Aminoamidines

8.* Synthesis of bicyclic nitrogen- and phosphorus, nitrogen-containing compounds from 2-arylaminomethylimidazolines

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N-Aryl-substituted 5-oxo-tetrahydroimidazo[1,5-*a*]imidazoles, tetrahydroimidazo[1,2-*c*][1,3,2λ^3]- and -[1,2-*c*][1,3,2λ^5]diazaphospholes, as well as 6-oxo- and 5,6-dioxohexahydroimidazo[1,2-*a*]pyrazines were synthesized using 2-arylaminomethylimidazolines as 1,4-binucleophiles.

Key words: 2-arylaminomethylimidazolines; heterocyclization; 5-oxo-5*H*-tetrahydroimidazo[1,2-*c*][1,3,2]diazaphosphole; 6-oxo- and 5,6-dioxohexahydroimidazo[1,2-*a*]pyrazine.

Acyclic amidines of α- and β-aminoacids (aminoamidines)[2—10] have been successfully used as 1,4- and 1,5-binucleophiles, respectively, in the syntheses of various 5—7-membered nitrogen-containing heterocycles. To construct condensed tricyclic systems, 2-aminoalkylbenzimidazoles, related to aminoamidines, have been utilized.[11—14] Patent information is available[15] on the synthesis of imidazo[1,5-*a*]imidazoles based on 2-amino-[bis-(fluoroalkyl)]methylimidazoles and acylating reagents.

2-Arylaminomethylimidazolines, which may be regarded as cyclic analogs of α-aminoamidines, are worth attention as starting compounds for obtaining biologically active compounds.[16—22] However, apart from a few examples,[16] they are not employed in organic synthesis. Meanwhile, it was recently shown[1] that 2-arylaminomethylimidazolines are typical binucleophiles which readily undergo acylation both at the imidazoline ring and at the α-amino group.

It has been found in the present work that 2-arylaminomethylimidazolines (**1—3**) react as 1,4-binucleophiles with such typical bielectrophiles as dichlorides of carboxylic and phosphonic acids, diamides of phosphonous acids, and methyl bromoacetate to give bicyclic condensed systems. The reactions of compounds **1** and **2** with oxalyl chloride in the presence of Et_3N give hexahydro-5,6-dioxoimidazo[1,2-*a*]pyrazines (**4**, **5**), while the reactions of **1** and **3** with phosgene under similar conditions result in 5-oxo-5*H*-tetrahydroimidazo[1,5-*a*]imidazoles (**6**, **7**) (Scheme 1, Table 1).

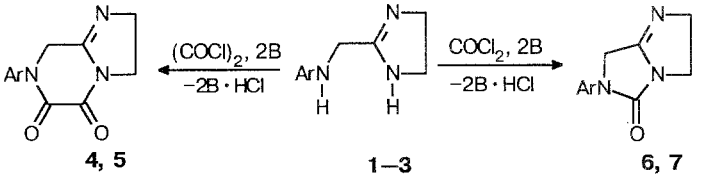
Probably, products of acylation at the highly nucleophilic N(1) atom of the imidazoline ring are formed first,[1] while subsequent intramolecular cyclization affords compounds **4—7**.

As one could expect, the reaction of imidazoline **1** with such an asymmetric bielectrophile as methyl bromoacetate proceeds in a more complicated way, although a bicyclic compound was also isolated in this case; structure **8** shown in Scheme 2 was ascribed to this compound based on its mass-spectrometric study. The isomeric structure **9** was ruled out because dissociative ionization of this compound cannot produce the $[PhN{=}C{=}O]^+$ ion with *m/z* 119 observed in the mass spectrum (EI) of the reaction product.

We have previously found[8] that *N*-aryl-substituted α-aminoamidines readily react with dichlorides of acids of tricoordinated phosphorus to give the corresponding

*For part 7, see Ref. 1.

Scheme 1



4, 5 **1—3** **6, 7**

Ar = Ph (**1**, **4**, **6**), *p*-MeC_6H_4 (**2**, **5**), *p*-ClC_6H_4 (**3**, **7**); B = Et_3N

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Table 1. Physicochemical and spectral properties of compounds **4—8**

Compound	Yield (%)	M.p./°C	IR, ν/cm^{-1}		^{1}H NMR, δ*	Found / Calculated (%)			Molecular formula
			C=N	C=O		C	H	N	
4	70	226—228	1647	1710, 1665	3.15—3.94 (m, 4 H, CH_2CH_2); 4.11 (m, 1 H, C(8)H); 4.30 (m, 1 H, C(8)H); 6.82—7.54 (m, 5 H, Ph)	62.46 62.88	4.52 4.80	18.50 18.34	$C_{12}H_{11}N_3O_2$
5	70.5	213—215	1645	1710, 1665	2.26 (s, 1.5 H, Me); 2.30 (s, 1.5 H, Me); 3.07—3.97 (m, 4 H, CH_2CH_2); 4.05—4.32 (m, 2 H, $C(8)H_2$); 7.12 (m, 4 H, C_6H_4)	64.55 64.20	5.04 5.35	16.90 17.28	$C_{13}H_{13}N_3O_2$
6	60	180—181	1678	1712	3.06—3.94 (m, 4 H, CH_2CH_2); 4.10—4.53 (m, 2 H, $C(7)H_2$); 6.77—7.53 (m, 5 H, Ph)	65.35 65.67	5.24 5.47	20.67 20.90	$C_{11}H_{11}N_3O$
7**	59	183—184	1682	1723	3.05—3.88 (m, 4 H, CH_2CH_2); 4.07—4.44 (m, 2 H, $C(7)H_2$); 7.43 (m, 4 H, C_6H_4)	56.28 56.05	4.34 4.25	17.56 17.83	$C_{11}H_{10}ClN_3O$
8***	27	312—316	1610	1665	4.17 (s, 4 H,CH_2CH_2); 4.50 (s, 2 H, $C(8)H_2$); 5.00 (s, 2 H, $C(5)H_2$); 7.37 (m, 5 H, Ph)	48.34 48.65	4.56 4.73	13.90 14.19	$C_{12}H_{13}N_3O \cdot HBr$

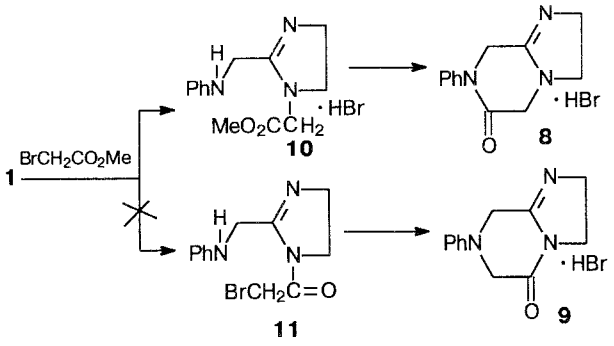
* The spectra of compounds **4—7** were obtained in DMSO-d_6 and those of **8** were obtained in CF_3COOH.
** Found (%): Cl, 14.73. Calculated (%): Cl, 15.07.
*** Found (%): Br, 26.58. Calculated (%): Br, 27.02.

Table 2. Physicochemical parameters of compounds **12—16**

Compound	Yield (%)	M.p./ °C	Found / Calculated (%)				Molecular formula
			C	H	N	P	
12	24	140—142	55.98 56.17	6.02 5.96	17.65 17.84	13.34 13.19	$C_{11}H_{14}N_3OP$
13	58	158—160 (0.07)*	—	—	18.26 18.02	13.15 13.30	$C_{12}H_{16}N_3P$
14	76.5	185—187	67.99 68.33	5.56 5.69	15.04 14.95	10.92 11.03	$C_{16}H_{16}N_3P$
15**	65	138—139	54.07 54.34	5.88 6.04	15.60 15.85	11.91 11.70	$C_{12}H_{16}N_3PS$
16***	77.5	180—182	61.03 61.34	5.02 5.11	13.51 13.42	10.16 9.90	$C_{16}H_{16}N_3PS$

* M.p. (*p*/Torr), n_D^{20} 1.6150.
** Found (%): S, 12.01. Calculated (%): S, 12.08.
*** Found (%): S, 10.22. Calculated (%): S, 10.22.

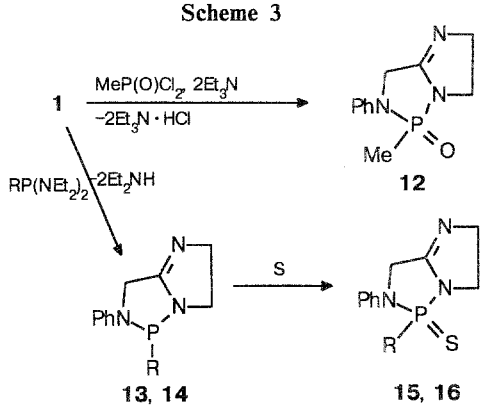
Scheme 2



1,3,2-diazaphospholanes, whereas such transformations are not characteristic of dichlorides of acids of tetracoordinated phosphorus.

Attempts to synthesize phosphorus-containing analogs of compounds **6** and **7** from imidazoline **1** and $EtOP(O)Cl_2$ or $EtNP(O)Cl_2$ also proved to be unsuccessful. A condensed phospholane (**12**) was isolated in a low yield only in the case of $MeP(O)Cl_2$. The reactions with $PhPCl_2$ and other P^{III}-based acid dichlorides could not be performed, either. However, if the approach without the use of HCl is utilized, *e.g.*, in the reaction of **1** with diamides of phosphonous acids, bicyclic diamidophosphonites **13** and **14** are smoothly formed. The latter readily add sulfur to give thiophosphonates **15** and **16** (Scheme 3, Table 2).

Scheme 3



R = Et (**13**, **15**), Ph (**14**, **16**)

Table 3. Mass spectra (EI) of compounds **5**, **7**, **8**, and **13**

Compound	MS, m/z (I_{rel} (%))
5	243 $[M]^+$ (42); 215 $[M-CO]^+$ (15); 187 $[M-2CO]^+$ (2); 186 $[M-2CO-H]^+$; 133 $[ArNCO]^+$ (13); 120 $[ArNH=CH_2]^+$ (26); 119 $[ArN=CH_2]^+$ (100); 106 $[ArNH]^+$ (78); 91 $[Ar]^+$ (34); 56 $[CH_2=N=C=O]^+$ (7)
7	237* $[M]^+$ (33); 235 $[M]^+$ (100); 207 $[M-CO]^+$ (3); 155* $[ArNCO]^+$ (15); 153 $[ArNCO]^+$ (42); 141* $[ArN=CH_2]^+$ (32); 139 $[ArN=CH_2]^+$ (100); 128* $[ArNH]^+$ (10); 126 $[ArNH]^+$ (32); 113* $[Ar]^+$ (15); 57 $[CH_2=N=C=OH]^+$ (12)
8**	215 $[M]^+$ (62); 187 $[M-CO]^+$ (13); 186 $[M-C_2H_4-H]^+$ (14); 119 $[ArNCO]^+$ (4); 106 $[ArNH=CH_2]^+$ (13); 105 $[ArN=CH_2]^+$ (100); 104 $[ArN=CH]^+$ (16); 96 $[M-ArNCO]^+$ (15); 77 $[Ar]^+$ (23); 56 $[CH_2N=C=O]^+$ (30)
13	233 $[M]^+$ (64); 205 $[M-C_2H_4]^+$ (25); 204 $[M-C_2H_5]^+$ (100); 123 $[ArN=PH]^+$ (17); 106 $[ArNH=CH_2]^+$ (10); 105 $[ArN=CH_2]^+$ (7); 104 $[ArN=CH]^+$ (8); 99 $[M-C_2H_5-ArN=CH_2]^+$ (38); 77 $[Ar]^+$ (24)

* Ions containing ^{37}Cl.
** In the chemical ionization mass spectrum, m/z 216 $[M+H]^+$ (100).

Bicyclic compounds **13** and **14** are much more stable in the air oxygen than the respective monocyclic analogs.[8] For example, compound **14** undergoes almost no oxidation in boiling benzene when a strong stream of air is passed for 2 h through the solution. Furthermore, compounds **13** and **14** could not be oxidated with DMSO.

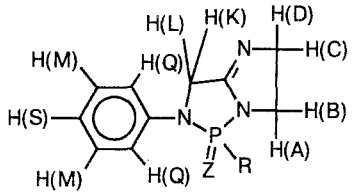
The structures of the compounds obtained were confirmed by mass spectrometric (Table 3) and NMR and IR absorption spectroscopic data (Tables 1, 4, and 5). The mass spectra (EI) of the compounds studied are characterized by the presence of intense peaks $[M]^+$, whereas those of oxo-derivatives **5**, **7**, and **8** display $[ArN=CH_2]^+$ ions, resulting from fragmentation of the ArN—CO and $ArNCH_2$—C moieties in the ring, as the most abundant components. Emission of $[ArNCO]^+$ and $[CO]^+$ ions from $[M]^+$ is quite typical of dissociative ionization of oxo-derivatives. The most intense peak (m/z 204) in the mass spectrum of compound **13** results from splitting off of an ethyl radical from $[M]^+$. The fragment ion that is next in intensity (m/z 99) results from abstraction of an $ArN=CH_2$ fragment from the ion with m/z 204. The intensity of the $[ArN=CH_2]^+$ ion peak is relatively small since the charge is predominantly located at the phosphorus-containing fragment.

The IR spectra of phosphorus-containing heterocycles **12**—**16** (see Table 4) contain a ν(C=N) absorption band at 1660—1680 cm^{-1}, whose intensity and frequency increase on going from P^{III} derivatives to four-coordinated phosphorus compounds.

Table 4. ^{31}P NMR and IR absorption spectra of compounds **12**—**16**

Compound	^{31}P NMR (δ)	IR (ν/cm^{-1})	
		C=N	P=X
12	25.05	1680	1242
13	105.0	1660	—
14	86.70	1663	—
15	79.50	1676	647
16	63.00	1680	652

Table 5. ^{1}H NMR spectra of compounds **12—16** (δ, *J*/Hz)*



Atom	Parameter	Compound				
		12	**13**	**14**	**15**	**16**
H(A)	δ	3.56	3.17	3.09	3.54	3.28
	$-^2J_{H(A)-H(B)}$	9.0	9.3	12.0	9.2	9.0
	$^3J_{PH(A)}$	19.4	9.3	11.0	9.6	9.0
	$^3J_{H(A)-H(C)}$	7.5	—	12.0	4.7	6.0
	$^3J_{H(A)-H(D)}$	3.0	—	7.0	—	—
H(B)	δ	3.63	3.24	3.14	3.71	3.75
	$^3J_{PH(B)}$	18.0	9.3	12.0	18.0	18.0
	$^3J_{H(B)-H(C)}$	3.0	—	2.0	1.7	1.5
	$^3J_{H(B)-H(D)}$	7.5	5.3	1.2	7.1	5.2
H(C)	δ	4.09	4.08	4.20	4.30	4.50
H(D)	δ	4.09	4.08	4.20	4.30	4.50
H(K)	δ	4.52	3.60	3.61	4.36	4.33
	$-^2J_{H(K)-H(L)}$	15.1	9.3	8.6	10.3	12.0
	$^3J_{PH(K)}$	5.4	14.7	18.9	6.2	5.8
H(L)	δ	4.43	3.64	3.58	4.20	4.19
	$^3J_{PH(L)}$	5.6	3.0	6.3	10.4	12.2
H(Q)	δ	7.15	7.27	7.37	7.31	7.05
	$^3J_{H(M)-H(Q)}$	8.0	11.2	6.8	—	7.8
H(M)	δ	7.33	6.72	7.23	7.31	7.22
	$J_{H(M)-H(S)}$	7.3	7.5	7.5	6.21	7.4
H(S)	δ	6.97	6.59	7.07	6.20	6.90
	$J_{H(Q)-H(S)}$	1.4	—	—	2.2	0.7
R H(α)	δ	1.81	1.53;1.71	7.49	2.44; 2.48	7.96
	$J_{H(\alpha)-H(\beta)}$	—	7.5	6.8	7.5	8.0
	$J_{PH(\alpha)}$	16.1		13.5	8.0;10.0	14.8
	$J_{H(\alpha)-H(\gamma)}$	—		2.3		1.6
	$^2J_{H(\alpha)-H(\alpha')}$	—	−14.9		−18.0	
H(β)	δ	—	0.96	6.89	1.03	7.40
	$J_{H(\beta)-H(\gamma)}$	—	11.2	9.0		7.6
	$^3J_{PCH_3}$				22.9	
H(γ)	δ	—	—	6.75	—	7.48

* The ^{1}H NMR spectra of compounds **13**, **14**, **15**, and **16** were recorded in $CDCl_3$ and that of **12** in DMSO-d_6.

The parameters of the NMR spectra of phosphorus-containing bicyclic compounds **12—16** are presented in Tables 4 and 5. Generally, the chemical shifts for phosphorus atoms (δ_P) in the systems considered are markedly smaller than those in the monocyclic analogs having an exocyclic C=N bond (*cf.* Ref. 8), which indicates stronger shielding of the P nucleus. Replacement of the carbonyl and dicarbonyl moieties by a P atom, whose nucleus manifests significant spin-spin interaction with the protons at C(3) and C(7) of the heterocycles (*cf.* compounds **4—7** and **12—16**), results in better resolution of the signals of the methylene fragments. The methylene protons at C(2) and C(3) form an ABCDX-type spin system, where AB are the geminal protons at C(3), CD are those at C(2), and X is a phosphorus nucleus. It should be noted that the C and D protons have equal values of δ but different vicinal coupling constants with nuclei A and B. The $^3J_{AC}$ and $^3J_{BD}$ constants are normally higher than $^3J_{AD}$ $^3J_{BC}$, which probably indicates that both proton pairs AC and BD have *trans*-positions.[23] Protons B, giving a resonance in a weaker field, have higher coupling constants with the phosphorus nucleus. The geminal protons at C(7) form a KLX spin system. The methylene protons of the ethyl

substituent in the spectra of compounds **13** and **15** become nonequivalent owing to the chirality of the phosphorus atom and steric hindrance of free rotation around the P—C exocyclic bond. Therefore, the spectrum of the ethyl moiety should be regarded as a $X\alpha\alpha'\beta_3$ system. The attribution of the signals in the ^1H NMR spectra of compounds **12—16** was consistent with data obtained in double homonuclear proton-proton resonance experiments.

Experimental

^1H NMR spectra were recorded on Bruker WM-250 and Varian T-60 spectrometers. ^{31}P NMR spectra were obtained on a Bruker CXP-100 instrument (36.5 MHz). IR spectra were recorded in vaseline oil on a UR-20 spectrophotometer. Mass spectra (EI) were obtained on a Hitachi M-80B mass-spectrometer using an ionization energy of 70 eV.

The starting **2-arylaminomethylimidazolines 1—3** were obtained by a procedure reported previously.[1]

7-Aryl-2,3,5,6,7,8-hexahydro-5,6-dioxoimidazo[1,2-*a*]pyrazines (4, 5). A solution of imidazoline **1** or **2** (8 mmol) and Et_3N (6 mL, 43 mmol) in THF (35 mL) was added at −20 ÷ −30 °C to a solution of oxalyl chloride (10 mmol) in THF (25 mL). The reaction mixture was stirred for 1 h at −20 °C and for 1 h at 20 °C. The precipitated mixture of compounds **4** or **5** with $Et_3N \cdot HCl$ was filtered off, washed with water and methanol. The undissolved compounds **4** or **5** were reprecipitated with methanol from DMF and dried *in vacuo* (the yields and melting points are given in Table 1).

6-Aryl-2,3,6,7-tetrahydro-5-oxo-5*H*-imidazo[1,5-*a*]imidazoles (6, 7). A solution of compound **1** or **3** (14 mmol) and Et_3N (8 mL, 58 mmol) in THF (15 mL) was added at −10 ÷ −15 °C to a solution of phosgene (20 mmol) in THF (20 mL). The reaction mixture was stirred for 1 h at −10 °C and kept for 20 h at 0—5 °C. The precipitate of $Et_3N \cdot HCl$ was filtered off, and the filtrate was concentrated *in vacuo*. The residue was dissolved with heating in methanol (~30 mL). Water (100—120 mL) was added to the cooled solution, and the suspension formed was centrifuged for ~40 min (3500—4000 rpm). The precipitate of compound **6** or **7** was dried with KOH and purified by reprecipitation with ether from 1,4-dioxane (the yields and melting points are given in Table 1).

7-Phenyl-2,3,5,6,7,8-hexahydro-6-oxoimidazo[1,2-*a*]pyrazine hydrobromide (8). A mixture of compound **1** (3.1 g, 17.7 mmol) and methyl bromoacetate (3.3 g, 21.6 mmol) in methanol (40 mL) was stirred for 8 h at 20 °C, boiled for 7 h, and kept for 2 days at 5 °C. The precipitated crystals of product **8** were filtered off and thoroughly ground. Admixtures were extracted with boiling ethanol (50 mL), and the product was dried *in vacuo* (the yield and melting point are given in Table 1).

5-Methyl-6-phenyl-2,3,6,7-tetrahydro-5-oxo-5*H*-imidazo[1,2-*c*][1,3,2λ^5]diazaphosphol (12). A solution of compound **1** (2.50 g, 18.9 mmol) and Et_3N (10.5 mL, 75 mmol) in THF (30 mL) was added at 0—5 °C to a solution of $MeP(O)Cl_2$ (3.20 g, 18.3 mmol) in THF (20 mL). The reaction mixture was stirred for 2 h at 20 °C, and the precipitate of $Et_3N \cdot HCl$ was filtered off. The filtrate was diluted with ether (150 mL) and kept for 10 days at 0÷−5 °C. The precipitated crystals of compound **12** were filtered off and purified by low-temperature recrystallization from a 1 : 3 THF—ether mixture.

5-Ethyl-6-phenyl-2,3,6,7-tetrahydro-5*H*-imidazo[1,2-*c*][1,3,2λ^3]diazaphosphol (13). A mixture of compound **1** (3.1 g, 17.7 mmol) and $EtP(NEt_2)_2$ (3.80 g, 18.6 mmol) was heated for 3 h at 80—90 °C (100—120 Torr) in a stream of argon. Product **13** was isolated by distillation of the reaction mixture *in vacuo*.

5,6-Diphenyl-2,3,6,7-tetrahydro-5*H*-imidazo[1,2-*c*][1,3,2λ^3]diazaphosphol (14). A mixture of compound **1** (6.6 g, 37.7 mmol) and $PhP(NEt_2)_2$ (9.8 g, 38.8 mmol) was heated in a stream of argon for 2 h at 90—100 °C and for 1 h at 120 °C (70 Torr) and then cooled. The crystals formed were triturated in ether (50 mL) and filtered off. Compound **14** obtained was recrystallized.

5-Ethyl-6-phenyl-2,3,6,7-tetrahydro-5-thioxo-5*H*-imidazo[1,2-*c*][1,3,2λ^5]diazaphosphol (15). A mixture of compound **13** (0.93 g, 3.6 mmol), finely divided sulfur (0.12 g, 3.8 mmol), and Et_3N (0.5 mL) in benzene (2 mL) was stirred for 14 h at 20 °C and then concentrated *in vacuo*. Methanol (10 mL) was added, excess sulfur was filtered off, and the filtrate was kept for 5 days at 0—5 °C. The precipitate of compound **15** was filtered off and recrystallized from methanol.

In a similar way, **5,6-diphenyl-2,3,6,7-tetrahydro-5-thioxo-5*H*-imidazo[1,2-*c*][1,3,2λ^5]diazaphosphol (16)** was obtained and recrystallized from a 1 : 1 benzene—ether mixture.

The yields, melting (boiling) points, and elemental analysis data for compounds **12—16** are given in Table 2.

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