382, 1366, 1096 (vs) cm^{-1}.

Cycloaddition of 4 to 6: 2-Diphenylphosphinyl-1,5,6,10b-tetrahydro-2*H*-isoxazolo[3,2-a]isoquinoline (24a and 24b) and 3-Diphenylphosphinyl-1,5,6,10b-tetrahydro-2*H*-isoxazolo[3,2-a]isoquinoline (25). The reaction mixture was purified by flash column chromatography (eluent dichloromethane-methanol 20:1).

24a + 24b + 25: oil, R_f = 0.2. Anal. (of the mixture) Calcd. for $C_{23}H_{22}NO_2P$: C, 73.58; H, 5.90; N, 3.73. Found: C, 73.50; H, 6.06; N, 3.28%. IR ($CDCl_3$): 3063, 2919, 1592, 1484, 1438, 1278, 1177 (vs), 1119 cm^{-1}. The mixture was further purified by crystallization from ligroin (75-120 °C).

24a: mp 151-153 °C.

Cycloaddition of 5 to 6: 2-Diphenylphosphinylhexahydro-2*H*-isoxazolo[2,3-a]pyridine (26a and 26b) and 3-Diphenylphosphinylhexahydro-2*H*-isoxazolo[2,3-a]pyridine (27a and 27b). The reaction mixture was purified by flash column chromatography (eluent chloroform-methanol 10:1).

26a + 26b + 27a + 27b: oil, R_f = 0.5. Anal. (of the mixture) Calcd. for $C_{19}H_{22}NO_2P$: C, 69.71; H, 6.77; N, 4.28. Found: C, 69.54; H, 7.02; N, 3.96%.

Cycloaddition of 3 to 28: 3-Diphenylphosphinyl-2,6,6-trimethylhexahydropyrrolo[1,2-b]isoxazole (37). Starting dipolarophile **28** contained 20% of the *E* isomer **29** that did not react in these conditions. The reaction mixture was purified by treatment with hot petroleum ether 40-70 °C. Repeated washing left a solid pure by chromatography.

37: mp 187-188 °C (from ligroin (75-125 °C)), sublimes. Anal. Calcd. for $C_{21}H_{26}NO_2P$: C, 70.97; H, 7.37; N, 3.94. Found: C, 71.23; H, 7.47; N, 4.71%, run in sealed aluminum holder. IR (CCl_4): 3064, 2937, 2900, 1605, 1438, 1198 (vs), 1160, 1117 cm^{-1}.

Cycloaddition of 3 to 29: 3-Diphenylthiophosphinyl-2,6,6-trimethylhexahydropyrrolo[1,2-b]isoxazole (38). The reaction mixture was purified by chromatography on a short pad of silica gel (eluent dichloromethane-methanol 10:1).

38: R_f = 0.6; mp 146-147.5 °C (from ligroin (75-120 °C)). Anal. Calcd. for $C_{21}H_{26}NOPS$: C, 67.90; H, 7.05; N, 3.77. Found: C, 67.54; H, 6.92; N, 3.86%. IR (CCl_4): 3061, 2972, 2936, 1536, 1438, 1097 (vs) cm^{-1}.

Cycloaddition of 3 to 30: 3-Diphenylphosphinyl-2,6,6-trimethylhexahydropyrrolo[1,2-b]isoxazole (39a and 39b). The reaction mixture was purified by flash column chromatography (eluent ethyl acetate).

39a: R_f = 0.2; mp 197-199 °C. Anal. Calcd. for $C_{21}H_{26}NO_2P$: C, 70.97; H, 7.37; N, 3.94. Found: C, 70.72; H, 7.05; N, 3.90%. IR (CCl_4): 3062, 2973, 1535, 1438, 1200 (vs), 1114 cm^{-1}.

39b: R_f = 0.1; mp 194-195 °C (Büchi). Anal. Calcd. for $C_{21}H_{26}NO_2P$: C, 70.97; H, 7.37; N, 3.94. Found: C, 70.86; H, 7.56; N, 3.84%. IR ($CDCl_3$): 3063, 2973, 2937, 1592, 1537, 1438, 1184 (vs), 1117 cm^{-1}.

Cycloaddition of 3 to 31: 6,6-Dimethyl-1-oxide-1-phenyloctahydro-1*H*-phospholo[2,3-d]pyrrolo[1,2-b]isoxazole (40). The reaction mixture was purified by flash column chromatography (eluent dichloromethane-methanol 20:1).

40: oil, R_f = 0.25. Anal. Calcd. for $C_{16}H_{22}NO_2P$: C, 65.96; H, 7.61; N, 4.81. Found: C, 65.50; H, 7.82; N, 4.79%. IR ($CDCl_3$): 3060, 2972, 1601, 1438, 1258, 1182 (vs) cm^{-1}.

Cycloaddition of 3 to 32: 6,6-Dimethyl-2-diphenylphosphinyl-3-phenylsulfonylhexahydropyrrolo[1,2-b]isoxazole (41) and 6,6-Dimethyl-3-diphenylphosphinyl-2-phenylsulfonylhexahydropyrrolo[1,2-b]isoxazole (42). The reaction mixture was purified by flash column chromatography (eluent ethyl acetate-petroleum ether 1:1). Anal. (of the mixture) Calcd. for $C_{26}H_{28}NO_4PS$: C, 64.85; H, 5.86; N, 2.91. Found: C, 64.99; H, 6.01; N, 2.57%.

41: yield 38 %; R_f = 0.2; mp 199-200 °C (from ligroin (75-120 °C)). IR ($CDCl_3$): 3160, 3064, 2980, 1600, 1438, 1322, 1197 (vs), 1159 (vs), 1149 (vs), 1122 cm^{-1}.

42: yield 27 %; R_f = 0.3; mp 190-191 °C (from ligroin (75-120 °C)). IR ($CDCl_3$): 3160, 3067, 2972, 1594, 1439, 1322, 1197 (vs), 1152 (vs), 1118 (vs) cm^{-1}.

Cycloaddition of 3 to 34: 6,6-Dimethyl-3-diphenylphosphinyl-2-phenylsulfenylhexahydropyrrolo[1,2-b]isoxazole (43a and 43b). The reaction mixture was purified by flash column chromatography (eluent dichloromethane-methanol 20:1).

43a + 43b: R_f = 0.3. The mixture was further purified by crystallization from ligroin (75-120 °C). **43a**: mp 187-188 °C. Anal. Calcd. for $C_{26}H_{28}NO_2PS$: C, 69.47; H, 6.27; N, 3.11. Found: C, 69.87; H, 6.41; N, 2.82%. IR ($CDCl_3$): 3064, 2974, 1585, 1438, 1189 (vs), 1117, 1069, 1024 cm^{-1}.

Cycloaddition of 3 to 35: 2-Diethylphosphonyl-6,6-dimethylhexahydropyrrolo[1,2-b]isoxazole (44) and 3-Diethylphosphonyl-6,6-dimethylhexahydropyrrolo[1,2-b]isoxazole (45). The reaction mixture was purified by flash column cromatography (eluent dichloromethane-methanol 15:1).

44 + 45: oil, R_f = 0.35. Anal. (of the mixture) Calcd. for $C_{12}H_{24}NO_4P$: C, 51.98; H, 8.72; N, 5.05. Found: C, 51.85; H, 8.83; N 5.08%. IR (CCl_4): 2976, 2872, 1630, 1466, 1367, 1245 (vs), 1029 (vs) cm^{-1}.

Cycloaddition of 3 to 36: 6,6-Dimethylhexahydropyrrolo[1,2-b]isoxazol-2-yltriphenylphosphonium bromide (46). The reaction mixture, after 6 h (90 % conversion), was immediately purified by flash column chromatography (eluent dichloromethane-methanol 10:1).

46: viscous oil, R_f = 0.2. Decomposes in solution, and on storing for a long period.

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