

CYCLOADDITIONS OF VINYL ISOCYANATE AND ISOTHIOCYANATE WITH  
OXOVINYLLIDENE- AND PHENYLIMINOVINYLLIDENETRIPHENYLPHOSPHORANES.  
NEW SYNTHESIS AND CRYSTAL STRUCTURE OF POLYSUBSTITUTED  
PYRIDINE DERIVATIVES.

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Abstract - Oxovinylidenetriphenylphosphorane **1** and N-phenyl-  
iminovinylidenetriphenylphosphorane **2** enter cycloaddition re-  
actions with vinyl isocyanate **3** and vinyl isothiocyanates **4**  
and **5** giving exclusively [4+2]cycloaddition products, i.e. de-  
rivatives of 3-triphenylphosphoranopyrid-2-one **6** and **15** or  
3-triphenylphosphoranopyridine-2-thione (**8**, **9** and **17**), in con-  
trast with alkyl or aryl isocyanates or isothiocyanates. The  
structure of the obtained cycloadducts was determined by spec-  
tral methods and confirmed by desulfuration of the pyridine-  
-2-thione derivative **8** and X-ray diffraction analysis of 4-  
-phenylimino-3-triphenylphosphoranopyrid-2-one **15** and 4-phenyl-  
imino-3-triphenylphosphoranopyridine-2-thione **17**.

Isocyanates and isothiocyanates in which the heterocumulene grouping is conjugated with another multiple bond (e.g. C=C, C=O, C=S, C=N) may react in cycloaddition reactions with double or triple bonds with varying periselectivity: they can act either as a  $2\pi$  electron component and afford different [2+2] cycloadducts or as a  $4\pi$  electron component and give [4+2] cycloadducts<sup>1,2</sup>. Thus, for example, treatment of alkenyl isothiocyanates with ynamines results in [2+2] cycloaddition to the N=C bond<sup>2a</sup> (i), with carbodiimides in [2+2] cycloaddition to the C=S bond<sup>2b</sup> (ii) whereas with tetracyanoethylene in [4+2] cycloaddition to the C=C-N=C azadiene grouping<sup>2d</sup> (iii) (Fig. 1). These reactions are interesting both from mechanistic and synthetic standpoint because they can lead to various four-membered as well as six-membered cycloadducts.

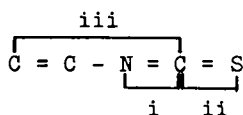
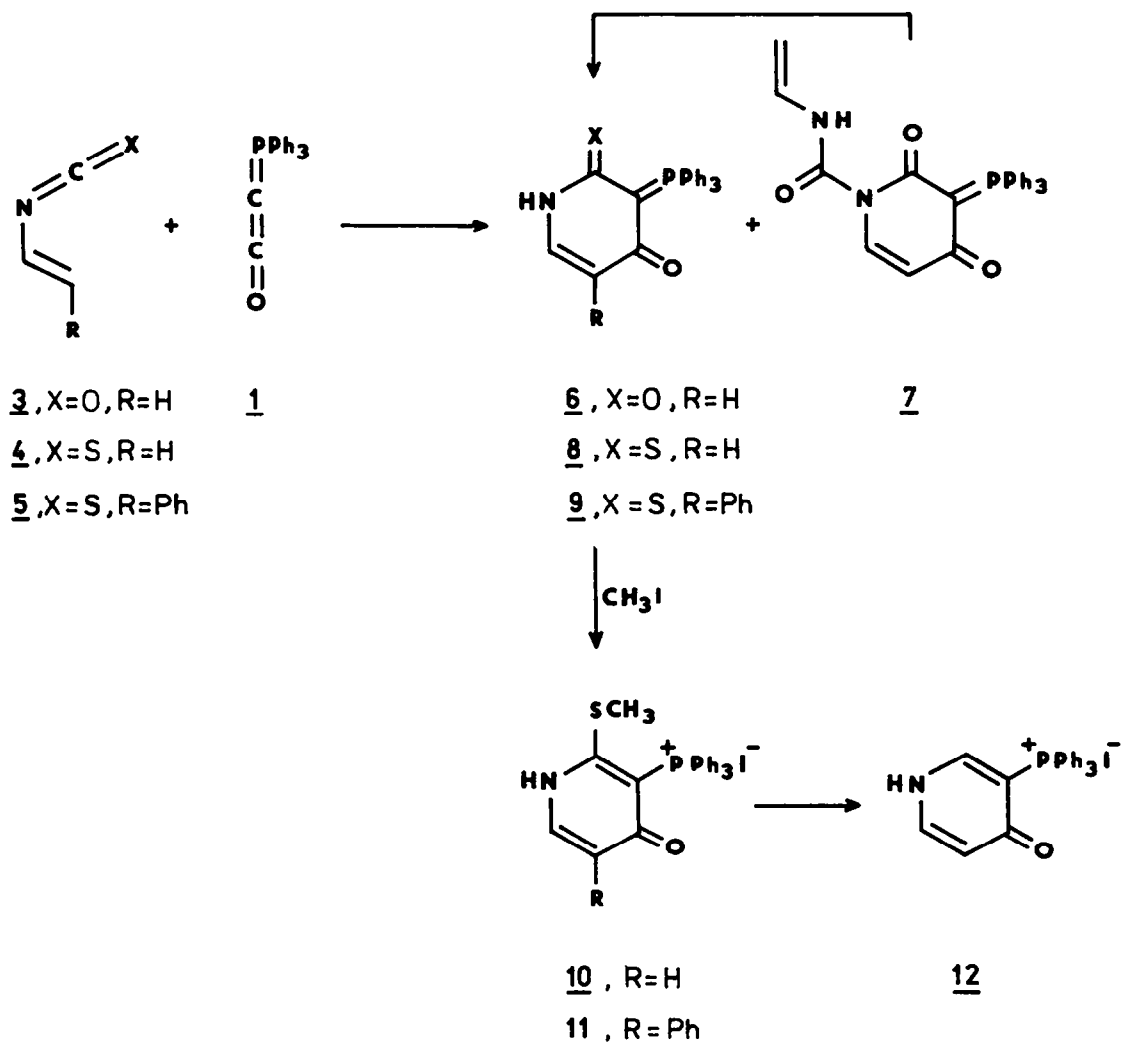


Fig.1 Cycloaddition possibilities in vinyl isothiocyanates

In spite of some attempts to predict which of the possible thermic pericyclic processes should prevail in the given reaction<sup>2d,3</sup>, no generally valid rules for such prediction can be formulated so far. Our present paper concerns cycloaddition reactions of vinyl isocyanate and isothiocyanate with oxovinylidenetriphenylphosphorane 1 and N-phenyliminovinylidenetriphenylphosphorane 2.

## RESULTS AND DISCUSSION

Reaction of phosphorane 1 with an equimolar amount of vinyl isocyanate 3 afforded a mixture of two products 6 and 7 which were separated by crystallization (Scheme 1).

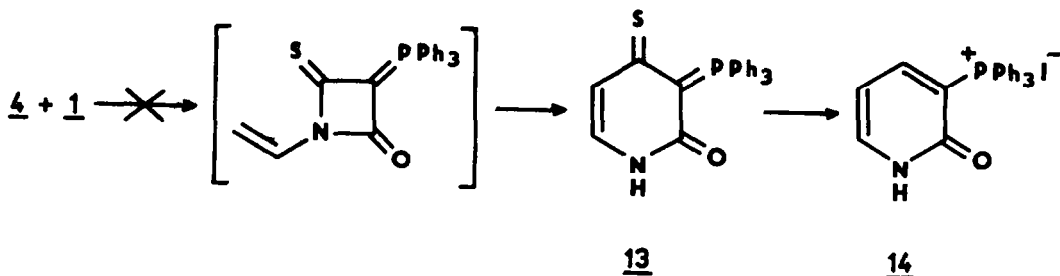


Scheme 1

According to NMR spectra, both compounds were pyridine-2,4-dione derivatives but, moreover, compound 7 contained a vinyl group. Reaction of two equivalents of isocyanate 3 with one equivalent of 1 afforded predominantly compound 7 (according to NMR spectra); however, attempted crystallization of 7 resulted in a mixture of 6 and 7. On heating to 120 °C in vacuo or refluxing in decalin, compound 7 was converted into 6. All these facts confirm that compound 7 arises from 6 by reaction with another molecule of isocyanate 3. On heating, the product 7 liberates vinyl isocyanate 3 and the derivative 6 is recovered. The fact that mass spectra of 6 and 7 are completely identical (at 70 eV) shows that (under conditions of the measurement) compound 7 liberates vinyl isocyanate under formation of 6.

The reaction of phosphorane 1 with vinyl isothiocyanate 4 afforded 8 as the sole product in 94% yield. As shown by mass spectra, the product 8 is a 1:1 adduct of the starting compounds. No vinyl grouping was detected by the <sup>1</sup>H NMR spectra, and thus the product cannot be a [2+2] cycloadduct (iminothietane or azetidione derivative). Reaction of 8 with methyl iodide led to the S-methyl derivative 10 (NMR signals of CH<sub>3</sub>: δ<sub>H</sub> 2.75, δ<sub>C</sub> 18.8) which was soluble enough to allow measurement of its <sup>13</sup>C NMR spectrum. Styryl isothiocyanate 2 reacted with 1 analogously to furnish only one product 9 which was S-methylated to 11 (CH<sub>3</sub> signals: δ<sub>H</sub> 2.8, δ<sub>C</sub> 19.2). The NMR spectra of 10 and 11 indicate that both compounds are similar pyridine derivatives.

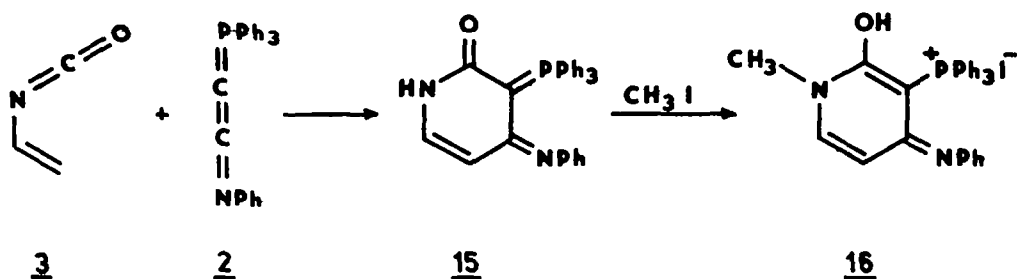
As follows from our previous experience with the reaction of vinyl isothiocyanate 4 with an ynamine<sup>2a</sup>, the reaction of 4 with 1 could be a [2+2] cycloaddition to the N=C bond of the -NCS group (Scheme 2).



Scheme 2

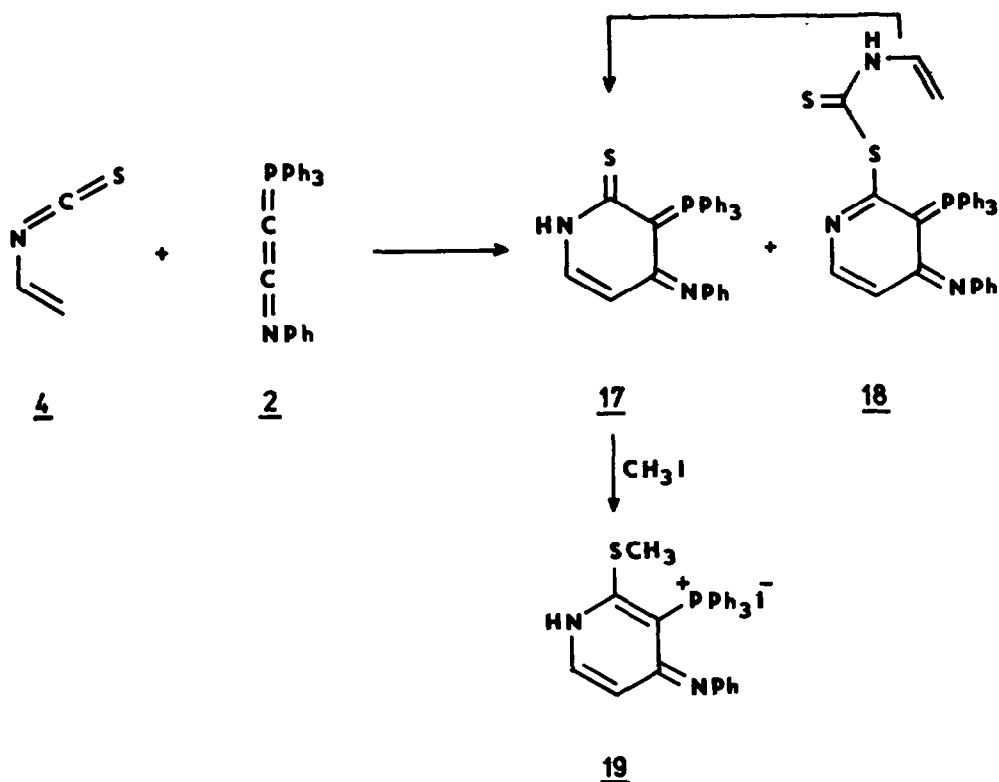
The arising unstable azetidione derivative could be stabilized by opening the four-membered ring followed by electrocyclization to give compound 13, isomeric with 8. The usual spectral methods were not capable of discrimination between structures 8 or 13. To confirm the structure of the obtained cycloadducts 8 and 9 we removed the -SCH<sub>3</sub> group in compound 10 by reduction with Raney nickel and measured the <sup>1</sup>H NMR spectrum of the obtained product 12. The C<sub>5</sub> proton signals (δ<sub>H</sub> 6.48 dd, J<sub>H,H</sub> = 7 Hz, J<sub>H,P</sub> = 6 Hz) did not differ significantly from those of the corresponding proton in 10 (δ<sub>H</sub> 6.28 dd, J<sub>H,H</sub> = 7 Hz, J<sub>H,P</sub> = 3 Hz). This confirms that 8 is indeed a [4+2] cycloadduct since if the original product was 13, its Raney nickel reduction would afford compound 14 with a new proton on the C<sub>4</sub> carbon atom and coupling constants of the proton on C<sub>5</sub> carbon atom would be markedly different.

Reaction of vinyl isocyanate 3 with iminovinylidetriphenylphosphorane 2 afforded only one product, isolated in 85% yield. Its X-ray diffraction analysis revealed the [4+2] cycloadduct structure 15 (see Fig.2). Its methylation gave N-methyl derivative 16 (NMR signals of the CH<sub>3</sub> group: δ<sub>H</sub> 3.44, δ<sub>C</sub> 36.9) (Scheme 3).



Scheme 3

Equimolar amounts of vinyl isothiocyanate **4** and phosphorane **2** afforded a mixture of two products of identical mass spectra (at 70 eV). According to <sup>1</sup>H NMR spectra, one of the products contained a vinyl group whereas the other did not. In an attempted measurement of <sup>13</sup>C NMR spectrum of the vinyl-containing compound in deuteriochloroform, the spectrum changed with time and after standing at room temperature for two days, the chloroform solution afforded the second reaction product in a 90% yield. These facts, together with the presence of an NH band in the IR spectrum (3385 cm<sup>-1</sup>) of the vinyl-containing compound, confirm that this compound is not a product of [2+2] cycloaddition to the -NCS group but compound **18** formed from **17** by reaction with further molecule of vinyl isothiocyanate **4** (Scheme 4).



Scheme 4

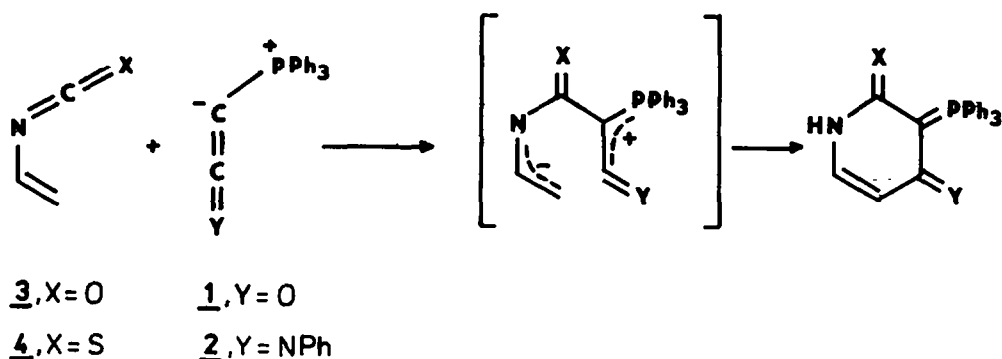
On standing in chloroform solution or during mass spectra measurements, compound 18 loses vinyl isothiocyanate 4 under formation of 17 whose structure was confirmed by X-ray diffraction (see Fig.2). Methylation of 17 with methyl iodide afforded the S-methyl derivative 19 (NMR signals of the CH<sub>3</sub> group:  $\delta_{\text{H}}$  2.2,  $\delta_{\text{C}}$  15.9).

It is worth mentioning that the obtained phosphonium compounds 19, 16, 12, 11 and 10 are not very stable because their mass spectra exhibited no molecular peak (although measured by the chemical ionization method), the dominant peak being due to the M<sup>+</sup>-HI ion or, in the case of 10, M<sup>+</sup>-CH<sub>3</sub>I ion.

It was of interest to compare our results with those obtained by Bestmann and coworkers in reactions of vinylidenephosphoranes 1 and 2 with alkyl, aryl, acyl, thioacyl and imidoyl isocyanates and isothiocyanates<sup>4</sup>. Thus, oxovinylidene-triphenylphosphorane 1 reacted with alkyl and aryl isocyanates or isothiocyanates to give 1:2 adducts with six-membered ring. The reaction took place at the C=N bond of the isocyanates and the C=S bond of the isothiocyanates. On the other hand, N-phenyliminovinylidene-triphenylphosphorane 2 reacted with the same heterocumulenes under formation of stable [2+2] cycloadducts, the isocyanates again reacting at the C=N bond whereas the isothiocyanates at the C=S bond<sup>4</sup>. When the -NCO or -NCS group was conjugated with a polar multiple bond C=Y (Y = O, S, NR), 1 reacted unequivocally with the heterodiene grouping Y=C-N=C under formation of [4+2] cycloadducts<sup>2h</sup>. Iminovinylidene-triphenylphosphorane 2 reacted either similarly to 1 to give [4+2] cycloadducts or, with some isothiocyanates (depending on the character of Y), to afford [2+2] cycloadducts arising by addition to the C=S bond<sup>2h</sup>. As follows from our results, contrary to alkyl or aryl isocyanates or isothiocyanates<sup>4</sup>, vinyl isocyanate and vinyl isothiocyanate react selectively with phosphorus ylides of ketene 1 and ketene imine 2 in a [4+2] cycloaddition reaction.

Giffard and Cousseau<sup>2d</sup>, on the basis of the present results on cycloadditions of alkenyl isothiocyanates, remark upon the fact that reactions with typical electron-poor dienophiles (e.g. tetracyanoethylene) prefer [4+2] cycloaddition whereas with electron-rich dienophiles (ynamine) [2+2] cycloadditions are frequently favoured. If the periselectivity of the cycloaddition to heterocumulenes were influenced only by electron density of the dienophile, we could expect that reactions of 3 and 4 with vinylidenephosphoranes 1 and 2 (which can be regarded as electron-rich dienophiles) would also afford [2+2] cycloadducts. However, as mentioned above, we observed the exclusive formation of [4+2] cycloadducts.

As revealed by the X-ray diffraction analysis<sup>4a</sup>, phosphoranes 1 and 2 exist predominantly in the ylide mesomeric form (Scheme 5), unfavourable for a concerted cycloaddition mechanism. We may thus assume that cycloaddition of the mentioned



Scheme 5

phosphoranes with the heterocumulenes 3 and 4 proceeds very probably by a dipolar mechanism, with a primary attack by the ylide carbon atom at the -NCX carbon atom, followed by cyclization of the ambidental anion to give the six-membered ring product (Scheme 5). The formation of [4+2] cycloadducts in the reaction of alkenyl isothiocyanates with dienophiles of various types (tetracyanoethylene and vinylidene-triphenylphosphoranes) probably reflects the fact that the periselectivity of cycloaddition reaction is influenced not only by the electronic character of the dienophile but also by the reaction mechanism (concerted or dipolar).

#### Crystallographic Structure of Compounds 15 and 17

Perspective views of the compounds 15 and 17 are depicted in Fig.2. Tables 1 and 2 show the atomic fractional coordinates; interatomic distances are given in Tables 3 and 4 and bond angles in Tables 5 and 6. Supplementary data (thermal parameters and structure factors) are available from the Cambridge Crystallographic Data Centre respectively from the British Library, Lending Division, on request.

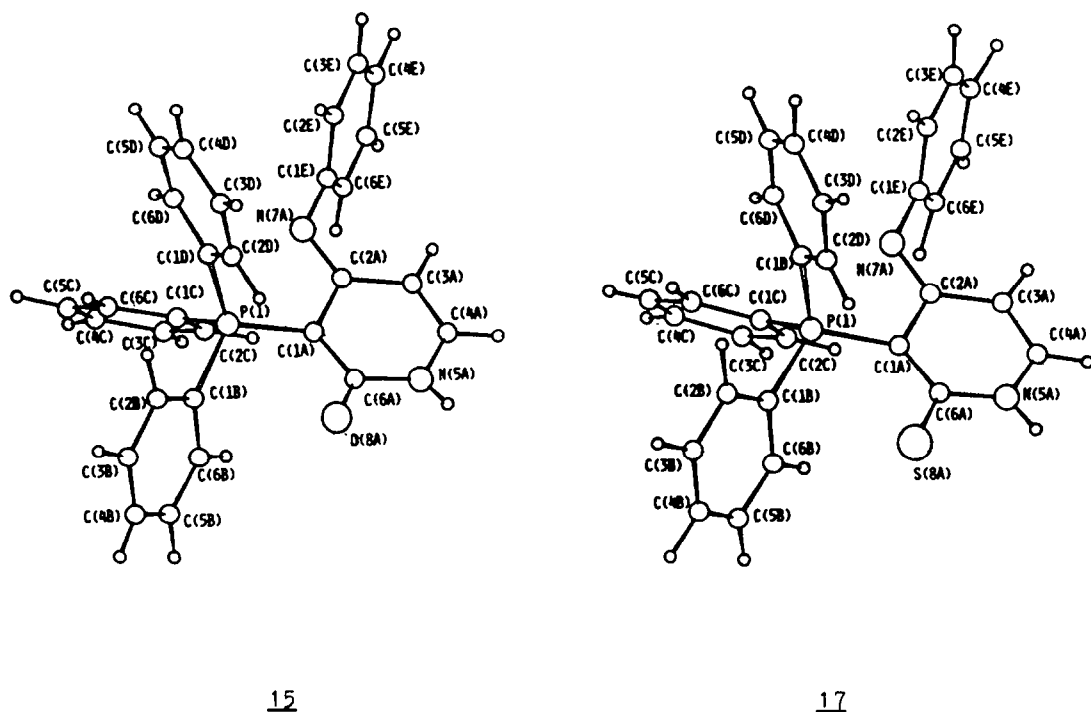


Fig.2 Perspective views of compound 15 and 17

As shown in Fig.2 the two structures are similar. Replacement of the exocyclic sulfur atom by oxygen has only negligible effect on the molecular conformation which can be described by dihedral angles between the mean molecular planes passing through the individual rings (A to E). The dihedral angles are as follows: For compound 15 :

$A-B = 66.0(1)^\circ$	$A-C = 59.3(1)^\circ$	$A-D = 79.9(1)^\circ$	$A-E = 76.4(1)^\circ$
	$B-C = 99.2(1)^\circ$	$B-D = 62.1(1)^\circ$	$B-E = 14.9(2)^\circ$
		$C-D = 54.1(1)^\circ$	$C-E = 96.8(2)^\circ$
			$D-E = 51.4(1)^\circ$

Table 1. Atomic fractional coordinates of compound 15 with e.s.d. in parentheses

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
P(1)	.2414( 1)	.1606( 1)	.2221( 1)	C(2E)	.3702( 3)	.5159( 3)	.0683( 2)
C(1A)	.1622( 2)	.2012( 2)	.1290( 1)	C(3E)	.3941( 4)	.6327( 4)	.0391( 3)
C(2A)	.1847( 2)	.3201( 2)	.0947( 1)	C(4E)	.3336( 3)	.7331( 3)	.0451( 2)
C(4A)	.0505( 2)	.2772( 2)	-.0200( 2)	C(5E)	.2498( 3)	.7202( 3)	.0818( 2)
C(3A)	.1195( 2)	.3566( 2)	.0177( 2)	C(6E)	.2262( 2)	.6045( 3)	.1109( 2)
N(5A)	.0361( 1)	.1614( 2)	.0108( 1)	H(3A)	.1328(21)	.4337(28)	-.0067(19)
C(6A)	.0949( 2)	.1148( 2)	.0827( 1)	H(4A)	.0071(19)	.2980(24)	-.0757(16)
N(7A)	.2621( 2)	.3818( 2)	.1325( 1)	H(5A)	.0003(22)	.1097(27)	-.0217(20)
O(8A)	.0849( 1)	.0025( 2)	.0998( 1)	H(2B)	.3241(25)	-.0791(27)	.2834(19)
C(1B)	.1954( 2)	.0260( 2)	.2698( 1)	H(3B)	.2614(26)	-.2342(35)	.3559(23)
C(2B)	.2518( 3)	-.0783( 3)	.2920( 2)	H(4B)	.0872(25)	-.2318(34)	.3806(22)
C(3B)	.2135( 4)	-.1741( 4)	.3349( 3)	H(5B)	-.0042(27)	-.0601(32)	.3511(21)
C(4B)	.1200( 3)	-.1652( 4)	.3553( 2)	H(6B)	.0617(24)	.1079(29)	.2767(21)
C(5B)	.0649( 2)	-.0620( 4)	.3356( 2)	H(2C)	.1318(23)	.3822(26)	.2463(20)
C(6B)	.1010( 2)	.0335( 3)	.2922( 2)	H(3C)	.1260(27)	.5142(33)	.3616(21)
C(1C)	.2440( 2)	.2747( 2)	.3045( 1)	H(4C)	.2316(23)	.4858(30)	.4866(22)
C(2C)	.1765( 2)	.3710( 3)	.2977( 2)	H(5C)	.3579(21)	.3281(25)	.5039(20)
C(3C)	.1734( 3)	.4506( 3)	.3648( 2)	H(6C)	.3590(21)	.1785(29)	.3848(18)
C(4C)	.2398( 3)	.4333( 3)	.4389( 2)	H(2D)	.3214(23)	-.0253(28)	.1318(18)
C(5C)	.3060( 2)	.3369( 3)	.4472( 2)	H(3D)	.4910(22)	-.0748(26)	.1055(18)
C(6C)	.3089( 2)	.2562( 3)	.3806( 2)	H(4D)	.6266(25)	.0645(28)	.1620(20)
C(1D)	.3679( 2)	.1303( 2)	.2056( 1)	H(5D)	.6016(27)	.2240(32)	.2455(23)
C(2D)	.3839( 2)	.0288( 2)	.1559( 2)	H(6D)	.4399(25)	.2807(33)	.2746(22)
C(3D)	.4789( 2)	.0032( 3)	.1397( 2)	H(2E)	.4131(23)	.4392(28)	.0654(18)
C(4D)	.5584( 2)	.0770( 3)	.1743( 2)	H(3E)	.4582(28)	.6379(31)	.0139(25)
C(5D)	.5437( 2)	.1756( 3)	.2233( 3)	H(4E)	.3541(23)	.8177(32)	.0205(20)
C(6D)	.4476( 2)	.2054( 3)	.2374( 2)	H(5E)	.2037(24)	.7994(32)	.0902(20)
C(1E)	.2844( 2)	.5000( 2)	.1031( 2)	H(6E)	.1662(24)	.6044(28)	.1407(20)

For compound 17 :

$$\begin{array}{llll}
 \text{A-B} = 62.6(1)^\circ & \text{A-C} = 58.6(1)^\circ & \text{A-D} = 82.6(1)^\circ & \text{A-E} = 75.9(1)^\circ \\
 & \text{B-C} = 96.0(1)^\circ & \text{B-D} = 62.1(1)^\circ & \text{B-E} = 19.1(2)^\circ \\
 & & \text{C-D} = 56.4(1)^\circ & \text{C-E} = 92.9(2)^\circ \\
 & & & \text{D-E} = 47.2(2)^\circ
 \end{array}$$

In both structures the substituted pyridine rings are not planar, with a value of  $\sum(\delta)^2$  of 1034.7 and 1120.5 for compounds 15 and 17, respectively. In the first structure the atoms O(8A) and N(7A) are .2306(22) and .2101(29) Å out of the mean plane passing through the hetero ring. In the structure 17 the out-of-plane deviations for S(8A) and N(7A) (.3545(15) and .2393(30) Å) are significantly increased, in accord with the assumption that the negative charge in the compound 17 is localized on the sulfur atom more than on the oxygen atom in the compound 15.

The bond distances P-C are close to the mean value of 1.805(4) Å, just expected for the P(Ph) groups, with the exception of the bond distance P(1)-C(1A) which is 1.767(3) Å in compound 17 and even shorter (1.750(2) Å) in compound 15.

Small but significant differences, observed in the conformations of the heterocyclic ring are accounted in the puckering parameters<sup>5</sup> which are

$$\begin{array}{lll}
 Q = 0.96(4) \text{ \AA}, & \Phi = 169(2)^\circ, & \Theta = 132(2)^\circ \\
 Q = 0.172(4) \text{ \AA}, & \Phi = 178(14)^\circ, & \Theta = 110(15)^\circ
 \end{array}$$

Table 2. Atomic fractional coordinates of compound 17 with e.s.d. in parentheses

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
P(1)	.2472( 1)	.1718( 1)	.2355( 1)	C(2E)	.3891( 3)	.5050( 4)	.0840( 3)
C(1A)	.1719( 2)	.2061( 3)	.1428( 2)	C(3E)	.4194( 4)	.6172( 5)	.0541( 3)
C(2A)	.1970( 2)	.3231( 3)	.1080( 2)	C(4E)	.3605( 5)	.7198( 5)	.0569( 3)
C(3A)	.1382( 2)	.3585( 3)	.0321( 2)	C(5E)	.2755( 4)	.7135( 4)	.0897( 4)
C(4A)	.0716( 3)	.2807( 3)	-.0045( 2)	C(6E)	.2435( 3)	.6023( 4)	.1200( 3)
N(5A)	.0563( 2)	.1666( 3)	.0268( 2)	H(3A)	.1530(23)	.4322(32)	.0042(20)
S(8A)	.0943( 1)	-.0302( 1)	.1165( 0)	H(4A)	.0311(22)	.2978(28)	-.0587(19)
C(1B)	.2020( 2)	.0428( 3)	.2890( 2)	H(5A)	.0139(28)	.1085(36)	-.0068(24)
C(2B)	.2619( 3)	-.0544( 4)	.3170( 2)	H(2B)	.3379( 3)	-.0562( 4)	.3056( 2)
C(3B)	.2230( 4)	-.1486( 4)	.3610( 3)	H(3B)	.2735(32)	-.2247(44)	.3867(27)
C(4B)	.1280( 4)	-.1441( 5)	.3768( 3)	H(4B)	.0969(30)	-.2196(40)	.4137(25)
C(5B)	.0690( 3)	-.0463( 5)	.3505( 2)	H(5B)	.0020(31)	-.0389(39)	.3597(24)
C(6B)	.1049( 2)	.0492( 4)	.3065( 2)	H(6B)	.0592( 2)	.1271( 4)	.2865( 2)
C(1C)	.2482( 2)	.2901( 3)	.3128( 2)	H(2C)	.1376(24)	.3977(31)	.2560(20)
C(2C)	.1807( 3)	.3852( 4)	.3056( 2)	H(3C)	.1210(31)	.5358(40)	.3629(25)
C(3C)	.1787( 3)	.4669( 4)	.3718( 3)	H(4C)	.2341(26)	.5192(36)	.4888(23)
C(4C)	.2439( 4)	.4525( 5)	.4423( 3)	H(5C)	.3452(31)	.3440(40)	.4916(26)
C(5C)	.3087( 4)	.3574( 5)	.4490( 2)	H(6C)	.3620(28)	.2104(36)	.3911(23)
C(6C)	.3116( 3)	.2745( 4)	.3850( 2)	H(2D)	.3241(25)	-.0105(32)	-.1500(20)
C(1D)	.3707( 2)	.1393( 3)	.2151( 2)	H(3D)	.4964(30)	-.0594(40)	.1098(26)
C(2D)	.3851( 2)	.0365( 3)	.1679( 2)	H(4D)	.6272(27)	.0676(33)	.1543(21)
C(3D)	.4786( 3)	.0109( 4)	.1471( 2)	H(5D)	.6039(30)	.2482(38)	.2382(24)
C(4D)	.5568( 3)	.0852( 4)	.1733( 3)	H(6D)	.4336(28)	.2807(37)	.2735(24)
C(5D)	.5425( 3)	.1884( 4)	.2193( 3)	H(2E)	.4344(28)	.4358(37)	.0836(23)
C(6D)	.4493( 2)	.2160( 3)	.2394( 2)	H(3E)	.4876(34)	.6106(43)	.0353(27)
C(6A)	.1089( 2)	.1226( 3)	.0970( 2)	H(4E)	.3865(34)	.7997(47)	.0248(28)
N(7A)	.2720( 2)	.3815( 2)	.1457( 2)	H(5E)	.2325(35)	.7845(48)	.1033(29)
C(1E)	.3006( 3)	.4959( 3)	.1153( 2)	H(6E)	.1766(29)	.5944(37)	.1553(24)

for compounds 15 and 17, respectively, and which in both cases indicate half-chair conformations.

#### EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. NMR spectra were recorded on a TESLA BS 567-A spectrometer (operating frequency was 100.034 MHz and 25.156 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively) in the indicated solvents. Chemical shifts are reported in the  $\delta$  scale with tetramethylsilane as internal standard; interaction constants  $J_{\text{CP}}$  (Hz) are given in parentheses. IR spectra were determined on a Specord IR-75 spectrometer. Mass spectra were taken on JEOL DX 303/DA 5000 instrument at 70 eV or by the direct chemical ionization (DCI) method.

#### Materials

Benzene was dried over Na wire and distilled prior to use. All starting compounds were prepared according to the described procedures: vinyl isocyanate 3, b.p. 40–42 °C and vinyl isothiocyanate 4, b.p. 38–40 °C/70 mm Hg (ref.<sup>2a</sup>); 2-phenylethenyl isothiocyanate 2, b.p. 84–86 °C/0.25 mmHg (ref.<sup>6</sup>); oxovinylidenetriphenylphosphorane 1, m.p. 170–172 °C (ref.<sup>7</sup>) and N-phenyliminovinylidenetriphenylphosphorane 2, m.p. 150–152 °C (ref.<sup>8</sup>).



Table 3. Interatomic distances (Å) for compound 15 with e.s.d. in parentheses

P(1) - C(1A)	1.750( 2)	C(1C) - C(2C)	1.373( 4)
P(1) - C(1B)	1.800( 3)	C(1C) - C(6C)	1.400( 3)
P(1) - C(1C)	1.807( 2)	C(2C) - C(3C)	1.388( 5)
P(1) - C(1D)	1.808( 3)	C(3C) - C(4C)	1.384( 5)
C(1A) - C(2A)	1.446( 3)	C(4C) - C(5C)	1.361( 5)
C(1A) - C(6A)	1.422( 3)	C(5C) - C(6C)	1.389( 5)
C(2A) - C(3A)	1.453( 3)	C(1D) - C(2D)	1.394( 3)
C(2A) - N(7A)	1.302( 3)	C(1D) - C(6D)	1.375( 4)
C(3A) - C(4A)	1.334( 4)	C(2D) - C(3D)	1.384( 4)
C(4A) - N(5A)	1.366( 3)	C(3D) - C(4D)	1.377( 4)
N(5A) - C(6A)	1.387( 3)	C(4D) - C(5D)	1.358( 5)
C(6A) - O(8A)	1.250( 3)	C(5D) - C(6D)	1.396( 4)
N(7A) - C(1E)	1.407( 3)	C(1E) - C(2E)	1.385( 5)
C(1B) - C(2B)	1.369( 4)	C(1E) - C(6E)	1.390( 4)
C(1B) - C(6B)	1.389( 4)	C(2E) - C(3E)	1.398( 6)
C(2B) - C(3B)	1.390( 6)	C(3E) - C(4E)	1.368( 6)
C(3B) - C(4B)	1.365( 7)	C(4E) - C(5E)	1.375( 6)
C(4B) - C(5B)	1.344( 6)	C(5E) - C(6E)	1.386( 5)
C(5B) - C(6B)	1.379( 5)		

Table 4. Interatomic distances (Å) for compound 17 with e.s.d. in parentheses

P(1) - C(1A)	1.767( 3)	C(1C) - C(2C)	1.382( 5)
P(1) - C(1B)	1.808( 4)	C(1C) - C(6C)	1.388( 5)
P(1) - C(1C)	1.809( 4)	C(2C) - C(3C)	1.409( 6)
P(1) - C(1D)	1.798( 3)	C(3C) - C(4C)	1.378( 7)
C(1A) - C(2A)	1.456( 5)	C(4C) - C(5C)	1.358( 8)
C(1A) - C(6A)	1.404( 4)	C(5C) - C(6C)	1.391( 6)
C(2A) - C(3A)	1.448( 4)	C(1D) - C(2D)	1.390( 5)
C(2A) - N(7A)	1.295( 4)	C(1D) - C(6D)	1.379( 4)
C(3A) - C(4A)	1.330( 5)	C(2D) - C(3D)	1.393( 5)
C(4A) - N(5A)	1.371( 5)	C(3D) - C(4D)	1.366( 6)
N(5A) - C(6A)	1.366( 4)	C(4D) - C(5D)	1.382( 7)
C(6A) - S(8A)	1.711( 4)	C(5D) - C(6D)	1.389( 5)
N(7A) - C(1E)	1.416( 4)	C(1E) - C(2E)	1.377( 6)
C(1B) - C(2B)	1.381( 5)	C(1E) - C(6E)	1:405( 6)
C(1B) - C(6B)	1.395( 4)	C(2E) - C(3E)	1.399( 7)
C(2B) - C(3B)	1.399( 6)	C(3E) - C(4E)	1.382( 8)
C(3B) - C(4B)	1.358( 8)	C(4E) - C(5E)	1.344( 9)
C(4B) - C(5B)	1.372( 7)	C(5E) - C(6E)	1.401( 7)
C(5B) - C(6B)	1.392( 6)		

#### Cycloadditions of Vinylidenephosphoranes 1 and 2 with Vinylheterocumulenes 3, 4 and 5. General procedure :

A solution of the vinylheterocumulene in benzene was added under nitrogen to an ice-cooled solution of the phosphorane in benzene. After stirring at room temperature for the time specified, the solvent was evaporated in vacuo and the residue crystallized. Starting amounts, reaction times, yields and spectral data of the obtained products are given below.

3-Triphenylphosphorano-2,4-pyridinedione (6) and 1-(N-Ethenylcarbamoyl)-3-triphenylphosphorano-2,4-pyridinedione (7)

From 1 (5 mmol) and 3 (10 mmol), 1h, yield 98%, m.p. 115-123 °C. Crystallization of 2g from methanol-ether afforded 6 (0.6 g), m.p. 293-294 °C, 7 (0.4 g), m.p. 123-126 °C and a mixture of 6 and 7 (0.9 g).

A solution of 7 (0.2 g) in decalin (6 ml) was heated to 170 °C for 1 h. The solvent was evaporated in vacuo and the residue was crystallized from chloroform-benzene-heptane, affording 0.13 g (80%) of 6, m.p. 293-294 °C.

Compound 6 :

For C<sub>23</sub>H<sub>18</sub>O<sub>2</sub>NP (371.38) calcd.: 74.39 %C, 4.89 %H, 3.77 %N, found: 74.53 %C, 5.05 %H, 3.52 %N. <sup>1</sup>H NMR (isopropanol, d<sub>8</sub>): 5.6 (dd, 1H, C<sub>5</sub>-H), 7.0 (d, 1H, C<sub>6</sub>-H), 7.5 (m, 15H, Ph-H); <sup>13</sup>C NMR (CDCl<sub>3</sub> + CD<sub>3</sub>OD): 181.7 (3.6 Hz, C<sub>4</sub>), 165.8 (11.4 Hz, C<sub>2</sub>),

Table 5. Bond angles ( $^{\circ}$ ) for compound 15 with e.s.d. in parentheses

C(1C) - P(1) - C(1D)	109.3(1)	C(1B) - C(6B) - C(5B)	120.8(3)
C(1B) - P(1) - C(1D)	108.9(1)	P(1) - C(1C) - C(6C)	118.9(2)
C(1B) - P(1) - C(1C)	101.1(1)	P(1) - C(1C) - C(2C)	121.5(1)
C(1A) - P(1) - C(1D)	112.1(1)	C(2C) - C(1C) - C(6C)	119.2(2)
C(1A) - P(1) - C(1C)	113.5(1)	C(1C) - C(2C) - C(3C)	120.6(2)
C(1A) - P(1) - C(1B)	111.3(1)	C(2C) - C(3C) - C(4C)	119.6(3)
P(1) - C(1A) - C(6A)	122.4(1)	C(3C) - C(4C) - C(5C)	120.5(3)
P(1) - C(1A) - C(2A)	114.4(1)	C(4C) - C(5C) - C(6C)	120.2(3)
C(2A) - C(1A) - C(6A)	122.2(1)	C(1C) - C(6C) - C(5C)	119.8(2)
C(1A) - C(2A) - N(7A)	118.4(1)	P(1) - C(1D) - C(6D)	122.8(2)
C(1A) - C(2A) - C(3A)	115.5(2)	P(1) - C(1D) - C(2D)	118.1(2)
C(3A) - C(2A) - N(7A)	126.1(2)	C(2D) - C(1D) - C(6D)	119.1(2)
C(2A) - C(3A) - C(4A)	119.7(2)	C(1D) - C(2D) - C(3D)	120.4(2)
C(3A) - C(4A) - N(5A)	123.2(2)	C(2D) - C(3D) - C(4D)	119.8(3)
C(4A) - N(5A) - C(6A)	122.5(2)	C(3D) - C(4D) - C(5D)	120.3(3)
C(1A) - C(6A) - N(5A)	115.6(2)	C(4D) - C(5D) - C(6D)	120.5(3)
N(5A) - C(6A) - O(8A)	117.7(2)	C(1D) - C(6D) - C(5D)	119.9(3)
C(1A) - C(6A) - O(8A)	126.7(1)	N(7A) - C(1E) - C(6E)	122.7(2)
C(2A) - N(7A) - C(1E)	120.2(2)	N(7A) - C(1E) - C(2E)	119.5(2)
P(1) - C(1B) - C(6B)	117.8(2)	C(2E) - C(1E) - C(6E)	117.7(2)
P(1) - C(1B) - C(2B)	123.5(2)	C(1E) - C(2E) - C(3E)	120.4(3)
C(2B) - C(1B) - C(6B)	118.4(2)	C(2E) - C(3E) - C(4E)	120.5(4)
C(1B) - C(2B) - C(3B)	119.9(4)	C(3E) - C(4E) - C(5E)	120.0(3)
C(2B) - C(3B) - C(4B)	120.6(4)	C(4E) - C(5E) - C(6E)	119.5(3)
C(3B) - C(4B) - C(5B)	120.1(4)	C(1E) - C(6E) - C(5E)	121.8(3)
C(4B) - C(5B) - C(6B)	120.2(3)		

Table 6. Bond angles ( $^{\circ}$ ) for compound 17 with e.s.d. in parentheses

C(1C) - P(1) - C(1D)	110.4(1)	C(1B) - C(6B) - C(5B)	118.5(3)
C(1B) - P(1) - C(1D)	109.0(1)	P(1) - C(1C) - C(6C)	117.5(2)
C(1B) - P(1) - C(1C)	100.6(1)	P(1) - C(1C) - C(2C)	121.9(2)
C(1A) - P(1) - C(1D)	109.8(1)	C(2C) - C(1C) - C(6C)	120.1(3)
C(1A) - P(1) - C(1C)	114.0(1)	C(1C) - C(2C) - C(3C)	119.1(3)
C(1A) - P(1) - C(1B)	112.7(1)	C(2C) - C(3C) - C(4C)	120.2(4)
P(1) - C(1A) - C(6A)	125.2(2)	C(3C) - C(4C) - C(5C)	120.0(4)
P(1) - C(1A) - C(2A)	112.6(2)	C(4C) - C(5C) - C(6C)	121.0(4)
C(2A) - C(1A) - C(6A)	121.0(3)	C(1C) - C(6C) - C(5C)	119.5(3)
C(1A) - C(2A) - N(7A)	117.0(3)	P(1) - C(1D) - C(6D)	122.8(2)
C(1A) - C(2A) - C(3A)	116.0(2)	P(1) - C(1D) - C(2D)	117.8(2)
C(3A) - C(2A) - N(7A)	126.9(3)	C(2D) - C(1D) - C(6D)	119.3(2)
C(2A) - C(3A) - C(4A)	119.5(3)	C(1D) - C(2D) - C(3D)	119.9(3)
C(3A) - C(4A) - N(5A)	122.4(3)	C(2D) - C(3D) - C(4D)	120.6(3)
C(4A) - N(5A) - C(6A)	123.1(3)	C(3D) - C(4D) - C(5D)	119.6(4)
C(1A) - C(6A) - N(5A)	116.5(3)	C(4D) - C(5D) - C(6D)	120.3(3)
N(5A) - C(6A) - S(8A)	116.0(2)	C(1D) - C(6D) - C(5D)	120.3(3)
C(1A) - C(6A) - S(8A)	127.4(2)	N(7A) - C(1E) - C(6E)	121.7(3)
C(2A) - N(7A) - C(1E)	120.0(3)	N(7A) - C(1E) - C(2E)	119.4(3)
P(1) - C(1B) - C(6B)	117.1(2)	C(2E) - C(1E) - C(6E)	118.8(3)
P(1) - C(1B) - C(2B)	122.2(2)	C(1E) - C(2E) - C(3E)	120.5(4)
C(2B) - C(1B) - C(6B)	120.6(3)	C(2E) - C(3E) - C(4E)	119.6(5)
C(1B) - C(2B) - C(3B)	119.1(4)	C(3E) - C(4E) - C(5E)	120.6(5)
C(2B) - C(3B) - C(4B)	120.6(4)	C(4E) - C(5E) - C(6E)	120.8(4)
C(3B) - C(4B) - C(5B)	120.4(4)	C(1E) - C(6E) - C(5E)	119.5(4)
C(4B) - C(5B) - C(6B)	120.8(4)		

139.3 ( $C_6$ ), 105.1 (7.4 Hz,  $C_5$ ), 82.2 (112.1 Hz,  $C_3$ ),  $Ph_3P$  carbons: 123.1 (93.4 Hz,  $C_{ipso}$ ), 133.8 (10.7 Hz,  $C_{ortho}$ ), 129.1 (12.9 Hz,  $C_{meta}$ ), 133.1 (2.7 Hz,  $C_{para}$ ); IR (KBr): 1607, 1533, 1480, 1426, 1386, 1100  $cm^{-1}$ ; mass (70 eV): 371 ( $M^+$ , 42), 370 (100), 301 (10), 293 (10), 183 (15).

Compound 7 :

For  $C_{26}H_{21}O_3N_2P$  (440.44), calcd.: 70.90 %C, 4.81 %H, 6.36 %N, found: 71.18 %C, 4.63 %H, 6.52 %N;  $^1H$  NMR ( $CDCl_3$ ): 4.5 (m, 2H, vinyl  $CH_2$ ), 5.8 (dd, 1H,  $C_5-H$ ), 6.8 (m, 1H, vinyl CH), 7.6 (m, 15H, Ph-H), 8.2 (d, 1H,  $C_6-H$ ), 11.6 (d, 1H, NH);  $^{13}C$  NMR ( $CDCl_3$ ): 182.0 (5.6 Hz,  $C_4$ ), 166.8 (10.4 Hz,  $C_2$ ), 150.8 (N-CO-N), 134.0 ( $C_6$ ), 128.9 (vinyl CH), 112.2 (9.4 Hz,  $C_5$ ), 97.5 (vinyl  $CH_2$ ), 79.4 (114.6 Hz,  $C_3$ ),  $Ph_3P$  carbons: 123.8 (93.9 Hz,  $C_1$ ), 133.6 (9.4 Hz,  $C_0$ ), 128.9 (11.3 Hz,  $C_m$ ), 132.7 ( $C_p$ ); IR ( $CHCl_3$ ): 3410, 1707, 1630, 1540, 1490, 1343, 1100  $cm^{-1}$ ; mass (70 eV):

identical with that of 6.

4-Oxo-3-triphenylphosphorano-2-pyridinethione (8)

Prepared from 1 (3.5 mmol) and 4 (3.5 mmol), 12 h, 94 % of compound 8, m.p. 322-324 °C (acetic acid). For  $C_{23}H_{18}ONSP$  (387.44) calcd.: 71.30 %C, 4.68 %H, 3.62 %N, found: 71.73 %C, 4.85 %H, 3.38 %N;  $^1H$  NMR (DMSO): 5.9 (dd, 1H,  $C_5$ -H), 7.9 (m, Ph-H), 10.9 (broad d, 1H, NH); IR (KBr): 1607, 1514, 1435, 1356, 1290, 1214, 1135, 1100  $cm^{-1}$ ; mass (70 eV): 387 ( $M^+$ , 100), 386 (66), 311 (10), 310 (49), 278 (21), 232 (12), 200 (10), 193 (10), 186 (25), 185 (12), 183 (30).

4-Oxo-5-phenyl-3-triphenylphosphorano-2-pyridinethione (9)

From 1 (3 mmol) and 5 (3 mmol), 12 h, 73 % of compound 9, m.p. 291-293 °C (chloroform-benzene-heptane). For  $C_{29}H_{22}ONSP$  (463.54) calcd.: 75.14 %C, 4.78 %H, 3.02 %N, found: 75.34 %C, 4.93 %H, 2.95 %N;  $^1H$  NMR (DMSO): 7.4 - 8.1 (m, Ph-H +  $C_6$ -H), 11.3 (broad s, NH); IR (KBr): 1613, 1506, 1480, 1433, 1273, 1257, 1100  $cm^{-1}$ ; mass (70 eV): 463 ( $M^+$ , 100), 462 (72), 387 (12), 386 (41), 384 (10), 355 (10), 354 (40), 262 (30), 231 (22), 183 (37).

4-Phenylimino-3-triphenylphosphorano-2-pyridone (15)

From 2 (1.6 mmol) and 3 (1.6 mmol), 16 h, 85 % of compound 15, m.p. 267-269 °C (ethanol). For  $C_{29}H_{23}ON_2P$  (446.49) calcd.: 78.01 %C, 5.19 %H, 6.27 %N, found: 78.34 %C, 5.02 %H, 6.03 %N;  $^1H$  NMR (DMSO): 5.5 (dd, 1H,  $C_5$ -H), 6.2 (broad d, 2H, Ph-H +  $C_6$ -H), 6.8 (m, 4H, Ph-H), 7.6 (m, Ph-H); IR (KBr): 1633, 1603, 1580, 1525, 1476, 1394, 1355, 1099  $cm^{-1}$ ; mass (70 eV): 446 ( $M^+$ , 68), 445 (100), 369 (21), 185 (12), 183 (18), 77 (11).

4-Phenylimino-3-triphenylphosphorano-2-pyridinethione (17) and 2-(N-Ethenyldithiocarbamoyl)-4-phenylimino-3-triphenylphosphoranyridine (18)

Prepared from 2 (1.3 mmol) and 4 (1.3 mmol), 1.5 h. The residue in benzene (5 ml) was rapidly heated to the boil and the undissolved material was filtered while hot. Yield 31 % of 17, m.p. 250-253 °C. On addition of heptane, the mother liquors deposited compound 18 (29 %), m.p. 127-130 °C.

Compound 17 :

$^1H$  NMR ( $CDCl_3$ ): 5.6 (dd, 1H,  $C_5$ -H), 5.9 (broad d, 2H, Ph-H +  $C_6$ -H), 6.85 (m, 4H, Ph-H), 7.3 - 8.0 (m, Ph-H);  $^{13}C$  NMR ( $CDCl_3$ ): 178.6 (18.8 Hz,  $C_2$ ), 156.3 (5.6 Hz,  $C_4$ ), 135.1 ( $C_6$ ), 102.4 (7.5 Hz,  $C_5$ ), 89.9 (125.8 Hz,  $C_3$ ),  $Ph_3P$  carbons: 126.1 (95.8 Hz,  $C_1$ ), 133.2 (9.4 Hz,  $C_0$ ), 128.4 (13.1 Hz,  $C_m$ ), 131.5 ( $C_p$ ), Ph-N carbons: 150.6 ( $C_1$ ), 121.1 ( $C_0$ ), 128.5 ( $C_m$ ), 121.2 ( $C_p$ ); IR ( $CHCl_3$ ): 3393, 1626, 1580, 1550, 1513, 1486, 1473  $cm^{-1}$ ; mass (70 eV): 462 ( $M^+$ , 73), 386 (25), 385 (100), 383 (10), 353 (10), 307 (12), 277 (43), 276 (24), 243 (10), 231 (27), 192 (10), 185 (13), 183 (30), 77 (16).

Compound 18 :

$^1H$  NMR ( $CDCl_3$ ): 4.5 (m, 2H, vinyl  $CH_2$ ), 6.4 (m, 1H, vinyl CH), 6.8 - 8.0 (m, Ph-H +  $C_5$ -H +  $C_6$ -H); IR ( $CHCl_3$ ): 3385, 1673, 1613, 1583, 1565, 1470, 1093  $cm^{-1}$ ; mass (70 eV): identical with the spectrum of 17.

Methylation of the prepared cycloadducts. General procedure :

A mixture of the triphenylphosphoranyridine, methyl iodide and methanol was stirred at room temperature for the time specified. Methanol and excess methyl iodide were evaporated in vacuo and the residue was crystallized. The amount of starting compounds and methanol, reaction time, yield and spectral data of the obtained products are given below.

3-(2-Methylthio-4-oxo)pyridyltriphenylphosphonium Iodide (10)

From 8 (2.5 mmol), methyl iodide (11.9 mmol) and methanol (8 ml), 16 h, 73 % of 10, m.p. 175-177 °C (methanol-ethyl acetate-hexane). For  $C_{24}H_{21}ONSPI$  (529.38) calcd.: 54.45 %C, 4.00 %H, 2.65 %N, found: 54.32 %C, 3.85 %H, 2.31 %N;  $^1H$  NMR

(CDCl<sub>3</sub>): 2.8 (s, 3H, CH<sub>3</sub>S-), 6.3 (dd, 1H, C<sub>5</sub>-H), 7.8 (m, Ph-H), 8.3 (d, 1H, C<sub>6</sub>-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 177.7 (3.4 Hz, C<sub>4</sub>), 161.6 (14.1 Hz, C<sub>2</sub>), 141.0 (C<sub>6</sub>), 115.9 (3.8 Hz, C<sub>5</sub>), 101.3 (110.8 Hz, C<sub>3</sub>), 18.8 (CH<sub>3</sub>S-), Ph<sub>3</sub>P carbons: 120.8 (93.9 Hz, C<sub>1</sub>), 133.7 (11.3 Hz, C<sub>0</sub>), 129.9 (13.1 Hz, C<sub>m</sub>), 134.3 (3.8 Hz, C<sub>p</sub>); IR (CHCl<sub>3</sub>): 1634, 1581, 1505, 1432, 1286, 1100 cm<sup>-1</sup>; mass (70 eV): identical with spectrum of 8; mass (DCI): 416 (23), 402 (M<sup>+</sup>-HI, 49), 388 (M<sup>+</sup>-CH<sub>3</sub>I, 100), 279 (14), 185 (10), 79 (47).

### 3-(2-Methylthio-4-oxo-5-phenyl)pyridyltriphenylphosphonium Iodide (11)

From 9 (1.4 mmol), methyl iodide (2.8 mmol), in methanol (5 ml), 4 h, 94 %, m.p. 275-278 °C (chloroform - heptane). For C<sub>30</sub>H<sub>25</sub>ONSPI (605.48) calcd.: 59.51 %C, 4.16 %H, 2.31 %N, found: 59.28 %C, 3.95 %H, 2.12 %N; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.8 (s, 3H, CH<sub>3</sub>S-), 7.5 (m, Ph-H), 8.5 (d, 1H, C<sub>6</sub>-H), 11.7 (broad d, 1H, NH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 176.5 (2.8 Hz, C<sub>4</sub>), 159.7 (15 Hz, C<sub>2</sub>), 138.6 (C<sub>6</sub>), 127.5 (5.6 Hz, C<sub>5</sub>), 101.7 (112.7 Hz, C<sub>3</sub>), 19.2 (CH<sub>3</sub>S-), Ph<sub>3</sub>P carbons: 121.4 (93.9 Hz, C<sub>1</sub>), 133.7 (9.4 Hz, C<sub>0</sub>), 129.7 (13.1 Hz, C<sub>m</sub>), 134.1 (C<sub>p</sub>), Ph-C<sub>5</sub> carbons: 134.2, 132.4, 128.3; IR (CHCl<sub>3</sub>): 1628, 1564, 1521, 1428, 1284, 1100 cm<sup>-1</sup>; mass (70 eV): identical with spectrum of 9.

### 3-(2-Hydroxy-1-methyl-4-phenylimino)pyridyltriphenylphosphonium Iodide (16)

From 15 (0.6 mmol), methyl iodide (2.8 mmol), in methanol (5 ml), 3 days, 77 % of compound 16, m.p. 310-312 °C (chloroform-benzene). For C<sub>30</sub>H<sub>26</sub>ON<sub>2</sub>PI (588.43) calcd.: 61.24 %C, 4.45 %H, 4.76 %N, found: 61.03 %C, 4.15 %H, 4.58 %N; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 3.4 (s, 3H, CH<sub>3</sub>N-), 6.1 (m, 2H, Ph-H + C<sub>5</sub>-H), 7.1 (m, 5H, Ph-H + C<sub>6</sub>-H), 7.6 - 8.2 (m, Ph-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 163.0 (7.5 Hz) and 161.2 (3.8 Hz), C<sub>2</sub> and C<sub>4</sub>, 146.4 (C<sub>6</sub>), 97.6 (9.4 Hz, C<sub>5</sub>), 79.7 (112.7 Hz, C<sub>3</sub>), 36.9 (CH<sub>3</sub>N-), Ph<sub>3</sub>P carbons: 120.7 (93.9 Hz, C<sub>1</sub>), 133.7 (9.4 Hz, C<sub>0</sub>), 130.5 (13.4 Hz, C<sub>m</sub>), 134.6 (C<sub>p</sub>), Ph-N carbons: 136.0 (C<sub>1</sub>), 124.5 (C<sub>0</sub>), 129.9 (C<sub>m</sub>), 127.2 (C<sub>p</sub>); IR (CHCl<sub>3</sub>): 3466, 1633, 1592, 1539, 1500, 1100 cm<sup>-1</sup>; mass (DCI): 462 (32), 461 (M<sup>+</sup>-HI, 100), 460 (68), 447 (M<sup>+</sup>-CH<sub>3</sub>I, 9), 305 (10), 277 (38), 276 (16), 185 (20).

### 3-(2-Methylthio-4-phenylimino)pyridyltriphenylphosphonium Iodide (19)

From 17 (0.6 mmol), methyl iodide (1.1 mmol) in methanol (5 ml), 1 h, 77 % of compound 19, m.p. 157-159 °C (ethyl acetate). For C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>SPI (604.49) calcd.: 59.61 %C, 4.34 %H, 4.63 %N, found: 59.35 %C, 4.12 %H, 4.28 %N; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.2 (s, 3H, CH<sub>3</sub>S-), 7.0 (m, Ph-H + C<sub>5</sub>-H), 7.5 - 8.1 (m, Ph-H), 8.25 (d, 1H, C<sub>6</sub>-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 167.7 (7.5 Hz, C<sub>2</sub>), 157.7 (5.6 Hz, C<sub>4</sub>), 152.7 (C<sub>6</sub>), 110.7 (6.4 Hz, C<sub>5</sub>), 96.6 (95.8 Hz, C<sub>3</sub>), 15.9 (CH<sub>3</sub>S-), Ph<sub>3</sub>P carbons: 120.2 (90.1 Hz, C<sub>1</sub>), 134.5 (11.3 Hz, C<sub>0</sub>), 130.4 (13.1 Hz, C<sub>m</sub>), 134.8 (C<sub>p</sub>), Ph-N carbons: 138.6 (C<sub>1</sub>), 121.8 (C<sub>0</sub>), 129.2 (C<sub>m</sub>), 125.0 (C<sub>p</sub>); IR (CHCl<sub>3</sub>): 3400, 1550, 1440, 1426, 1393, 1340, 1093 cm<sup>-1</sup>; mass (DCI): 479 (10), 478 (34), 477 (M<sup>+</sup>-HI, 100), 476 (73), 465 (14), 463 (M<sup>+</sup>-CH<sub>3</sub>I, 45), 462 (26), 461 (28), 399 (10), 385 (10), 294 (10), 293 (40), 292 (20), 279 (29), 277 (17), 262 (20), 217 (22), 215 (10), 201 (11), 200 (17), 185 (14), 143 (18), 142 (10), 123 (10).

### 3-(4-Oxo)pyridyltriphenylphosphonium Iodide (12)

A solution of 10 (0.8 g, 1.5 mmol) in ethanol (15 ml) was refluxed with Raney nickel (W-2, 3 g) under nitrogen for 5 h. The nickel was removed by filtration and the solvent was evaporated. Thin-layer chromatography on silica gel (eluent ethanol-ethyl acetate 1 : 1) followed by crystallization from benzene-hexane afforded 0.21 g (30 %) of 12, m.p. 280-282 °C.

For C<sub>23</sub>H<sub>19</sub>ONPI (483.29) calcd.: 57.16 %C, 3.96 %H, 2.90 %N, found: 56.94 %C, 3.74 %H, 2.71 %N; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.5 (dd, 1H, C<sub>5</sub>-H), 7.4 - 7.8 (m, Ph-H + C<sub>2</sub>-H), 8.1 (d, 1H, C<sub>6</sub>-H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 178.5 (3.8 Hz, C<sub>4</sub>), 155.3 (13.1 Hz, C<sub>2</sub>), 151.3 (C<sub>6</sub>), 119.0 (9.4 Hz, C<sub>5</sub>), 100.7 (95.8 Hz, C<sub>3</sub>), Ph<sub>3</sub>P carbons: 121.1 (92.0 Hz,

( $C_1$ ), 133.9 (11.3 Hz,  $C_O$ ), 129.5 (13.1 Hz,  $C_m$ ), 133.8 ( $C_p$ ); IR ( $CHCl_3$ ): 1585, 1513, 1472, 1433, 1106  $cm^{-1}$ ; mass (DCI): 384 (22), 357 (28), 356 ( $M^+ - HI, 100$ ), 355 (15).

### X - Ray Structure Analysis

Data collection :

Lattice parameters were determined from 30 and 28 ( $\Theta, X, \Phi$ )<sub>h,k,l</sub> reflections (for compound 15 and 17, respectively) collected on a Siemens AED single crystal diffractometer using a package of Data Collection control programs<sup>9</sup>. Single crystal specimens of about 0.4 x 0.6 x 0.5 mm and 0.3 x 0.4 x 0.6 mm were used. For compound 17 a total of 4575 reflections were collected at room temperature using Ni-filtered Cu -  $K_\alpha$  radiation in the  $\Theta - 2\Theta$  step-scanning mode operating in the range  $3^\circ \leq \Theta \leq 65^\circ$ . Symmetry dependent reflections (3372) with  $I \geq 3\sigma_{(I)}$ , ( $\sigma_{(I)}$  based on counting statistics) were retained as observed but 3237 symmetry independent reflections (internal R = 0.03) were used in the refinement. Data collection for compound 15 was performed in the range  $3^\circ \leq \Theta \leq 70^\circ$ , collecting 4831 reflections of which 3355 had  $I \geq 3\sigma_{(I)}$  and the 3229 symmetry independent reflections (internal R = 0.02) were used in the refinement. For both the structures the method described in ref. 10 was used to calculate the intensities I from profile analysis. One standard reflection was collected every 50  $I_{h,k,l}$  measurements to monitor crystal decomposition and instrumental linearity. The intensities were corrected for Lorenz and polarization effects. No corrections were made for absorption effects.

Crystal data for compound 15 :

Chemical formula:  $C_{29}H_{23}N_2OP$ ; formula weight: 446.5; crystal system and lattice parameters: monoclinic,  $a = 13.544(4) \text{ \AA}$ ,  $b = 10.743(3) \text{ \AA}$ ,  $c = 16.182(4) \text{ \AA}$ ,  $\beta = 99.79(4)^\circ$ ;  $U = 2320(9) \text{ \AA}^3$ ;  $Z = 4$ ;  $D = 1.266 \text{ g.cm}^{-3}$ ; space group:  $P2_1/c$  (from systematic absences); Cu -  $K_\alpha$  radiation  $\lambda = 1.5418 \text{ \AA}$ ;  $\mu$  (Cu- $K_\alpha$ ) =  $12.16 \text{ cm}^{-1}$ .

Crystal data for compound 17 :

Chemical formula:  $C_{29}H_{23}N_2SP$ ; formula weight: 462.5; crystal system and lattice parameters: monoclinic,  $a = 13.671(2) \text{ \AA}$ ,  $b = 10.891(3) \text{ \AA}$ ,  $c = 16.439(3) \text{ \AA}$ ,  $\beta = 97.33(3)^\circ$ ;  $U = 2427.6(9) \text{ \AA}^3$ ;  $Z = 4$ ;  $D = 1.266 \text{ g.cm}^{-3}$ ; space group:  $P2_1/c$  (from systematic absences); Cu -  $K_\alpha$  radiation  $\lambda = 1.5418 \text{ \AA}$ ;  $\mu$  (Cu- $K_\alpha$ ) =  $19.26 \text{ cm}^{-1}$ .

Structure solution and refinement :

The structures were solved and refined using the SHELX system of crystallographic computer programs<sup>11</sup>. Geometrical calculations were performed using a suitable program<sup>12</sup>. From direct methods, the analysis of the E-map computed with the most consistent set of signs revealed about 50% of the atoms. The structures were completed by some cycles of isotropic temperature factors and differences  $F_o - F_c$  Fourier maps. The atomic parameters were refined using anisotropic temperature factors with cycles of block matrix least squares calculations. The refinements were stopped at  $R = 0.043$ ,  $R_w = 0.043$  (unit weights) and  $R = 0.048$ ,  $R_w = 0.048$  (unit weights) for compounds 17 and 15, respectively. The maximum residual in the final  $\Delta F$  maps were 0.25 and 0.27  $e.\text{\AA}^{-3}$ , respectively. The plots of  $|\Delta F|$  as a function of the scattering angle, magnitude of F and Miller indexes reveal a linear trend.

All the calculations were performed on a Gould 32/77 computer at Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Parma.

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