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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### ORGANIC PHOSPHORUS COMPOUNDS 106.<sup>1</sup> A <sup>31</sup>P-NMR STUDY OF PHOSPHINOUS-, PHOSPHINIC-, AND THIOPHOSPHINIC AMIDES

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# ORGANIC PHOSPHORUS COMPOUNDS 106.<sup>1</sup> A <sup>31</sup>P-NMR STUDY OF PHOSPHINOUS-, PHOSPHINIC-, AND THIOPHOSPHINIC AMIDES

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*(Received April 16, 1996)*

Dedicated in friendship to Professor John G. Verkade  
 on the occasion of his 60th birthday

The synthesis, physical, chemical and spectroscopic properties of eight different types of phosphinous-, phosphinic- and thiophosphinic amides are reported. It is shown that the <sup>31</sup>P-chem. shifts of tertiary amides are at lower magnetic field than that of secondary amides. As an exception, in the bis(tertiary butyl) series this trend is reversed.

**Key words:** Phosphinous amides, phosphinic amides, thiophosphinic amides, sterically hindered amides, <sup>31</sup>P-chem. shifts.

## INTRODUCTION

Although several phosphinous-, phosphinic- and thiophosphinic amides have been prepared and their <sup>1</sup>H and <sup>31</sup>P-chemical shifts reported in the literature,<sup>2,3</sup> no systematic study has been made. It seemed of interest to prepare several different classes of compounds including sterically hindered ones and to determine their <sup>31</sup>P-chemical shifts. It was hoped to derive at some generalizations and forecasts concerning the <sup>31</sup>P-chemical shifts of phosphorus amides.

## RESULTS AND DISCUSSION

We have prepared eight different classes of phosphorus amide compounds and measured their <sup>1</sup>H and <sup>31</sup>P-chemical shifts. Since the different types of compounds could not be prepared by the same procedure, we shall discuss each class separately below.

### 1. Derivatives of Chloromethyl-Phenylphosphinic Acid, 1

The amides of this acid were readily prepared by the interaction of the phosphinic chloride<sup>4</sup> with amines in an inert organic solvent.

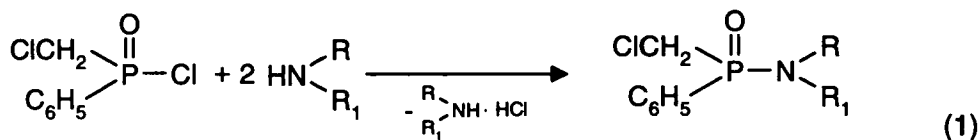

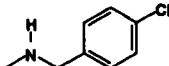
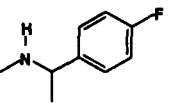
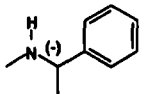
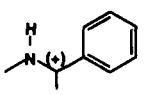
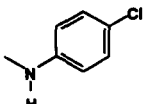
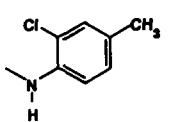
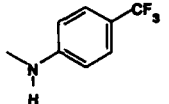
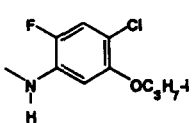

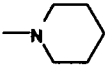
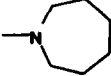
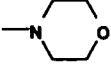
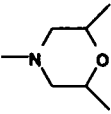
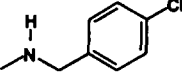
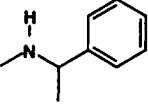
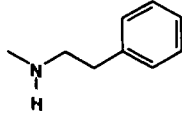
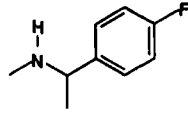
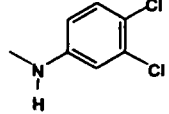


TABLE I  
Physical and spectroscopic properties of phenyl-  
chloromethylphosphinic amides

$\begin{array}{c} \text{ClCH}_2 \\   \\ \text{C}_6\text{H}_5 \\   \\ \text{P} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{X} \end{array} \end{array}$			
X	yield in %	m.p. °C	<sup>31</sup> P
-N(C <sub>3</sub> H <sub>7</sub> -n) <sub>2</sub>	50.0	oil	31.48
-N(C <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	65.0	oil	31.53
-NHC <sub>4</sub> H <sub>9</sub> -t	43.0	oil	22.44
-NHC <sub>6</sub> H <sub>13</sub> -n	52.0	oil	26.39
-NHCH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	53.0	oil	27.10
-NHCH(CH <sub>3</sub> )CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	34.0	82	25.86
	53.0	oil	26.41
	52.0	oil	27.18
	58.8	101-104	25.4 <sup>a</sup> 25.1
	47.0	A 155-160 <sup>a</sup> B 78-80 <sup>a</sup>	25.51 25.39
	58.8	A 164 <sup>a</sup> B 78 <sup>a</sup>	25.52 25.50
	32.2	192	21.31
	49.0	resin	22.39
	37	85	22.41
	32	solid	22.37

a) stereoisomers; diastereomer A and B

TABLE IIa  
Physical and spectroscopic properties of diphenylphosphinous  
amides

$\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{P}-\text{X} \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array}$			
X	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> P
$-\text{N}(\text{C}_2\text{H}_5)_2$	82.9	117-122/0.04	61.56
$-\text{N}(\text{C}_3\text{H}_7-n)_2$	52.8	121-126/0.02	62.1
$-\text{N}(\text{C}_4\text{H}_9-n)_2$	72.3	139-142/0.06	62.17
	70.3	131-136/0.08	47.33
	36.7	133-139/0.04	62.81
	85.6	(59-65)	64.46
	89.7	(77-79)	62.92
	34.9	131-138/0.01	63.45 61.54
	67.5	165/0.08	42.96
	21.6	220-230/0.1	36.36
	21.6	180-183/0.08	41.45
	99.0	oil	36.32
	100.0	oil	29.85

The physical properties together with the  $^{31}\text{P}$ -chem. shifts of the prepared compounds are listed in Table I.

## 2. Derivatives of Diphenylphosphinic Acid, 2

The amides of this acid were readily obtained by the interaction of the corresponding chlorides with amines in an inert organic solvent.<sup>2,4</sup>

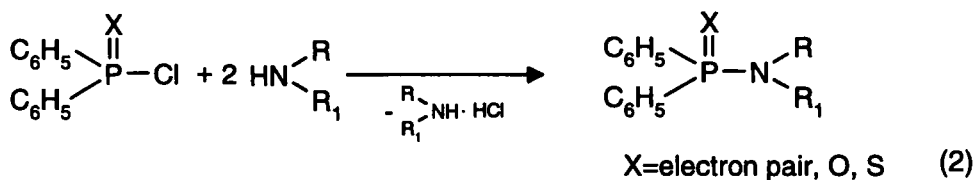


TABLE IIb  
Physical and spectroscopic properties of diphenylphosphinic amides



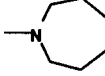
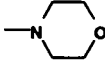
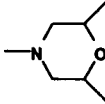
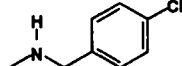
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{P}=\text{O} \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array} - \text{X}$			
X	yield in %	m.p. °C	$^{31}\text{P}$
$-\text{N}(\text{C}_2\text{H}_5)_2$	31.1	133-137	30.73
$-\text{N}(\text{C}_3\text{H}_7-n)_2$			30.77
$-\text{N}(\text{C}_4\text{H}_9-n)_2$	78.9	oil	30.65
$-\text{N}(\text{C}_5\text{H}_{11}-n)_2$	57.8	oil	30.58
$-\text{N}(\text{C}_6\text{H}_{13}-n)_2$	33.8	oil	30.62
	65.5	81-87	25.54
	58.9	107-110	29.18
			30.73
	66.9	resin	29.19
			28.89
			24.43

TABLE IIb (Continued)

	25.5	158-162	22.80
	67.2	136-139	23.89
-NHC <sub>6</sub> H <sub>13</sub> - <sup>n</sup>	84.5	68-71	23.75
-NHCH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	62.8	93-96	23.81
-NHCH(CH <sub>3</sub> )CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	54.0	82-85	22.88
	36.7	127-128	23.27
	70.2	157-159	22.68
	52.5	200-201	22.83
	81.0	249-254	20.57
	38.0	244-246	20.61

The physical properties together with the <sup>31</sup>P-chem. shifts of the prepared compounds are listed in Tables IIa, IIb and IIc.

### 3. Derivatives of *tert*.-butyl-phenylphosphinic Acid, **3**

The amides of this acid were also readily prepared by the interaction of the corresponding chlorides<sup>4</sup> with amines in an inert organic solvent.

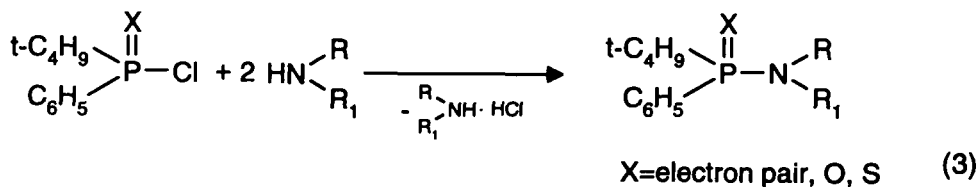


TABLE IIc  
Physical and spectroscopic properties of diphenylthiophosphinic  
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
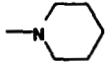
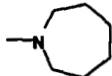
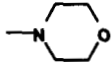
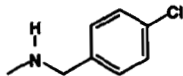
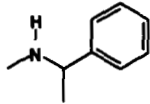
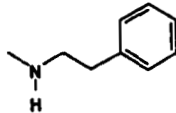
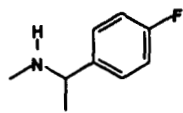
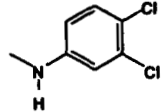
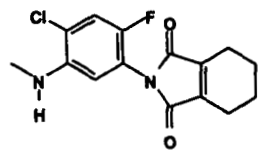

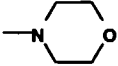
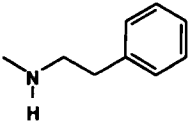
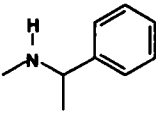
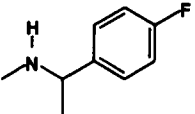
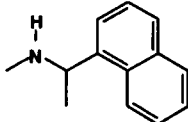
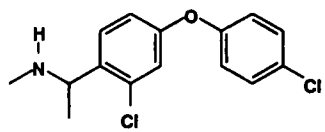
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \text{P}(=\text{S})-\text{X}$			
X	yield in %	m.p. °C	<sup>31</sup> P
-M(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	65.7	73-75	68.74
-M(C <sub>3</sub> H <sub>7</sub> -n) <sub>2</sub>			68.96
-M(C <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	83.0	oil	69.06
	63.8	107	65.35
	48.5	98-99	67.83
	74.5	79-85	70.62
	41.7	96-102	67.92
	78.4	95-103	60.46
	62.3	71-73	58.95
	50.4	100-101	59.63
	82.2	113-114	59.0
	82.0	168-175	53.49
	41.0	213-215	53.87

TABLE IIIa  
Physical and spectroscopic properties of *t*-butyl-phenylphosphinous amides

$\begin{array}{c} \text{t-Bu} \\ \diagup \\ \text{C}_6\text{H}_5 - \text{P} - \text{X} \end{array}$			
X	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> P
-Cl	85.1	114-119/15	107.9
-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	85.3	78-82/0.5	81.47
-N(C <sub>3</sub> H <sub>7</sub> - <i>n</i> ) <sub>2</sub>	69.5	105-108/0.04	81.56
-N(C <sub>4</sub> H <sub>9</sub> - <i>n</i> ) <sub>2</sub>	57.4	107-112/0.04	81.8
-N(C <sub>6</sub> H <sub>13</sub> - <i>n</i> ) <sub>2</sub>	83.0	160/0.04	81.77
	82.0	135-140/0.1	65.18
	100	oil	83.12
-NHC <sub>6</sub> H <sub>13</sub> - <i>n</i>	86.7	180/0.04	53.14
	99.3	oil	53.31
	82.7	170/0.08	48.45; 47.37 <sup>a</sup>
	71.6	170-175/0.08	48.17; 47.56 <sup>a</sup>
	99.0	oil	48.54; 47.86 <sup>a</sup>
	93.0	oil	48.0; 47.50 <sup>a</sup>

a) diastereoisomers



The physical properties together with the  $^{31}\text{P}$ -chem. shifts of the prepared compounds are listed in Tables IIIa, IIIb and IIIc.

#### 4. Derivatives of *tert*.-pentyl-phenylphosphinic Acid, 4

The phosphinic chloride was obtained by a Kinnear-Perren reaction as shown<sup>5</sup>:

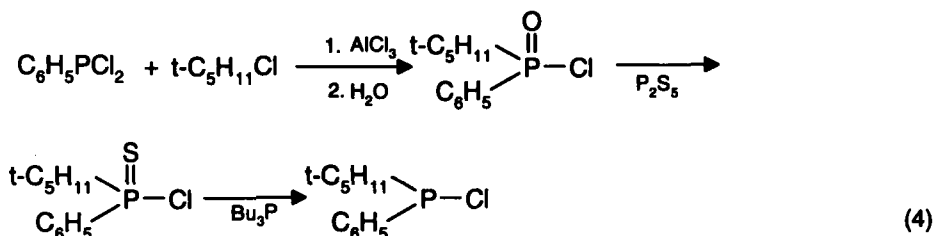


TABLE IIIb  
Physical and spectroscopic properties of *t*-butyl-phenylphosphinic amides


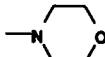
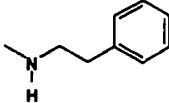
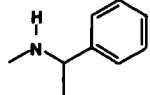
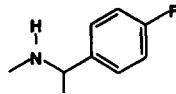
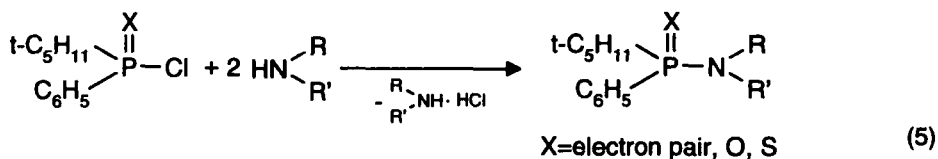
$\begin{array}{c} t\text{-Bu} \\ \diagup \\ \text{C}_6\text{H}_5 \end{array} \text{P}(=\text{O})\text{X}$			
X	yield in %	b.p. °C/torr (m.p.)	$^{31}\text{P}$
-Cl	75.0	105-107/0.03	71.5
-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	54.3	oil	46.68
-N(C <sub>3</sub> H <sub>7</sub> -n) <sub>2</sub>	59.7	oil	46.37
-N(C <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	67.1	oil	46.42
-N(C <sub>6</sub> H <sub>13</sub> -n) <sub>2</sub>	54.1	oil	46.02
	39.8	oil	44.24
	24.3	(71-78)	45.26
-NHC <sub>6</sub> H <sub>13</sub> -n	68.7	resin	42.53
			42.8
	70.5	(124-135) °	42.33:40.60
	65.3 <sup>a</sup>	A(208) B(145-152)	42.29 40.77

TABLE IIIb (Continued)

	37.0	(166-169) <sup>a</sup>	42.52;40.81
	60.8 <sup>a</sup>	A(119-123) B(158-161)	41.98 40.5
	58.7	(133-137) <sup>a</sup>	42.5;41.0 <sup>b</sup>
	57.1	(148-150) <sup>a</sup>	42.22;40.49
	53.9	A(150-152) B(152-154)	42.06 40.44
	58.8 <sup>a</sup>	A(157-160) B(108-119)	42.04 40.59
	62.1 <sup>a</sup>	A(89-93) B(184-185)	42.11 40.31
	44.0	(161-173) <sup>a</sup>	41.6;40.36

The phosphinic chloride gave on sulfurization with  $P_2S_5$  the thiophosphinic chloride which when treated with tributylphosphine<sup>6</sup> produced the phosphinous chloride. Treatment of these chlorides with amines afforded the amides.



The physical properties together with the <sup>31</sup>P-chem shifts of the prepared compounds are listed in Tables IVa, IVb and IVc.

TABLE IIIb (Continued)

$\begin{array}{c} \text{t-Bu} \\ \diagup \\ \text{C}_6\text{H}_5 \\ \diagdown \\ \text{P} \\ \diagup \\ \text{O} \\ \diagdown \\ \text{X} \end{array}$			
X	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> P
	26.9	(212-214) °C	42.54°
	47.9	(107-108) °C	42.1; 41.87
	64.0	(154-156) °C	42.5; 40.9
	85.4	(178-185)	39.76

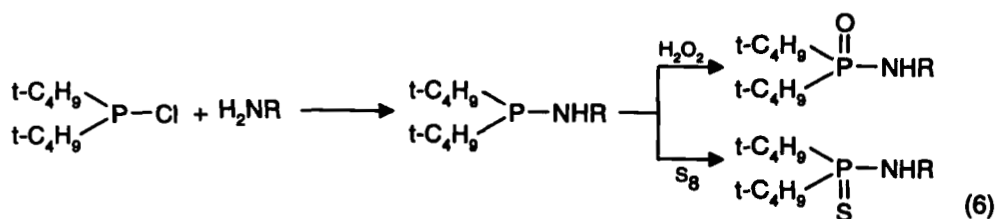
a) stereoisomeric mixture (diastereoisomers)

b) oxidation with air; when oxidised with H<sub>2</sub>O<sub>2</sub> only one signal at 40.81 was observed (only one stereoisomer)

c) only one diastereoisomer formed

### 5. Derivatives of bis-(*tert*.-butyl)Phosphinic Acid, 5

Since it is known from the literature that bis-(*tert*.-butyl)phosphinic- and thiophosphinic chlorides do not react with amines, these compounds were obtained by oxidation or sulfurization of bis-(*tert*.-butyl)phosphinous amides.<sup>7,8</sup> The latter were prepared by the interaction of bis-(*tert*.-butyl)phosphinous chloride<sup>4</sup> and amines in an inert organic solvent.



The physical properties together with the <sup>31</sup>P-chem shifts of the prepared compounds are listed in Tables Va, Vb and Vc.

TABLE IIIc  
Physical and spectroscopic properties of *t*-butyl-phenylthiophosphinic amides

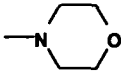
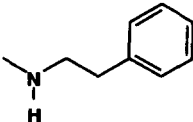
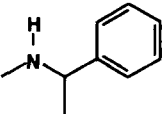
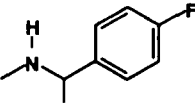
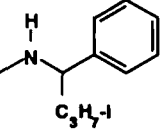
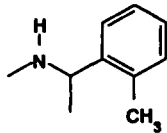
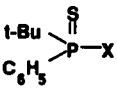
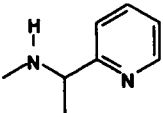
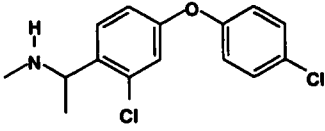
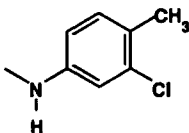
$\begin{array}{c} \text{S} \\ \parallel \\ \text{t-Bu} \text{---} \text{P} \text{---} \text{X} \\   \\ \text{C}_6\text{H}_5 \end{array}$			
X	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> P
-Cl	85.4	100-104/0.04 (71-73)	114.9
-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	94.6	160/0.08 (76-77)	90.0
-N(C <sub>3</sub> H <sub>7</sub> - <i>n</i> ) <sub>2</sub>	70.7	oil	90.27
-N(C <sub>4</sub> H <sub>9</sub> - <i>n</i> ) <sub>2</sub>	86.2	180/0.1	90.4
-N(C <sub>6</sub> H <sub>13</sub> - <i>n</i> ) <sub>2</sub>	64.0	oil	90.36
	44.1	(123-125)	88.89
-NHC <sub>6</sub> H <sub>13</sub> - <i>n</i>	80.8	(65-67)	80.66
	66.2	(64-66)	80.61
	47.2	(81-84) <sup>a</sup>	80.87; 78.09
	53.7	(79-81) <sup>a</sup>	80.86; 78.29
	55.1	(123-125) <sup>a</sup>	81.0; 80.0
	54.2 <sup>a</sup>	A (204-207) B (87-99)	81.68 78.0

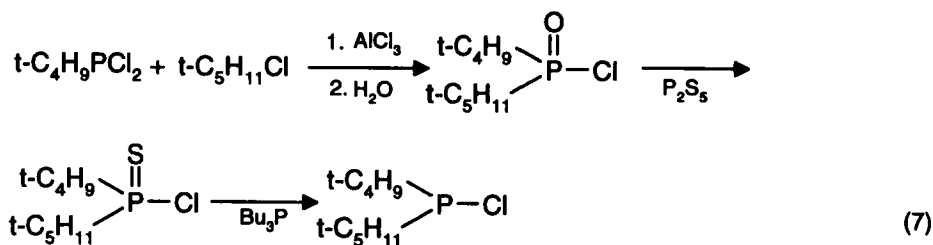
TABLE IIIc (Continued)

X		yield in %	b.p. °C/torr (m.p.)	31P
		40.9	oil <sup>a</sup>	78.87;78.55
		62.0	(138-140) <sup>a</sup>	81.1;78.7
		76.9	(179-184)	73.08

a) stereoisomeric mixture (diastereoisomers)

6. Derivatives of *tert*.-butyl-*tert*.-pentylphosphinic Acid, 6

The phosphinic chloride was obtained by a Kinnear-Perren reaction as shown<sup>5</sup>:



This phosphinic chloride was then sulfurized and reduced to the phosphinous chloride.<sup>6</sup> Treatment of this chloride with amines gave the phosphinous amides which on oxidation or sulfurization produced *t*-butyl-*t*-pentylphosphinic- and -thiophosphinic amides, respectively.

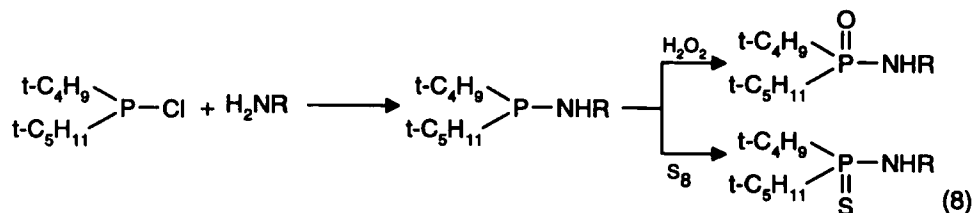
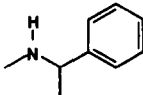
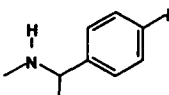
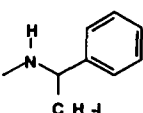
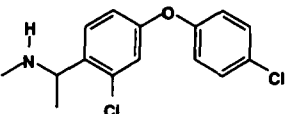


TABLE IVa  
Physical and spectroscopic properties of *t*-pentyl-phenylphosphinous amides

$\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{t-Pentyl} \text{---} \text{P} \text{---} \text{X} \end{array}$			
X	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> P
Cl	62.0	74-77/0.02	108.3
-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	64.7	78/0.01	81.2
-N(C <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	100	oil(crude)	81.1
-N(C <sub>6</sub> H <sub>13</sub> -n) <sub>2</sub>	100	oil(crude)	81.5
-N(C <sub>8</sub> H <sub>17</sub> -n) <sub>2</sub>	100	oil(crude)	81.7
	100	oil(crude) <sup>a</sup>	46.96;46.0
	100	oil(crude) <sup>a</sup>	46.9;46.1
	63.0	140/0.05 <sup>a</sup>	47.1;46.1
	95.0	oil <sup>f</sup>	46.48;46.08

a) stereoisomeric mixture (diastereoisomers)

The physical properties together with the <sup>31</sup>P-chem. shifts of the prepared compounds are listed in Tables VIa and VIb.

#### 7. Derivatives of 1-hydroxy-2,2,3,4,4-pentamethylphosphetane-1-oxide, 7

1-Chloro-2,2,3,4,4-pentamethylphosphetane-1-oxide was obtained in the reaction of 2,2,4-trimethylpentene-2 with PCl<sub>3</sub> and AlCl<sub>3</sub> as described.<sup>9</sup>

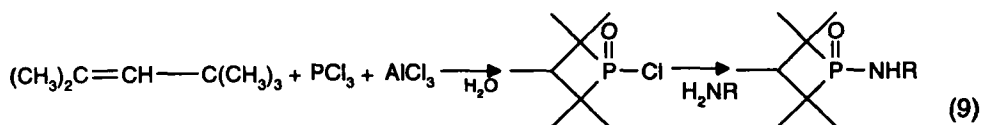
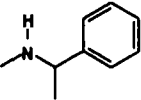
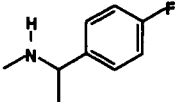
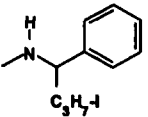
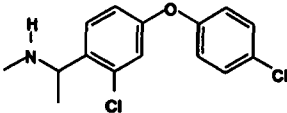
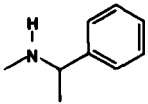
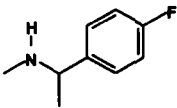
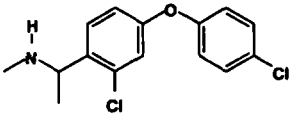


TABLE IVb  
Physical and spectroscopic properties of *t*-pentyl-phenylphosphinic-amides

$\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{P}=\text{O} \\ \diagdown \\ \text{t-Pentyl} \end{array} \text{---X}$			
X	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> P
Cl	97.0	oil	72.33
-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	60.0	oil	46.97
-N(C <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	45.0	oil	47.15
-N(C <sub>6</sub> H <sub>13</sub> -n) <sub>2</sub>	36.0	oil	46.45
-N(C <sub>8</sub> H <sub>17</sub> -n) <sub>2</sub>	36.0	oil	46.45
-NHC <sub>6</sub> H <sub>13</sub> -n	58.0	oil	42.90
	54.0	(125-130) <sup>a</sup>	42.41;40.69
	71.0	(118-120) <sup>a</sup>	43.05;41.50
	71.0 <sup>a</sup>	A (118-124) B (151-153)	42.75 41.11
	47.0 <sup>a</sup>	A (166-168) B (150-154)	43.00 41.34

<sup>a</sup>) stereoisomeric mixture (diastereoisomers)

TABLE IVc  
Physical and spectroscopic properties of *t*-pentyl-phenylthiophosphinic amides

$\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{P} \begin{array}{c} \text{S} \\ \parallel \\ \text{X} \end{array} \\ \diagdown \\ \text{t-Pentyl} \end{array}$			
X	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> p
Cl	81.0	oil	116.8
-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	85.0	oil	91.91
-N(C <sub>4</sub> H <sub>9</sub> - <i>n</i> ) <sub>2</sub>	32.0	oil	92.37
-N(C <sub>6</sub> H <sub>13</sub> - <i>n</i> ) <sub>2</sub>	53.5	oil	92.25
-N(C <sub>8</sub> H <sub>17</sub> - <i>n</i> ) <sub>2</sub>	56.7	oil	92.23
	38.0	(75-79) °	84.23;81.34
	68.5	(158-162) °	82.65;79.97
	59.0	(115-119) °	82.72;80.06

a) stereoisomeric mixture (diastereoisomers)

Some of the phosphinic amides were obtained directly by the reaction of the phosphinic chloride with amines in a bomb tube.<sup>10</sup> However, most of the amides could only be prepared by reaction of the phosphinous chloride (or phosphinous amide) with amines followed by oxidation or sulfurization, respectively.

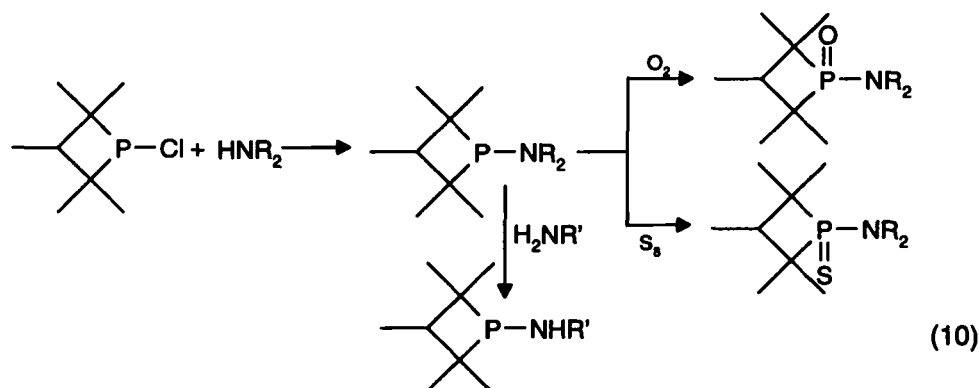
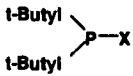
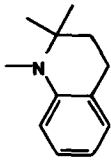
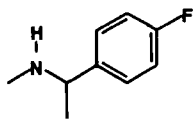
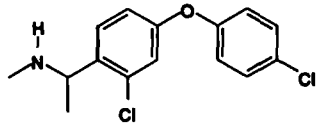
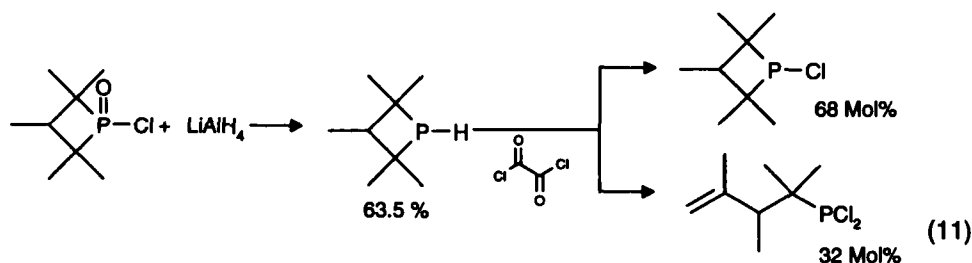




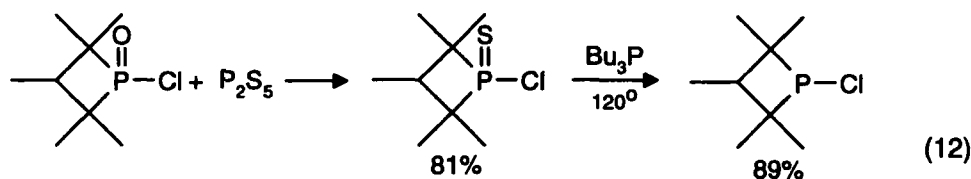
TABLE Va  
Physical and spectroscopic properties of di-*t*-butylphosphinous amides

X			b.p. °C/torr	<sup>31</sup> P
	yield			
	99.0		oil	67.0
	100		oil(crude)	72.35
	89.5		oil	74.66

Whereas chlorination of pentamethylphosphetane caused partial ring cleavage,<sup>11</sup> (Equation 11) the phosphinous chloride was obtained



in high yield by reduction of the corresponding thiophosphinic chloride with tributylphosphine.<sup>6</sup>



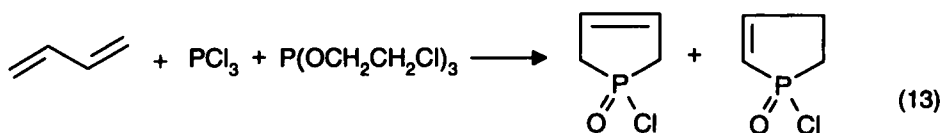
The physical properties together with the <sup>31</sup>P-chem shifts of the prepared compounds are listed in Tables VIIa, VIIb and VIIc.

TABLE Vb  
Physical and spectroscopic properties of di-*t*-butylphosphinic amides

$\begin{array}{c} \text{t-Butyl} \\ \diagup \\ \text{P}=\text{O} \\ \diagdown \\ \text{t-Butyl} \end{array} \text{---X}$		yield	b.p. °C/torr	<sup>31</sup> P
X				
		32.0	(159-163)	53.8
		37.5	(106-208)	55.79
		15.0	(145-149)	55.27
		27.5	(175-178)	55.47

### 8. Derivatives of 1-hydroxyphospholene-1-oxide, 8

The synthesis of 1-chlorophospholene-1-oxide was carried out as described in the literature.<sup>12,13</sup>



With the conditions we used only the 1-chloro-3-phospholene-1-oxide was formed. The phosphinic chloride reacted directly with amines in inert organic solvents to give the corresponding amides.

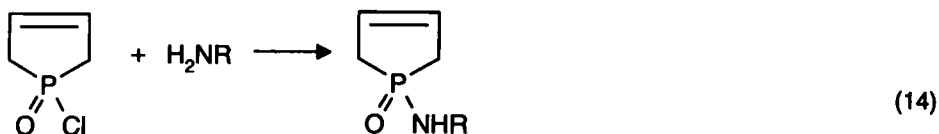


TABLE Vc  
Physical and spectroscopic properties of di-*t*-butylthiophosphinic amides

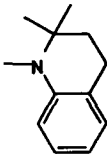
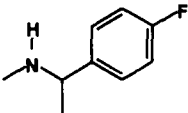
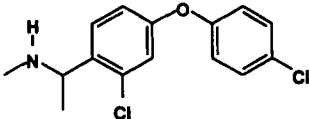
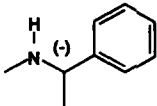
$\begin{array}{c} \text{t-Butyl} \\ \text{t-Butyl} \end{array} \begin{array}{c} \text{S} \\ \parallel \\ \text{P}-\text{X} \end{array}$		yield	m.p.	<sup>31</sup> P
X				
		60.0	135-138	95.29
		30.6	126-128	96.54
		24.5	129-131	97.18


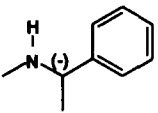
TABLE VIa  
Physical and spectroscopic properties of *t*-butyl-*t*-pentylphosphinous amides

$\begin{array}{c} \text{t-Butyl} \\ \text{t-Pentyl} \end{array} \begin{array}{c} \text{P}-\text{X} \end{array}$		yield	b.p. °C/torr	<sup>31</sup> P
X				
Cl		47.0	77-78/0.08 <sup>b</sup>	147.63;146.85
		100	oil <sup>a</sup>	66.14;64.88

<sup>a</sup>) stereoisomeric mixture (diastereoisomers)

<sup>b</sup>) cis/trans

TABLE VIb  
Physical and spectroscopic properties of *t*-butyl-*t*-pentylphosphinic amides

			
X	yield	b.p. °C/torr (m.p.)	<sup>31</sup> P
Cl	40.0	90/0.08 <sup>b</sup>	95.75;94.92
	26.5	(148-152) <sup>a</sup>	55.7;55.1

a) stereoisomeric mixture (diastereoisomers)

b) *cis/trans*

The physical properties together with the <sup>31</sup>P-chem shifts of the prepared compounds are listed in Table VIII.

### <sup>31</sup>P-CHEMICAL SHIFTS

From the <sup>31</sup>P-chem. shifts range of the various compound types given in Table IX the following conclusion can be drawn:

In all compounds except the bis-(*tert.*-butyl) series the <sup>31</sup>P-chem. shifts of the tertiary amides are at lower field than that of secondary amides which are lower than that of secondary aryl amides. Remarkably the <sup>31</sup>P-chem. shifts of the pyrrolidino amides of the compounds given in the Tables IIa, IIb, IIc, IIIa and IIIb are at higher field than all the other tertiary amides. In the bis-(*tert.*-butyl) series the <sup>31</sup>P-chem shifts of the tertiary amides given in Tables Va, Vb and Vc are at higher field than that of the secondary amides. The secondary aryl amides are not available yet.

### BIOLOGICAL ACTIVITY

Several of the hindered phosphinic- and thiophosphinic amides show herbicidal and insecticidal activity. A report describing these activities is in preparation.<sup>15</sup>

### EXPERIMENTAL

Phosphorus NMR-spectra were recorded using a Bruker WP 80 spectrometer at 32.28 MHz (ref. 85% H<sub>3</sub>PO<sub>4</sub>), and <sup>1</sup>H-NMR spectra were recorded with a Varian EM 360 spectrometer at 60 MHz or a Bruker WM 250/250 MHz spectrometer (ref. (CH<sub>3</sub>)<sub>4</sub>Si). The chemical shifts are reported in ppm, with negative

values being upfield of the standard, and positive downfield. All reactions were run under an atmosphere of argon.

**Preparation of Starting Materials.**  $(C_6H_5)_2PCl$ ,  $(C_6H_5)_2P(O)Cl$ ,  $(C_6H_5)_2P(S)Cl$ ,  $ClCH_2(C_6H_5)P(O)Cl$ ,  $ClCH_2(C_6H_5)P(S)Cl$  and 1-chloro-2,2,3,4,4-pentamethylphosphetan-1-oxide were prepared according to literature methods.<sup>4</sup>  $ClCH_2(C_6H_5)PCl$ , *t*-Bu-PhPCl, *t*-pentyl-phenylPCl, *t*-butyl-*t*-pentylPCl and 1-chloro-2,2,3,4,4-penta methylphosphetan were obtained from the corresponding thiophosphinic chlorides by reduction with tributylphosphine.<sup>6</sup> In contrast to a report<sup>11</sup> in which the 1-chloro-2,2,3,4,4-pentamethylphosphetan was obtained from the corresponding secondary phosphine with chlorine which also effected partial ring cleavage, no such cleavage was observed when the thiophosphinic chloride was reduced with tributylphosphine.

**1-Chloro-2,2,3,4,4-pentamethylphosphetan-1-sulfide, 1**

A mixture of 48.66 g (0.25 mol) of 1-chloro-2,2,3,4,4-pentamethylphosphetan-1-oxide<sup>9</sup> and 13.34 g of  $P_2S_5$  (20% excess) was stirred at 170–180°C for 15 h. Then the crude reaction product was vacuum distilled to give 43.1 g of 1, b.p. 160–163°C/50 torr; it solidified on standing. Lit.<sup>11</sup> m.p. 118–120°C (trans).

TABLE VIIa  
Physical and spectroscopic properties of 1-amino-2,2,3,4,4-pentamethylphosphetan

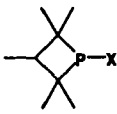
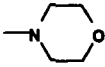
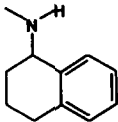
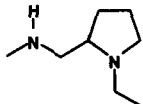
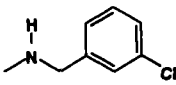
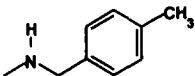
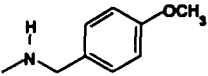
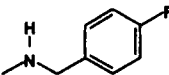
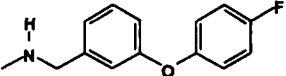
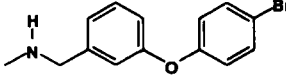
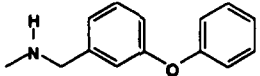
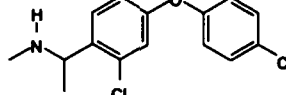
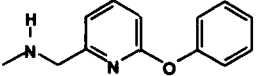
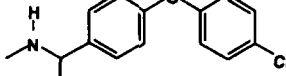
			
X	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> P
-N(CH <sub>3</sub> ) <sub>2</sub>			127.5;99.8 trans ; cis
-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	72.3	112-115/14	92.76;77.55
-N(C <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	92.8	oil	128.4;97.2
-N(C <sub>4</sub> H <sub>9</sub> -i) <sub>2</sub>	90.0	oil	130.9;94.5
	95.3	oil	128.0;97.2
-NHC <sub>8</sub> H <sub>17</sub> -n	85.5	oil	75.4
	79.6	oil	94.31;73.99
	90.5	oil	95.1;76.29
	57.6	93/0.04	78.22;66.1

TABLE VIIa (Continued)

	64.5	96/0.04	77.8;65.2
	60.5	102/0.04	77.4;62.3
	68.1	95/0.04	77.8;65.7
	70.2	oil	78.45
	71.3	oil	98.1;78.5
	95.0	oil(crude)	97.9;78.4
	98.5	oil	91.3;70.06
	98.0	oil	97.75;78.26
	97.5	oil	90.72;70.39

<sup>31</sup>P-NMR (in CDCl<sub>3</sub>)δ: 134.2 and 130.19 (ratio trans: cis = 2:1); impurity 124.2; Lit.<sup>11</sup> 137.

<sup>1</sup>H-NMR (in CDCl<sub>3</sub>)δ: 0.97 (dd, *J* 7, 3H); 1.35 (d, *J* 24, 6H); 1.4 (d, *J* 21, 6H); 2.3 (m, 1H) (main isomer); 1.0 (dd, 3H); 1.4 (d, 6H); 1.45 (d, 6H); 2.15 (m, 1H) (minor isomer).

#### 1-Chloro-2,2,3,4,4-pentamethylphosphetane, 2

A mixture of 31.61 g (0.15 mol) of 1 and 39.2 ml of tributylphosphine (6% excess) is stirred for 3 h at 170–180°C and then fractionated to give 23.9 g (89.2%) of 2, a clear liquid, b.p. 87–90°C/20 torr (Lit.<sup>11</sup> 87°C/20 torr).

<sup>1</sup>H-NMR (in CDCl<sub>3</sub>)δ: 0.75 (d, *J* 7, 3H); 1.2 (d, *J* 21, 6H); 1.1 (d, *J* 9, 6H); 2.77 (q, *J* 7, 1H); the minor isomer showed its presence through shoulders on the doublets at 1.1 and 1.2 (ratio main isomer:minor isomer ~3:1).

<sup>31</sup>P-NMR (in CDCl<sub>3</sub>)δ: 169.51 and 149.35 (~3:1); impurity at 129.3.

#### 1-Diethylamino-2,2,3,4,4-pentamethylphosphetane, 3

A mixture of 269 g (1.5 mol) of 2 and 343 ml of diethylamine (10% excess) in 1000 ml of toluene is

refluxed for 16 h, then the yellow suspension is filtered and the filtrate fractionally distilled to give 233.5 g (72.3%) of **3**, a clear liquid, b.p. 112–115°C/14 torr.

<sup>1</sup>H-NMR (in CDCl<sub>3</sub>)δ: 0.7–1.7 (m, 22H); 3.1 (2q, NCH<sub>2</sub>, 4H).

<sup>31</sup>P-NMR (in CDCl<sub>3</sub>)δ: 92.76 and 77.55 (ratio 5:1).

*1-Diethylamino-2,2,3,4,4-pentamethylphosphetane-1-oxide, 4*

On letting **3** stand at room temperature in an open flask it is oxidized quantitatively to the oxide **4**.

<sup>31</sup>P (in CDCl<sub>3</sub>)δ: 57.47 (Lit.<sup>10</sup> 56.23).

*1-Diethylamino-2,2,3,4,4-pentamethylphosphetane-1-sulfide, 5*

To a stirred solution of 5.38 g (0.025 mol) of **3** in 25 ml of toluene is added with stirring at 20°C 0.8 g of sulfur. An exothermic reaction ensues. Stirring is continued for 1 h at 20°C, then the solvent evaporated and the residue kugelrohr distilled. There is obtained 4.2 g (68%) of **5**, a colorless oil, b.p. 160°C/0.06 torr.

TABLE VIIb  
Physical and spectroscopic properties of 1-amino-2,2,3,4,4-pentamethylphosphetan-1-oxide

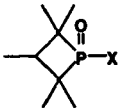

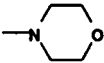
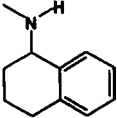
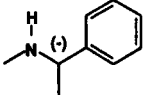
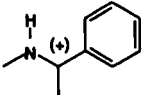
X			
	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> P
-N(CH <sub>3</sub> ) <sub>2</sub>	21.6	(90-92)	53.4
-N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	86.0	(155-157)	56.23
-N(C <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	80.0	oil	57.0
-N(C <sub>4</sub> H <sub>9</sub> -i) <sub>2</sub>	39.8	oil	53.7
	46.1	(81-83)	56.88;55.74
	13.6	(73-77)	56.9;55.2
-NHC <sub>8</sub> H <sub>17</sub> -n	47.0	oil	51.47;50.19
	31.2	(198-200)	51.4;51.03
	38.7	(147-149)	51.25;50.79
	37.2		51.2;50.8

TABLE VIIb (Continued)

	65.9	(158-159)	51.47
	18.7	(111-120)	52.28;51.02
			50.5
			50.4
			52.1;50.85
	82.0	(92-95)	52.1;50.89
	15.5	(112-114)	52.4;51.08
	28.7	(105-107)	52.0;50.8
	74.0	(138-141)	50.97;50.52

<sup>1</sup>H-NMR (in CDCl<sub>3</sub>)δ: 0.65–2.0 (m, 22H); 2.8 (2q, NCH<sub>2</sub>, 4H).

<sup>31</sup>P-NMR (in CDCl<sub>3</sub>)δ: 104.98 and 96.95 (ratio 5:1).

C<sub>12</sub>H<sub>26</sub>NPS (247.38) calc.: C 58.3, H 10.6, N 5.7, S 13.0, P 12.5%; found: C 57.5, H 10.4, N 5.4, S 13.1, P 12.7%.

#### 1-Phenylamino-2,2,3,4,4-pentamethylphosphetane, 6

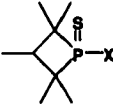
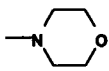
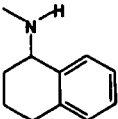
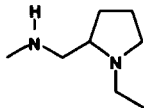
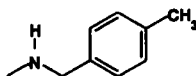
A mixture of 2.15 g (0.01 mol) of 3 and 0.91 ml of aniline is stirred and heated to 150°C for 0.5 h. Then the volatile material is distilled off and the residue kugelrohr distilled. There is obtained 1.7 g (72.3%) of 6, a yellow oil, b.p. 150°C/0.06 torr.

<sup>1</sup>H-NMR (in CDCl<sub>3</sub>)δ: 0.8 (d, *J* 7, 3H); 1.03 (d, *J* 8, 6H); 1.13 (d, *J* 17, 6H); 1.9 (2q, *J* 7 and 2, 1H); 4.27 (br.d, *J* 8, NH); 6.5–7.3 (m, 5H).

<sup>31</sup>P-NMR (in CDCl<sub>3</sub>)δ: 56.59 and 49.44 (ratio 6:1).



TABLE VIIc  
Physical and spectroscopic properties of 1-amino-2,2,3,4,4-pentamethylphosphetan-1-sulphide

			
X	yield in %	m.p. °C <sup>a</sup>	<sup>31</sup> P
-N(CH <sub>3</sub> ) <sub>2</sub>	87.8	90-92	113.27;108.44
-N(C <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	81.0	oil	105.0
-N(C <sub>4</sub> H <sub>9</sub> -i) <sub>2</sub>	76.7	oil	108.2;105.55
	45.5	54-56	106.2;101.8
-NHC <sub>8</sub> H <sub>17</sub> -n	83.0	48-50	95.25;91.49
	75.4	122-124	94.67;89.75
	32.0	156-157	96.0;93.0
	54.2	75-77	95.9;92.3

*Tert.-butyl-phenylthiophosphinic chloride, 7*

A mixture of 54.16 g (0.25 mol) of *t*-butyl-phenylphosphinic chloride (obtained according to Kinnear-Perren from PhPCl<sub>2</sub>, *t*-BuCl and AlCl<sub>3</sub>)<sup>3</sup> and 13.34 g (20% excess) of P<sub>2</sub>S<sub>5</sub> is stirred and heated to 160°C for 5 h. Fractional distillation yields 49.7 g of **7**, b.p. 100–104°C/0.04 torr; it solidifies of standing, m.p. 71–73°C (lit.<sup>14</sup> m.p. 69–70°C).

<sup>1</sup>H-NMR (in CDCl<sub>3</sub>)δ: 1.3 (d, *J* 20, 9H); 7.4–8.3 (m, 5H).

<sup>31</sup>P-NMR (in CDCl<sub>3</sub>)δ: 114.91.

C<sub>10</sub>H<sub>14</sub>ClPS (232.71) calc.: C 51.61, H 6.07, Cl 15.24, S 13.78, P 13.31%; found: C 51.3, H 6.0, Cl 15.5, S 13.9, P 13.4%.

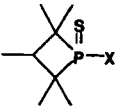
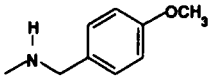
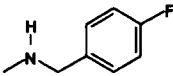
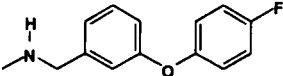
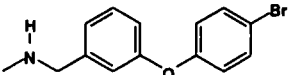
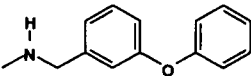
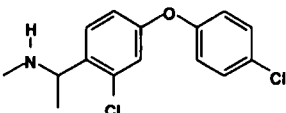
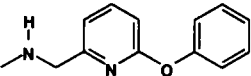
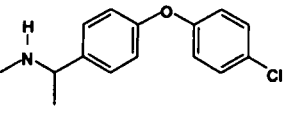
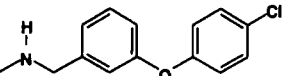
*Tert.-butyl-phenylchlorophosphine, 8*

A mixture of 93.1 g (0.4 mol) of **7** and 105 ml of tributylphosphine (5% excess) is heated with stirring to 180°C for 3 h. Fractional distillation yields 68.3 g (85.1%) of **8**, a clear liquid, b.p. 114–119°C/15 torr.

<sup>1</sup>H-NMR (in CDCl<sub>3</sub>)δ: 1.02 (d, *J* 14, 9H); 7.3–7.8 (M, 5H).

<sup>31</sup>P-NMR (in CDCl<sub>3</sub>)δ: 107.87.

TABLE VIIc (Continued)

			
X	yield in %	m.p. °C <sup>a</sup>	<sup>31</sup> P
	57.9	75-78	95.79;92.45
	51.2	99-103	96.29;92.45
	77.2	94-97	96.37;92.57
	57.0	87-90	96.44;92.6
	83.2	oil	96.3;92.5
	86.0	oil	95.32;90.53
	22.1	oil	94.91;91.98
	57.5	oil	94.85;89.93
	52.6	cis/trans 85-87 cis 96-98 trans 71-73	96.4;92.6 96.4 92.6

a) cis/trans mixture

TABLE VIII  
Physical and spectroscopic properties of 1-oxo-phospholene-amides

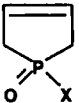
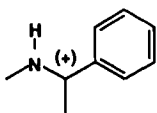
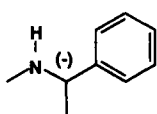
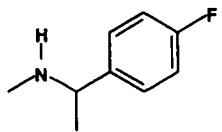
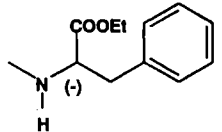
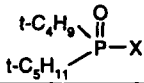
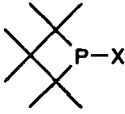
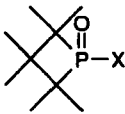
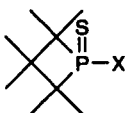

			
X	yield in %	b.p. °C/torr (m.p.)	<sup>31</sup> P
-N(C <sub>3</sub> H <sub>7</sub> -n) <sub>2</sub>	43.5	140/0.08	65.42
-N(C <sub>4</sub> H <sub>9</sub> -n) <sub>2</sub>	73.0	95/0.1 (59-63)	65.60
-NHC <sub>6</sub> H <sub>13</sub> -n	45.9	160/0.1 (solid)	63.35
-NHCH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	55.6	oil	63.81
-NHCH(CH <sub>3</sub> )CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	74.4	resin	62.21
	75.8	(57-60)	61.35
	75.8	(51-54)	61.89
	64.5	(72-73)	61.43
	54.4	(85-87)	63.38

TABLE IX

Range of the <sup>31</sup>P-chem-shifts of the various compound types given in Tables I to VIII

From Table	compound	X	range of <sup>31</sup> P-chem shifts
I		NR <sub>2</sub> NHR NHAryl	~31.5 25.1 to 27.1 (t-Bu 22.4) 21.3 to 22.4
IIa		NR <sub>2</sub> NHR NHAryl	61.5 - 64.4 (pyrrolidyl 47.33) 36.3 - 42.9 29.85
IIb		NR <sub>2</sub> NHR NHAryl	28.89 - 30.77 (pyrrolidyl 25.54) 22.68 - 24.43 20.6
IIc		NR <sub>2</sub> NHR NHAryl	67.83 - 70.62 (pyrrolidyl 65.35) 58.95 - 60.46 -53.6
IIIa		NR <sub>2</sub> NHR	81.47 - 83.12 (pyrrolidyl 65.18) 47.37 - 53.31
IIIb		NR <sub>2</sub> NHR NHAryl	45.26 - 46.68 (pyrrolidyl 44.24) 40.31 - 42.8 39.76
IIIc		NR <sub>2</sub> NHR NHAryl	88.89 - 90.4 78 - 81.68 73.08
IVa		NR <sub>2</sub> NHR	81.1 - 81.7 46.0 - 47.1
IVb		NR <sub>2</sub> NHR	46.45 - 47.15 40.69 - 43.05
IVc		NR <sub>2</sub> NHR	91.91 - 92.37 79.17 - 84.23
Va		NR <sub>2</sub> NHR	67 72.35 - 74.66
Vb		NR <sub>2</sub> NHR	53.8 55.27 - 55.79
Vc		NR <sub>2</sub> NHR	95.29 96.54 - 97.18
VIa		NHR	64.88 - 66.14

TABLE IX (Continued)

From Table	compound	X	range of $^{31}\text{P}$ -chem shifts
VIb		NHR	55.1 - 55.7
VIIa		NR <sub>2</sub> NHR NHAr <sub>yl</sub>	130.9 - 77.5 98.17 - 75.4 57.6
VIIb		NR <sub>2</sub> NHR NHAr <sub>yl</sub>	56.9 - 53.4 52.6 - 50.4 48.48 - 44.73
VIIc		NR <sub>2</sub> NHR NHAr <sub>yl</sub>	113.2 - 101.8 96.44 - 89.75 89.24 - 86.0
VIII		NR <sub>2</sub> NHR	65.5 63.38 - 61.35

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## REFERENCES

1. Part 105: L. Maier and P. J. Diel, *Phosphorus, Sulfur and Silicon*, **107**, 245 (1995).
2. L. A. Hamilton and P. S. Landis, in "Organic Phosphorus Compounds," G. M. Kosolapoff and L. Maier, eds., John Wiley & Sons, New York, N.Y., Vol. 4, p. 463, 1972; P. C. Crofts, *ibid.*, Vol. 6, p. 1, 1973.
3. R. S. Edmundson, in "CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data," J. C. Tebb, ed., CRC Press, Boca Raton, Chap. 12, p. 349, 1991; Y. Leroux, R. Burgada, St. G. Kleemann and E. Fluck, *ibid.*, Chap. 5, p. 93.
4. M. Field and R. Schmutzler in "Organic Phosphorus Compounds," G. M. Kosolapoff and L. Maier, eds., John Wiley & Sons, New York, N.Y., Vol. 4, pp. 75-255, 1972.
5. R. J. Brooks and C. A. Bunton, *J. Org. Chem.*, **40**, 2059 (1975).
6. H. E. Ulmer, L. C. D. Groenweghe and L. Maier, *J. Inorg. Nucl. Chem.*, **20**, 82 (1961).
7. W. Kuchen, D. Langsch and W. Peters, *Phosphorus, Sulfur and Silicon*, **54**, 55 (1990).
8. A. Brück, W. Kuchen and W. Peters, *Phosphorus, Sulfur and Silicon*, **107**, 129 (1995).
9. E. Jungermann, J. J. McBride Jr., R. Chutter and A. Mais, *J. Org. Chem.*, **27**, 606 (1962); *ibid.*, **27**, 1823 (1962).
10. J. Emsley and J. K. Williams, *J. Chem. Soc., Dalton*, 1576 (1973).
11. J. R. Corfield, R. K. Oram, D. J. H. Smith and S. Trippett, *J. Chem. Soc., Perkin I*, 713 (1972); *Chem. Commun.*, 1350 (1970).
12. K. Hunger, K. Hasseroth and F. Korte, *Tetrahedron*, **20**, 1593 (1964).
13. K. Moedritzer, *Syn. React. Inorg. Metal-Org. Chem.*, **5**, 45 (1975).
14. R. Luckenbach and H. H. Bechtolsheimer, *Z. Naturforsch.*, **32b**, 584 (1977).
15. L. Maier, publication in preparation.