Aminoamidines
6*. 4-Oxo- and 4-imino-1,3,2-diazaphospholanes and 4-imino-1,3,2-diazaphosphorinanes

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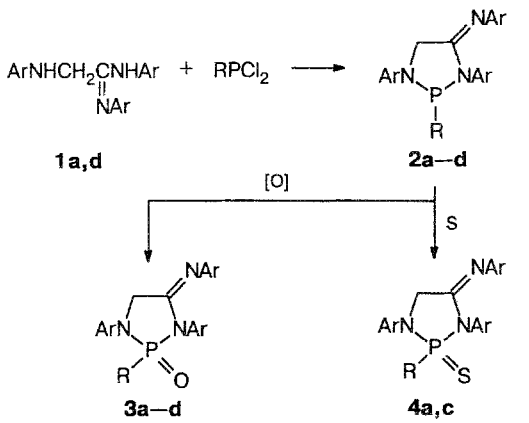
Reactions of *N*-aryl- and *N*-methyl-amidines and -amides of α-amino acids with $RPCl_2$ afford 4-aryl(methyl)imino and 4-oxo-1,3,2-diazaphospholanes. 4-Phenylimino-1,3,2-diazaphosphorinane was obtained in a similar way by the interaction of *N*(1),*N*(2)-diphenyl-β-anilinoisobutyramidine with $PhPCl_2$.

Key words: α-aminoamidine, β-aminoamidine, α-aminoamide, phosphorylation, synthesis, 1,3,2-diazaphospholane, 1,3,2-diazaphosphorinane.

The chemical behavior and synthetic potential of aminoamidines (AMAN) have not yet been properly and systematically studied. These compounds are the least known amino acid derivatives. The interaction of α- and β-AMAN with carbon electrophiles has been shown to be a convenient method for preparation of a number of five- to seven-membered diaza-heterocycles.[1–6] Reactions of AMAN with organoelement electrophiles have not yet been carried out. In this work we describe the preparation of phosphorus-containing heterocycles based on *N*,*N*(1),*N*(2)-triarylsubstituted α- and β-AMAN and some α-aminoamides (AMAD).

It is known that amidines with N—H bonds react readily with P^{III} acid chlorides or amides;[7,8] phosphorylation with dialkylphosphochloridates also proceeds effectively.[9] Triarylsubstituted α-AMAN[10] and β-AMAN[1] are smoothly acylated at the amino group.

However, reactions of *N*,*N*(1),*N*(2)-triarylglycinamidines (**1**) with of P^{III} acid monochlorides were found even at −30 °C to afford an unseparable mixture of unidentified products, though there was no appreciable interaction between α-AMAN **1** and $(Et_2N)_3P$ at 120—150 °C. Mono- and dichlorides of P^{IV} acids react ambiguously with AMAN and with substantial resinification. It turns out that the reactions of AMAN **1** with $RPCl_2$ proceed unexpectedly smoothly, and 1,3,2-diazaphospholanes (DAP) (**2**) are formed irrespective of the order of mixing the reagents. DAP **2a,c** were isolated in an analytically pure state, while **2b,d** ($\delta^{31}P$ (CH_2Cl_2) 96 and 124, respectively) were transformed into P^{IV} derivatives without purification. Like diamides of P^{III} acids, DAP **2** are readily oxidized with DMSO or atmospheric oxygen and add sulfur.



a: Ar = R = Ph; **b**: Ar = *p*-MeC_6H_4, R = Ph; **c**: Ar = Ph, R = EtO; **d**: Ar = Ph, R = Et.

Note that reactions of AMAN **1a** with $EtOP(O)Cl_2$ and $EtP(O)Cl_2$ yield DAP **3c,d** among other products, as indicated by their ^{31}P NMR spectra, but these reactions have no preparative value. Thus, it is reasonable to prepare 1,3-diaryl-4-arylimino-2-R-2-oxo(thioxo)-1,3,2-DAP via P^{III} derivatives **2**.

4-Oxo-derivatives of DAP **3,4** are valuable intermediates in the preparation of peptides.[11,12] This peptide synthesis, as reported previously,[11] consists of the interaction of α-AMAD with P^{IV} acid dichlorides at

* For communication 5 see ref. 1.

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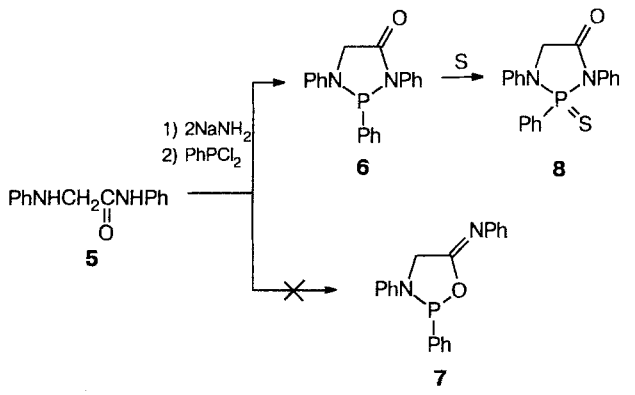
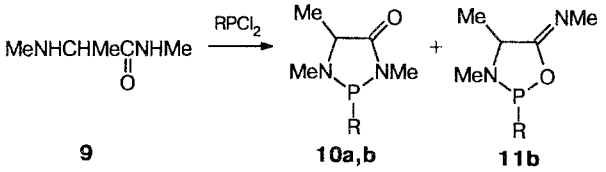
80—100 °C. The drastic reaction conditions result in considerable resinification and low yields of the target products. For this reason, taking into account the results obtained in phosphorylation of α-AMAN, attempts to synthesize 4-oxo-DAP with P^{IV} from amino acid amides and derivatives of P^{III} acids were considered worthwhile.

Note that phosphorylation of carboxamides usually occurs at the oxygen atom with the formation of Wilsmeier—Haack complexes[13,14] or the products of further transformations of O-derivatives.[15,16] Interaction of $(Et_2N)_3P$ with α-mercaptoacetanilide, however, leads to 4-oxo-1,3,2-thiazaphospholane.[17]

It turns out that the *N*-phenylglycine anilide (**5**) practically does not react with $(Et_2N)_3P$ at 120—160 °C, however, it interacts readily with PCl_3 in the presence of Et_3N even at 0 °C. As shown by ^{31}P NMR spectroscopy, the reaction results in a mixture of P^{IV} derivatives, with hydrogen phosphoryl compounds with δ 44.1 (J_{PH} = 598 Hz) and 34.6 (J_{PH} = 635 Hz), which are not DAP, as the predominant components of the mixture. $PhPCl_2$ reacts much less vigorously than PCl_3, though the reaction gives ~90 % 4-oxo-1,2,3-triphenyl-1,3,2-DAP (**6**) (δ 102) after 5—6 days at 20 °C, as indicated by ^{31}P NMR spectra. The formation of DAP **6** occurs much faster and equally unambiguously following prior dimetalation of AMAD **5** with $NaNH_2$. Isomeric oxazaphospholane (**7**) was in no case detected in the reaction mixtures by ^{31}P NMR. DAP **6** adds sulfur readily to form (**8**).



N-Methyl-*DL*-α-alanine methylamide (**9**) is much more reactive towards derivatives of P^{III} acids than *N*-aryl-substituted AMAD **5** and AMAN **1**. AMAD **9** reacts with PCl_3 in the presence of Et_3N at −30 °C to form 2-chloro-DAP (**10a**) as the only product, judging by ^{31}P NMR spectra. Partial decomposition of **10a** occurs upon vacuum distillation, which substantially decreases its yield. In the presence of the less electrophilic $EtOPCl_2$, in addition to *N,N*-disubstitution yielding DAP (**10b**) (~50 %, δP 110), *N,O*-cyclophosphorylation occurs to give oxazaphospholane (**11b**) (~50 %, δP 115). The isomers **10b** and **11b** could not be separated by vacuum distillation.



Chloride **10a** reacts with such a weak nucleophile as $(Me_3Si)_2NNa$ even at −40 °C. Though the reaction was carried out in the absence of oxygen, the ^{31}P NMR spectra of the reaction mixture exhibited only P^{IV} signals. Intermediate formation of DAP (**12**) and (**13**) was detected by mass-spectrometry (*m/z* 321[M+] and 249[M+], respectively). 2-Amino-2-oxo-DAP (**14**) (δ_P (CH_2Cl_2) 19, *m/z* 177[M+]) was isolated after hydrolysis of the reaction mixture by atmospheric moisture. The fact that no DAP containing P^{III} could be detected in the reaction mixture after the addition of $(Me_3Si)_2NNa$, may indicate that a strong oxidant is generated in the mixture *in situ*. It is known that P^{III} derivatives are easily oxidized by various oxygen-containing compounds, especially those having an X—O⁻ fragment.[18]

We assume that chloride **10a** can react with $(Me_3Si)_2NNa$ by two main routes: nucleophilic substitution at P^{III} leads to triamidophosphite **15**, whereas dehydrochlorination with abstraction of a proton from C(5) of the DAP affords an unstable mesoion of the type **16**. Triamidophosphite **15** is oxidized through the action of the intermediate **16** into amidophosphate **12**, which can be detected by ^{31}P NMR spectroscopy and mass-spectrometry. The hydrolysis of bis(trimethylsilyl)amidophosphate **12** yields the final product **14**.

Taking into account the above, notice that

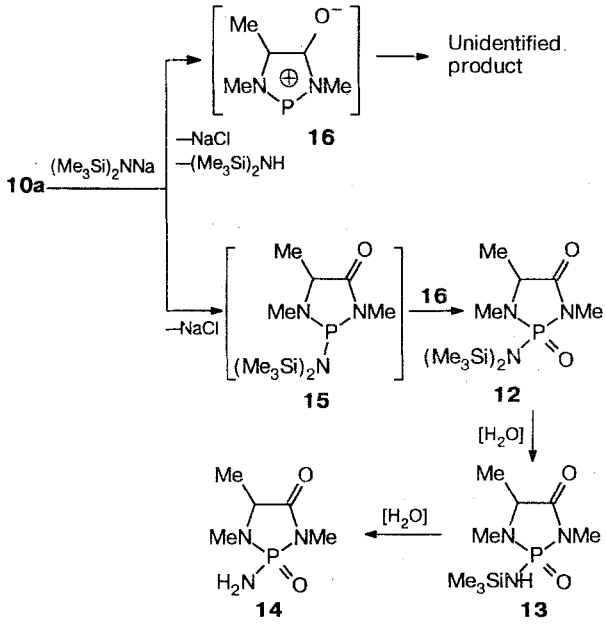


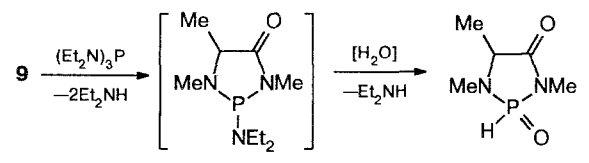
Table 1. Characteristics of the synthesized compounds

Compound	Yield (%)	M.p./°C (solvent)	Molecular formula	Found / Calculated (%)			
				C	H	N	P
2a	72	79—81 (benzene)	$C_{26}H_{22}N_3P$	79.90	5.31	10.31	8.04
				76.60	5.40	10.31	7.60
2c	96	[a]	$C_{22}H_{22}N_3OP$	70.94	6.14	11.44	8.60
				70.42	5.86	11.19	8.25
3a	53	175—177 (benzene)	$C_{26}H_{22}N_3OP$	73.61	5.22	9.64	7.42
				73.70	5.19	9.92	7.31
3b	56	176—178 (methanol)	$C_{29}H_{28}N_3OP$	74.86	6.50	9.16	6.70
				74.79	6.01	9.02	6.65
3c	50	193—195 (benzene—hexane)	$C_{22}H_{22}N_3O_2P$	67.30	6.09	10.99	7.74
				67.50	5.62	11.23	7.92
3d	27	124—126 (benzene—hexane)	$C_{22}H_{22}N_3OP$			11.54	8.12
						11.20	8.27
4a	66	217—218 (acetone)	$C_{26}H_{22}N_3PS$	[b]		9.34	7.03
						9.56	7.05
4c	55	197.5—199 (ethanol—benzene)	$C_{22}H_{22}N_3OPS$	[c]		10.45	7.84
						10.31	7.60
6	95	[a]	$C_{20}H_{17}N_2OP$	72.66	5.51	7.98	8.96
				72.28	5.12	8.45	9.33
8	61	208—209 (benzene)	$C_{20}H_{17}N_2OPS$	[d]		7.87	8.67
						7.69	8.51
10a	41	[e]	$C_5H_{10}ClN_2OP$	[e]		15.14	16.86
						15.51	17.17
14	26	187—188 (CH_2Cl_2—hexane)	$C_5H_{12}N_3O_2P$			23.42	17.30
						23.73	17.51
17	32	[f]	$C_5H_{11}N_2O_2P$	36.86	6.66	17.61	19.16
				37.04	6.79	17.28	19.13
20	93	62—65	$C_{28}H_{26}N_3P$	77.25	6.36	9.23	7.11
				77.24	5.98	9.65	7.13
21	79	209.5—210 (methanol—acetone)[g]	$C_{28}H_{26}N_3PS$	71.96	5.60	8.80	6.50
				71.95	5.57	8.99	6.64

[a] Viscous oil [b] Found (%): S, 7.44. Calculated (%): S, 7.29. [c] Found (%): S, 8.14. Calculated (%): S, 7.87. [d] Found (%): S, 9.08. Calculated (%): S, 8.80. [e] B.p. 82—83 °C / 0.65 Torr, n_D^{20} 1.5036. [f] B.p. 122 °C / 0.03 Torr. [g] Found (%): S, 7.15. Calculated (%): S, 6.85.

triamidophosphites (acyclic analogs of **15**) are generally oxidized by atmospheric oxygen with difficulty, while neither detection nor isolation of cyclic diamidophosphonites **2,6** offers problems.

Chloride **10a** was hydrolyzed readily, however we could not isolate the expected hydroxyphosphoryl compound **17**. Compound **17** was obtained by the reaction of AMAD **9** with $(Et_2N)_3P$ at 80 °C.



18 **17**

The initially formed cyclic triamidophosphite (**18**) is likely to react with **9** as a dehydrating agent; this is rather typical for reactions of carboxamides with electrophilic derivatives of P^{III} acids.

The physical properties and elemental analysis data of the DAP obtained are given in Table 1; Tables 2 and 3 present the NMR and IR spectral data. The spectral characteristics confirm the structures of the compounds synthesized.

Table 2 indicates that $\delta^{31}P$ decreases in the order δP^{III} 124—97 (**2, 6**) > δ(P=S) 71—64 (**4,8**) > δ(P=O) 36—85 (**3**), as is usually the case in ^{31}P NMR spectra of N-aryl-substituted DAP. The chemical shifts of the ring methylene protons lie within the range δCH_2 3.68—4.65. For some of the compounds studied these geminal protons are not equivalent and their spin-coupling constants are 13.8—15.6 Hz. The vicinal spin-coupling constants of the phosphorus atom with these nonequivalent protons are usually different and depend on the valent state of the phosphorus atom: $^3J_{HP^{III}} = 0.8 \div 3.2$, $^3J_{HP(S)} = 2.7 \div 11.0$, $^3J_{HP(O)} = 6.0 \div 9.9$ Hz, and on the environment of the phosphorus atom. Protons with greater δ have lower $^3J_{HCNP}$ values. When three or four nonequivalent aryl substituents are present in the ring, it

Table 2. ^{1}H NMR, ^{31}P NMR, and IR spectral data for N-aryl-substituted 1,3,2-DAP

Compound	^{31}P NMR, δ*	^{1}H NMR, δ, *J*/Hz**						IR, ν/cm^{-1}
		δH(**5a**)	$^3J_{PH(5a)}$	$^2J_{H(5a,5b)}$	δH(**5b**)	$^3J_{PH(5b)}$	δR, Ar	
2a	97.4	4.29	0.8	14.5	4.18	3.2	6.83—7.63 (m, Ph)	1497, 1594 (C=C arom.), 1648 (C=N)
2c	108.0	4.23	3.0	—	4.23	3.0	1.15 (t, Me), 3.73 (m, CH_2O, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 2.0), 6.47—7.63 (m, Ph)	1040 (P—O—C), 1515, 1590, 1610 (C=C arom.), 1655 (C=N)
2d	124.0	3.68	2.0	—	3.68	2.0	1.00 (m, Me), 1.75 (m, CH_2P), 6.36—7.66 (m, Ph)	1492, 1590, 1602 (C=C arom.), 1642 (C=N)
3a	18.7	4.46	6.0	—	4.46	6.0	6.76—7.89 (m, Ph)	1238 (P=O), 1488, 1495, 1503, 1595 (C=C arom.), 1687 (C=N)
3b	18.8, 19.2 (1:1)	4.41	6.8	—	4.41	6.8	2.15, 2.23, 2.26, 2.32 (c, Me), 6.41—7.79 (m, Ph + C_6H_4)	1233 (P=O), 1510, 1590, 1610 (C=C arom.), 1673 (C=N)
3c	8.2, 8.5 (1:1)	4.30	6.6	15.1	4.24	9.9	1.14 (t, Me), 4.12 (m, CH_2O, $^3J_{HH}$ = 7.2, $^3J_{PH}$ = 16.4), 6.84—7.66 (m, Ph)	1045 (P—O—C), 1275 (P=O), 1495, 1590 (C=C arom.), 1677 (C=N)
3d	36.0	4.23	7.0	—	4.23	7.0	0.93 (m, Me), 2.07 (m, CH_2P, $^3J_{PH}$ = 22.0, $^3J_{HH}$ = 7.0), 6.66—7.68 (m, Ph)	1230 (P=O), 1498, 1590, (C=C arom.), 1690 (C=N)
4a	70.9	4.59	2.7	15.0	4.49	11.0	6.90—7.69 (m, Ph)	653 (P=S), 1497, 1508, 1595 (C=C arom.), 1680 (C=N)
4c	64.0	4.38	8.3	13.8	4.32	8.3	1.25 (t, Me), 4.15 (m, CH_2O, $^3J_{PH}$ = 10.0, $^3J_{HH}$ = 8.0), 6.85—7.56 (m, Ph)	665 (P=S), 1027 (P—O—C), 1490, 1590 (C=C arom.), 1665 (C=N)
6	102.0	4.30	2.0	—	4.30	2.0	6.43—7.63 (m, Ph)	1498, 1597 (C=C arom.), 1690 (C=O)
8	68.8	4.65	2.6	15.6	4.55	10.7	6.89—7.96 (m, Ph)	655 (P=S), 1488, 1502, 1600 (C=C arom.), 1727 (C=O)

* In $CHCl_3$, except for compounds **2d**, **3d** (in CH_2Cl_2), and **8** (in dioxane). ** In $CDCl_3$, except for compound **8** (in dioxane-d_8). The spectra for DAP **2**, **3d** were recorded on a Varian T-60 instrument, those for other compounds were taken on a Bruker WM-250 spectrometer.

is difficult to analyze the corresponding regions of the ^{1}H NMR spectra.

The ^{31}P NMR spectra of **3b** and **3c** exhibit two signals of equal intensities, which may be associated with the presence of optical isomers that are possible because the phosphorus atom has four substituents or with the presence of *syn*- and *anti*-isomers in relation to the C=N bond. Table 3 indicates that methyl groups at different nitrogen atoms in methyl-substituted 4-oxo DAP **10a**, **14**, **17** are nonequivalent, and their J_{HP} are different. The shielding cone for the magnetically anisotropic C=O group **19** is such that the methyl group in the α-position in relation to C=O (MeN(3)) falls within the shielding area and has a lower δ value (2.15—2.73, $^3J_{HP}$ = 10÷16.4 Hz) than the MeN(1) group (δ 2.65—2.97, $^3J_{HP}$ = 8÷10.3 Hz); this is consistent with the data given in ref. 11. In the ^{1}H NMR spectra of compounds **10**, **14**, **17** (in $CDCl_3$) the signals of only a single stereoisomer could be observed, whereas in the spectrum of **10a** (3—5 % (v/v) in C_6D_6) all the signals are doubled, probably due to the presence of two isomers. The ratio of these isomers depends essentially on the concentration of **10a** in C_6D_6.

The most characteristic feature of the IR spectra of the DAP synthesized (Tables 2 and 3) is the presence of intense absorption bands (AB), ν(C=N) in the range of 1642—1690 cm^{-1} or ν(C=O) in the range of 1690—1727 cm^{-1}. The intensities and frequencies of these AB

Table 3. ^{1}H NMR spectral data for N-methyl-substituted 1,3,2-DAP

Compound	δ, *J*/Hz								Proportion of isomers (%)
	δMeC(5)	δHC(5)	$^3J_{HH}$	$^3J_{HC(5)N(1)P}$	δMeN(3)	$^3J_{HCN(3)P}$	δMeN(1)	$^3J_{H_3CN(1)P}$	
10a	1.39	3.50	7.0	14.0	2.64	15.0	2.97	9.0	100*
	1.06	3.07	6.6	13.6	2.16	16.4	2.67	10.3	66**
	1.52	4.16	7.1	14.0	2.15	16.0	2.65	10.0	34
14	1.37	3.66	7.0	—	2.65	10.0	2.63	9.0	100*
17	1.40	3.66	7.0	8.0	2.73	10.0	2.90	8.0	100*

* In $CDCl_3$, Varian T-60. ** In C_6D_6, Bruker WM-250.

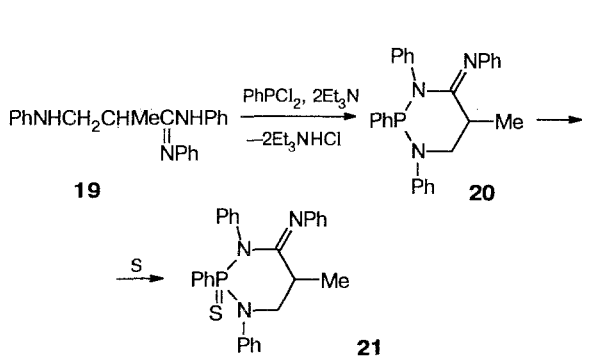
Table 4. ^{31}P NMR and IR spectral data for N-methyl-substituted 1,3,2-DAP

Compound	^{31}P NMR, δ	IR, ν/cm^{-1}
10a	152	1710, 1720 (C=O), 2825 (C—H_{MeN})
14	19	1243 (P=O), 1720 (C=O), 2400—3400 (N=H)
17	12	1264 (P=O), 1720 (C=O), 2390 (P—H), 2837 (C—H_{MeN})

Note. The spectra of DAP **10a** and **17** were measured without a solvent, that of **14** was taken in $CHCl_3$, ν_0 10.2 MHz. For compound **17** $^1J_{PH}$ = 650 Hz.

increase substantially with the transition from P^{III} derivatives **2, 6** to phosphoryl **3** and thiophosphoryl **4, 8** compounds. ν(C=O) AB of chloride **10a** is a clear doublet (Table 3); this supports the presence of the two isomers observed in C_6D_6 by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of a mixture of **10b** and **11b** is complicated due to the possible presence of two isomers for each, and can not be interpreted unambiguously. The IR spectrum of this mixture has a very intense asymmetric AB with the maximum at 1695—1700 cm^{-1}, which probably results from the superposition of ν(C=O) and ν(C=N) bands, an intense ν(P—O—C) AB at 1020 and 1038 cm^{-1}, and ν(C—H_{NMe}) bands of medium intensity at 2820 cm^{-1}.

β-AMAN **19** reacts with $PhPCl_2$ in the same manner as α-AMAN **1**, and 1,3,2-diazaphosphorinane **20** is formed in high yield. The latter adds sulfur to yield the corresponding cyclic thiophosphonate **21**.



The NMR and IR spectroscopic data for compounds **20, 21** (see Experimental) confirm their structures.

Experimental

IR spectra were measured on a UR-20 spectrometer, in vaseline oil for solids and in thin films for liquids. ^{1}H NMR spectra were recorded on Bruker WM-250 (250 MHz) and Varian T-60 (60 MHz) spectrometers at 20 °C. Solvents used are listed in Tables 2, 3; Me_4Si was used as the internal standard. ^{31}P NMR spectra were run on Bruker WM-250 (101.3 MHz) and YaMR KGU-4 (10.2 MHz) instruments using 85 % H_3PO_4 as the external standard. EI mass spectra were obtained on a MKh-1310 mass spectrometric system with direct sample injection, at an ionization potential of 70 eV, collector current 10 μA; the relative error of determination of ion masses (ΔM/M) was ≤ 1.10^{-5}.

All of the solvents were thoroughly dried prior to use, all manipulations were carried out under dry argon, unless otherwise stated.

α-AMAN **1** (ref. 20), β-AMAN **19** (ref. 1), α-AMAD **5** (ref. 20) were synthesized by the known procedures.

1,2,3-Triphenyl-4-phenylimino-1,3,2-diazaphospholane (2a). To a solution containing 15.05 g (50 mmol) of **1a** and 11.1 g (110 mmol) of Et_3N in 100 mL of benzene, 8.95 g (50 mmol) of $PhPCl_2$ in 20 mL of benzene was added at 10 °C, and the mixture was kept at 20 °C for 12 h. The precipitated $Et_3N \cdot HCl$ was filtered off and the filtrate was concentrated. The residue was dissolved in MeCN, precipitated with Et_2O, recrystallized from benzene, and dried *in vacuo* to give colorless crystals of **2a**.

DAP **2b—d** (oils) were prepared in a similar way.

2-Oxo-1,2,3-triphenyl-4-phenylimino-1,3,2-diazaphospholane (3a). A mixture of 2.0 g (4.9 mmol) of **2a** and 1.0 g (12.8 mmol) of DMSO in CH_2Cl_2 was kept for 12 h at 20 °C, evaporated *in vacuo*, and the residue was recrystallized from benzene and dried in air to yield colorless crystals of **3a**.

3c was synthesized in a similar manner. DAP **3b,d** were prepared by heating a benzene solution of DAP **2b,d** for 4—5 h at 40—50 °C under an anhydrous atmosphere. The benzene was evaporated and the residue was crystallized from MeOH

and recrystallized from the solvent mentioned in Table 1.

2-Thioxo-1,2,3-triphenyl-4-phenylimino-1,3,2-diazaphospholane (4a). A mixture of 2.0 g (4.9 mmol) of **2a** and 0.8 g (25 mmol) of powdered sulfur in 10 mL of benzene was refluxed for 2 h. The excess sulfur was filtered off, the filtrate was concentrated, and the residue was reprecipitated from MeCN with Et_2O, recrystallized from acetone, and dried in air.

DAP **4c** was prepared in a similar way (the mixture was refluxed for 4 h).

4-Oxo-1,2,3-triphenyl-1,3,2-diazaphospholane (6). A mixture of 9.2 g (4.07 mmol) of AMAD **5** and 3.2 g (82 mmol) of $NaNH_2$ in 50 mL of benzene was refluxed for 4 h, cooled to 10 °C, and 7.3 g (40.8 mmol) of $PhPCl_2$ in 20 mL of benzene was added to the mixture. This was stirred at 20 °C for 3 h, the precipitated NaCl was removed by centrifugation, the filtrate was concentrated *in vacuo*, and the residue was kept at 0.05 Torr for 3 h to yield DAP **6** as a viscous oil.

4-Oxo-2-thioxo-1,2,3-triphenyl-1,3,2-diazaphospholane (8) was prepared by addition of sulfur to DAP under conditions similar to those employed in the synthesis of **4a**.

***N*-Methyl-DL-α-alanine methylamide (9).** To a solution of 28.2 g (0.91 mol) of $MeNH_2$ in 100 mL of dry MeOH a solution of 41.05 g (0.246 mol) of methyl α-bromopropionate in 50 mL of MeOH was added at −5 ÷ −10 °C. The mixture was slowly heated to 40 °C, cooled to 20 °C, and stirred in a hermetically sealed flask at 20 °C for 3 days. To the reaction mixture, 14.2 g (0.246 mol) of KOH in 50 mL of MeOH was added with ice cooling. The precipitated KBr was filtered off and the solvent was evaporated. To remove the remaining KBr and H_2O, the residue was dissolved in 100 mL of *i*-PrOH and the solution was filtered and concentrated *in vacuo*. Distillation gave 21.3 g (75 %) of amide **9**, b.p. 73—75 °C (0.15 Torr), which crystallized on storage into a hygroscopic low-melting mass. ^{1}H NMR ($CDCl_3$); δ: 1.29 (d, 3H, 7, CH_3C); 2.00 (s, 1 H, NH); 2.40 (s, 3 H, CH_3N); 2.78 (s, 1.5 H) and 2.87 (s, 1.5 H, $CH_3NC(O)$); 3.08 (q, 1H, 7, CH); 7.67 (br s, 1 H, NHC(O). Found (%): C, 51.72; H, 10.34; N, 24.14. $C_5H_{12}N_{20}$. Calculated (%): C, 51.38; H, 10.18; N, 24.22.

2-Chloro-1,3,5-trimethyl-4-oxo-1,3,2-diazaphospholane (10a). To a solution of 8.4 g (61 mmol) of PCl_3 in 130 mL of ether a solution of 6.8 g (58.5 mmol) of amide **9** and 13.1 g (130 mmol) of Et_3N in 30 mL of ether was added at −20 ÷ −30 °C. The reaction mixture was stirred for 3 h at 20 °C, $Et_3N \cdot HCl$ was filtered off, and the solvent was evaporated *in vacuo*. Vacuum distillation of the residue gave 4.3 g (41 %) of DAP **10a**.

The reaction of α-AMAD **9** with $EtOPCl_2$ was carried out in the same way.

2-Amino-1,3,5-trimethyl-2,4-dioxo-1,3,2-diazaphospholane (14). To a solution of 1.12 g (6.2 mmol) of chloride **10a** in 20 mL of ether was added at −30 °C 1.13 g (6.3 mmol) of $(Me_3Si)_2NNa$ in 20 mL of ether. The reaction mixture was stirred for 3 h at 20 °C, filtered, the filtrate was concentrated *in vacuo*, and the residue was dissolved in a 2:1 Et_2O—CH_2Cl_2 mixture and evaporated in air. Reprecipitation of the crystals obtained with hexane from CH_2Cl_2 gave 0.29 g (26 %) of amide **14**. MS, *m/z* (I_{rel} (%)): 177 $[M]^+$ (40), 162 $[M-Me]^+$ (62), 149 $[M-C_2H_4]^+$ (14), 147 $[M-CH_2=NH-H]^+$ (29), 134 $[M-HNCO]^+$ (15), 93 $[MeNH(NH_2)PO]^+$ (14), 58 $[MeNCOH]^+$ (38), 57 $[MeNCO]^+$ (74), 56 $[CH_2NCO]^+$ (58), 42 $[NCO]^+$ (93), 31 $[MeNH_2]^+$ (100).

1,3,5-Trimethyl-2,4-dioxo-1,3,2-diazaphospholane (17). A mixture of 2.7 g (23.3 mmol) of AMAD **9** and 6.7 g (27.1 mmol) of $(Et_3N)_3P$ in 20 mL of benzene was heated under reflux for 4 h and evaporated. Fractionation of the residue *in vacuo* gave 1.2 g (32 %) of compound **17**. MS, *m/z* (I_{rel} (%)): 162 $[M]^+$ (19.5), 161 $[M-H]^+$ (6), 147 $[M-Me]^+$ (9), 134 $[M-C_2H_4]^+$ (13.5), 105 $[M-MeNCO]^+$ (12), 104 $[M-MeNCO-H]^+$ (16), 58 $[MeNCOH]^+$ (100), 57 $[MeNCO]^+$ (20), 56 $[CH_2NCO]^+$ (42), 42 $[NCO]^+$ (47.5), 30 $[MeNH]^+$ (59).

5-Methyl-1,2,3-triphenyl-4-phenylimino-1,3,2-diazaphosphorinane (20). To a solution of 5.2 g (15.8 mmol) of α-AMAN **19** and 4.8 g (47.5 mmol) of Et_3N in 50 mL of benzene, 3.0 g (16.7 mmol) of $PhPCl_2$ in 10 mL of benzene was added at 20 °C. The mixture was stirred for 3 h and filtered, the filtrate was evaporated, and the residue was kept for 2 h at 0.05 Torr to give **20** (a mixture of stereoisomers) as colorless glass (Table 1). ^{31}P NMR (CH_2Cl_2), δ: 90. ^{1}H NMR ($CDCl_3$), δ: 1.10 (d, 1.5H, 6, Me), 1.45 (d, 1.5H, 7, Me), 2.70—4.10 (m, 3H, CH_2CH); 6.45—7.85 (m, 20H, 4Ph). IR, ν/cm^{-1}: 1490, 1594 (C=C arom.), 1635 (C=N).

5-Methyl-1,2,3-triphenyl-4-phenylimino-2-thioxo-1,3,2-diazaphosphorinane (21). A mixture of 2.80 g (6.4 mmol) of **20**, 0.23 g (7.2 mmol) of powdered sulfur, and 0.36 g (3.6 mmol) of Et_3N was kept in 10 mL of benzene for 12 h at 20 °C, and refluxed for 1 h. The excess sulfur was filtered off, the filtrate was evaporated and the residue was crystallized from MeOH and recrystallized from a 2:3 MeOH — acetone mixture (Table 1). ^{31}P NMR ($CDCl_3$), δ: 67.4. ^{1}H NMR ($CDCl_3$), δ: 1.63 (d, J = 6.7, 3H, Me); 3.38 (m, 1H, HC-5); 3.46 (br.t, 1H, 15.8, 12.5, HC-6), 4.35 (d, 1H, 12.5, HC-6), 6.70—7.88 (m, 20H, 4Ph). IR, ν / cm^{-1}: 638 (P=S), 1494, 1593 (C=C arom), 1644 (C=N).

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