Chemistry of Heterocyclic Compounds, Vol. 39, No. 7, 2003

DIPYRROLO[1,2-*a*;2',1'-*c*]PYRAZINES. 6*. ELECTROPHILIC SUBSTITUTION IN A SERIES OF DIPYRROLO[1,2-*a*;2',1'-*c*]PYRAZINE AND 5,6-DIHYDRODIPYRROLO[1,2-*a*;2',1'-*c*]PYRAZINE DERIVATIVES. PHOSPHORYLATION OF DIPYRROLO[1,2-*a*;2',1'-*c*]PYRAZINES

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We have studied the behavior of asymmetrically substituted dipyrrolo[1,2-a;2',1'-c]pyrazines and their 5,6-dihydro analogs under phosphorylation reaction conditions.

Keywords: 5,6-dihydropyrrolo[1,2-*a*;2',1'-*c*]pyrazines, dipyrrolo[1,2-*a*;2',1'-*c*]pyrazines, phosphorylation.

Halides of trivalent phosphorus in basic media are effective phosphorylating reagents for a wide range of heterocyclic compounds*[2], including electron-rich compounds: pyrrole [2, 3], indole [4], furan, thiophene [5], thiazole [6]. So for example, N-methylpyrrole is easily phosphorylated by phosphorus tribromide and either 2-dibromophosphino-1-methylpyrrole or tris(1-methylpyrrolyl)-2-phosphine is obtained, depending on the ratio of the reagents [2]. Phosphorylation of 2,5-dimethyl-1-(*p*-tolyl)pyrrole by phosphorus trichloride leads to the monosubstitution product, repeated phosphorylation of which by phosphorus tribromide leads to diphosphine-substituted pyrrole [3]. In continuing research on the reactivity of the poorly studied heterocyclic system dipyrrolo[1,2-*a*;2',1'-*c*]pyrazine, we studied the behavior of this system under phosphorylation reaction conditions. It was shown earlier that acylation, aminomethylation, azo coupling, and nitration of dipyrrolo[1,2-*a*;2',1'-*c*]pyrazines initially occurs at the α-position of the pyrrole ring, and depending on the electrophilicity of the reagents, both monosubstituted and polysubstituted dipyrrolopyrazines are formed [7]. So acylation of dipyrrolopyrazines by trifluoroacetic anhydride led to the disubstitution products, while only the 3-monoacetyl derivatives were obtained in acylation by acetic anhydride.

In this work, we selected the chloride and bromide of trivalent phosphorus as the phosphorylating agents. As the substrates, we used 2-methyldipyrrolo[1,2-*a*;2',1'-*c*]pyrazine (**1a**), in which both α-positions of the pyrrole rings are free; 2,8-dimethyldipyrrolo[1,2-*a*;2',1'-*c*]pyrazine (**1b**), where only one α-position is free; and also their 5,6-dihydro analogs **1c,d**.

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* For Communication 5, see [1].

*[2] Considering the wide range of application of the phosphorylation reaction, we suggest calling this reaction the Tolmachev reaction.

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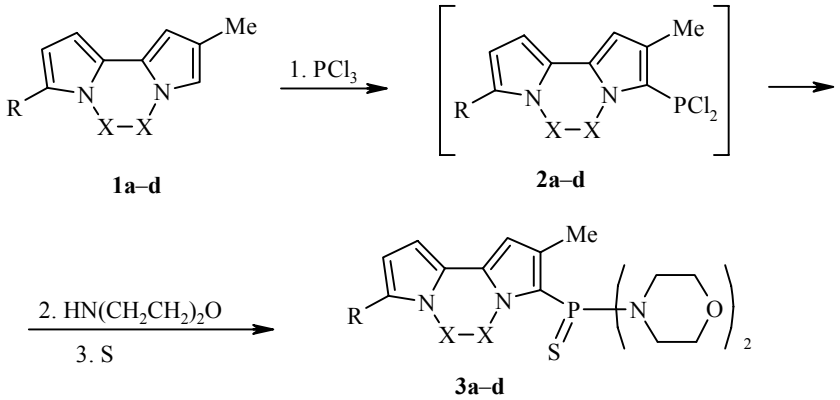
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1086-1095, July, 2003. Original article submitted November 3, 2000.

Phosphorylation of dipyrrolopyrazines and their 5,6-dihydro analogs by such a weak electrophilic agent as phosphorus trichloride occurs selectively, and leads to formation of only the monosubstitution products **3a-d**. And upon phosphorylation by phosphorus trichloride of the 2-methyl-substituted substrates **1a,c**, in which both α positions of the pyrrole rings of the molecule are free for electrophilic attack, we obtain only the 3-phosphorus-substituted derivatives.



3a–d

1-3 **a** R = H, X–X = –CH=CH–, **b** R = Me, X–X = –CH=CH–, **c** R = H, X–X = $–CH_2–CH_2–$, **d** R = Me, X–X = $–CH_2–CH_2$

In the case of aromatic dipyrrolopyrazines **1a,b**, increasing the amount of the reagent by a factor of two and even four compared with equimolar amounts increases the yield of products **3a,b** and does not result in obtaining the disubstitution products. In the case of 5,6-dihydrodipyrrolopyrazines **1c,d**, a change in the substrate-to-reagent ratio does not affect the yield of reaction products (Table 1).

The bromide of trivalent phosphorus is a stronger electrophilic reagent than the chloride, so the reaction of dipyrrolopyrazines with phosphorus tribromide does not occur so unambiguously as in the first case. In addition to the major monosubstitution products **3a-d**, the disubstitution products **4a-d** are formed. In practically all cases, in the reaction mixture we found significant amounts of trimorpholinophosphine sulfide **5,** the presence of which hindered separation and estimation of the yields of the latter since its chromatographic mobility is close to that of compounds **4a-d**. By varying the substrate-to-reagent ratio, we showed that with an increase in the amount of reagent for dipyrrolopyrazines **1a,b**, the yield of monosubstitution products decreases and the yield of disubstitution products increases, while for 5,6-dihydrodipyrrolopyrazines **1c,d** changing the ratio of the reagents did not affect the overall yield and ratio of the reaction products (Table 2). The yields of the monosubstituted products in the case of aromatic dipyrrolopyrazines **3a,b** (10% and 29% respectively) proved to be significantly lower than the yields of the corresponding 5,6-dihydro derivatives **3c,d** (41% and 63%).

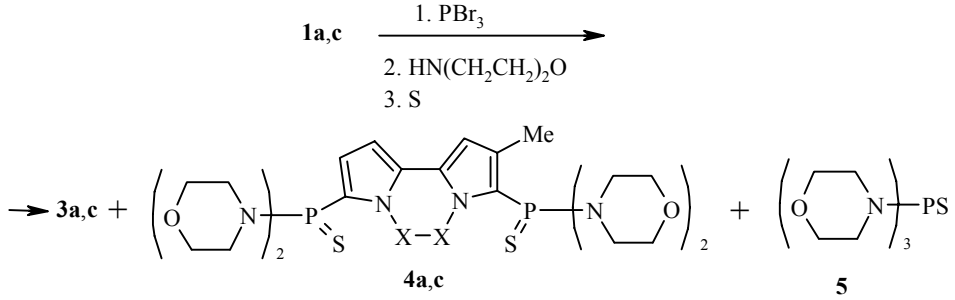
TABLE 1. Product Yields for Phosphorylation of Dipyrrolopyrazines and 5,6-Dihydrodipyrrolopyrazines by Phosphorus Trichloride

Synthesized compound	Yield, % (for substrate:reagent)		
	1:1	1:2	1:4
3a	10	22	73
3b	15	20	42
3c	41	41	41
3d	51	51	51

TABLE 2. Product Yields for Phosphorylation of Dipyrrolopyrazines and 5,6-Dihydrodipyrrolopyrazines by Phosphorus Tribromide

Starting compound	Substrate:reagent	Reaction product (yield, %)
1a	1:1	**3a** (16), **4a** ((traces))
	1:2	**3a** (10), **4a** (6)
	1:4	**3a** (8), **4a** (13)
1b	1:1	**3b** (26), **4b** (5)
	1:2	**3b** (15), **3e** ((traces)), **4b** (24)
		3b (21)*, **3e** (29)*, **4b** (20)*
1c	1:1	**3c** (40), **4c** (8)
	1:2	**3c** (41), **4c** (10)
	1:4	**3c** (38), **4c** (9)
1d	1:1	**3d** (39), **4d** ((traces))
	1:2	**3d** (51), **4d** ((traces))

* Yields of compounds obtained by procedure B.



4 a X–X = –CH=CH– , **c** X–X = $–CH_2–CH_2–$

We should note that in the case of compound **1b**, one more product appears in the reaction mixture: the 10-phosphine-substituted derivatives **3e**, and the ratio of the reaction products changes both when the reaction conditions change and when the substrate-to-reagent ratio changes. For normal addition (method A), the yields of compounds **3b** and **4b** are 15% and 24% respectively and compound **3e** is present in trace amounts. For reverse addition (method B), the yields of products **3b** and **4b** change insignificantly (21% and 20% respectively) and the yield of product **3e** increases up to 29%. Formation of the 10-acetyl-substituted dimethyldipyrrolopyrazine was observed earlier in acylation by acetic anhydride in the presence of magnesium perchlorate [8].

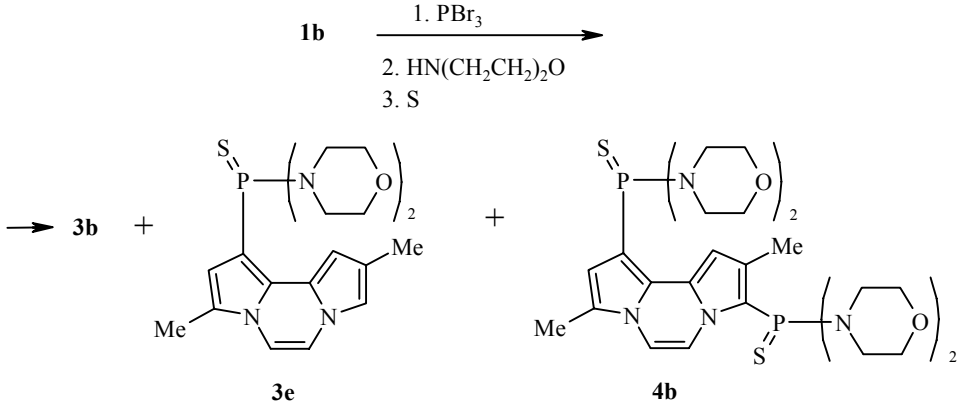


TABLE 3. ^{1}H and ^{31}P NMR Spectral Data for Compounds **3a-e, 4a-c**

Com-pound	Chemical shifts, δ, ppm (spin-spin coupling constant, *J*, Hz)									
	Pyrrole ring protons and substituents					Pyrazine ring protons		Morpholine ring protons		δ ^{31}P relative to H_3PO_4
	H (1)	R (2)	H(R) (8)	H (9)	H(R) (10)	H (5)	H (6)	OCH_2	NCH_2	
1	2	3	4	5	6	7	8	9	10	11
3a	6.40 (1H, dq, $J_{1,P}$ = 3.12, J_{1CH3} = 0.60)	2.54 (3H, dd, $J_{CH3,P}$ = 1.50, $J_{CH3,1}$ = 0.60)	7.32 (1H, dd, $J_{8,9}$ = 2.52, $J_{8,10}$ = 1.02)	6.58 (1H, dd, $J_{9,8}$ = 2.52, $J_{9,10}$ = 3.17)	6.66 (1H, dd, $J_{10,8}$ = 1.02, $J_{10,9}$ = 3.17)	8.63 (1H, d, $J_{5,6}$ = 6.29)	7.60 (1H, d, $J_{6,5}$ = 6.29)	3.67 (8H, m)	3.12, 3.25 (8H, m)	+58.08
3b	6.32 (1H, dq, $J_{1,CH3}$ = 0.80, $J_{1,P}$ = 3.57)	2.44 (3H, br. s)	2.48 (3H, d, $J_{CH3,9}$ = 1.10)	6.52 (1H, dq, $J_{9,10}$ = 3.62, $J_{9,CH3}$ = 1.10)	6.37 (1H, d, $J_{10,9}$ = 3.62)	8.65 (1H, d, $J_{5,6}$ = 6.34)	7.05 (1H, d, $J_{6,5}$ = 6.34)	3.66 (8H, m)	3.10, 3.25 (8H, m)	+67.10
3c	6.12 (1H, d, $J_{1,P}$ = 3.60)	2.33 (3H, d, $J_{CH3,P}$ = 0.83)	6.65 (1H, dd, $J_{8,9}$ = 2.50, $J_{8,10}$ = 1.49)	6.19 (1H, dd, $J_{9,10}$ = 3.50, $J_{9,8}$ = 2.50)	6.31 (1H, dd, $J_{10,9}$ = 3.50, $J_{10,8}$ = 1.49)	4.87 (2H, m)	4.16 (2H, m)	3.65 (8H, m)	3.08, 3.20 (8H, m)	+ 63.25
3d	6.08 (1H, dq, $J_{1,CH3}$ = 0.46, $J_{H,P}$ = 3.71)	2.33 (3H, dd, $J_{CH3,P}$ = 0.86, $J_{CH3,1}$ = 0.46)	2.26 (3H, d, $J_{CH3,9}$ = 0.82)	5.90 (1H, dq, $J_{9,10}$ = 3.55, $J_{9,CH3}$ = 0.82)	6.24 (1H, d, $J_{10,9}$ = 3.55)	4.83 (2H, m)	4.04 (2H, m)	3.64 (8H, m)	3.06, 3.19 (8H, m)	+63.32

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11
3e*	6.79 (1H, dq, $J_{1,3}$ = 1.50, $J_{1,CH3}$ = 0.50)	2.28 (3H, dd, $J_{CH3,1}$ = 0.50, $J_{CH3,3}$ = 0.91)	2.35 (3H, d, $J_{CH3,9}$ = 0.90)	6.50 (1H, dq, $J_{9,P}$ = 5.28, $J_{CH3,9}$ = 0.90)		6.82 (1H, d, $J_{5,6}$ = 6.10)	7.09 (1H, d, $J_{6,5}$ = 6.10)	3.66 (8H, m)	3.19, 3.28 (8H, m)	+65.62
4a	6.55 (1H, d, $J_{1,P}$ = 3.00)	2.50 (3H, br. s)		6.64 (1H, br. s)	7.00 (1H, br. s)	8.76 (1H, d, $J_{5,6}$ = 6.30)	8.42 (1H, d, $J_{6,5}$ = 6.30)	3.63-3.66 (16H, m)	3.08-3.14, 3.22-3.28 (16H, m)	+57.55, +54.66
4b	7.52 (1H, d, $J_{1,P}$ = 3.71)	2.41 (3H, br. s)	2.52 (3H, br. s)	6.55 (1H, d, $J_{9,P}$ = 4.91)		7.08 (1H, d, $J_{5,6}$ = 6.31, $J_{5,P}$ = 1.70)	8.86 (1H, d, $J_{6,5}$ = 6.31)	3.62-3.70 (16H, m)	3.11-3.19, 3.23-3.32 (16H, m)	+65.37, +58.13
4c	6.24 (1H, d, $J_{1,P}$ = 3.32)	2.30 (3H, br. s)		6.62 (1H, dd, $J_{9,10}$ = 3.40, $J_{9,P}$ = 2.57)	6.35 (1H, t, $J_{10,9}$ = 3.40, $J_{10,P}$ = 3.40)	4.84 (2H, m)	4.70 (2H, m)	3.66-3.68 (16H, m)	3.06-3.09, 3.20-324 (16H, m)	+62.85 +59.21

* δ H(3) 7.25 ppm (1H, br. s).

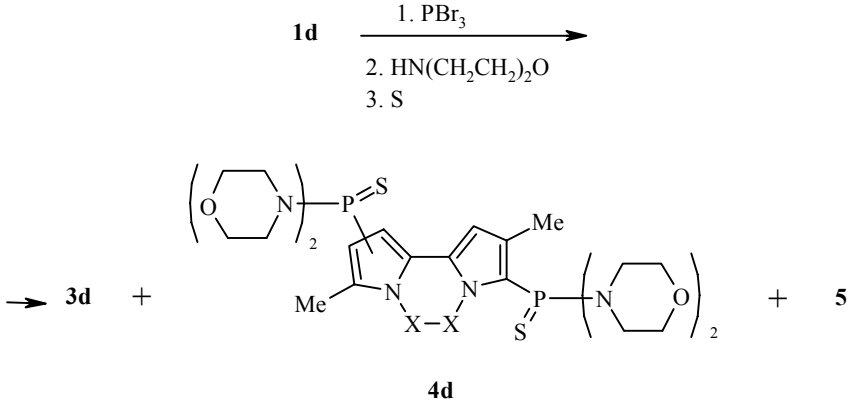
TABLE 4. ^{13}C NMR Spectra of Compounds **1b,d, 3a,c-e, 4a,b**

Com-pound	Chemical shifts, δ, ppm (spin-spin coupling constant, *J*, Hz)						
	C(1)	C(2)	C(3)	C(5)	C(6)	C(8)	C(9)
1b	100.02	122.02	109.52	112.06	110.98	122.17	107.67
1d	102.56 (J_{C1H1} = 168.5; J_{C1H3} = 7.1; $J_{C1CH3(2)}$ = 4.4)	119.39 (J_{C2H1} = 3.4; J_{C2H3} = 6.6; $J_{C2CH3(2)}$ = 6.6)	116.10 (J_{C3H3} = 182.4; J_{C3H1} = 6.4; $J_{C3CH3(2)}$ = 5.6)	43.77	41.08	126.58 (J_{C8H9} = 7.1; J_{C8H10} = 7.1; $J_{C8CH3(8)}$ = 7.1)	106.86 (J_{C9H9} = 168.9; J_{C9H10} = 4.0; $J_{C9CH3(8)}$ = 4.0)
3a	103.24 (J_{C1P} = 12.1)	133.24 (J_{C2P} = 13.7)	109.81 (J_{C3P} = 164.1)	111.47	111.61	114.86	110.70
3c	105.78 (J_{C1P} = 12.1)	130.08 (J_{C2P} = 13.9)	113.70 (J_{C3P} = 165.3)	44.12	44.09	119.75	109.04
3d	105.09 (J_{C1P} = 12.5)	130.91 (J_{C2P} = 13.6)	112.78 (J_{C3P} = 166.4)	43.90	41.08	127.88	107.35
3e	110.48	122.85	112.86	108.40	107.41	122.46 (J_{C8P} = 10.7)	115.26 (J_{C9P} = 11.9)
4a	104.24 (J_{C1P} = 11.7)	132.86 (J_{C2P} = 12.7)	110.70 (J_{C3P} = 166.5)	111.90	109.87	114.91 (J_{C8P} = 160.0)	121.73 (J_{C9P} = 12.5)
4b	110.30 (J_{C1P} = 11.8)	132.80 (J_{C2P} = 13.3)	110.69 (J_{C3P} = 163.1)	113.48	107.31	115.11 (J_{C8P} = 9.2)	123.30 (J_{C9P} = 12.5)

TABLE 4 (continued)

Com-pound	Chemical shifts, δ, ppm (spin-spin coupling constant, *J*, Hz)						
	C(10)	C(11)	C(12)	CH_3(2)	CH_3(8)	OCH_2	NCH_2
1b	97.71	123.36	124.50	12.12	11.27		
1d	100.64 (J_{C10H10} = 170.3; J_{C10H9} = 4.7)	124.35	125.67	11.84			
3a	100.82	122.69	129.37 (J_{C12P} = 8.7)	14.26	11.62	66.75 (J_{CP} = 7.1)	45.04
3c	103.00	123.6	131.72 (J_{C12P} = 10.4)	14.01		66.92 (J_{CP} = 7.8)	45.04
3d	103.19	122.67	132.21 (J_{C12P} = 10.4)	14.00	11.44	66.90 (J_{CP} = 7.5)	45.91
3e	101.35 (J_{C10P} = 155.6)	126.19 (J_{C11P} = 19.1)	122.74	12.28	11.41	66.87 (J_{CP} = 7.7)	45.47
4a	100.67 (J_{C10P} = 11.1)	127.72 (J_{C11P} = 8.5)	128.39 (J_{C12P} = 8.5)	13.98		66.28 (J_{CP} = 6.9)	44.57 44.67
4b	104.05 (J_{C10P} = 156.1)	124.75 (J_{C11P} = 20.3)	127.67 (J_{C12P} = 8.6)	14.37	14.00	66.83 (J_{CP} = 6.8)	45.09 45.47

2,8-Dimethyl-5,6-dihydrodipyrrolopyrazine (**1d**), when reacting with phosphorus tribromide, yields the monosubstitution product **3d**, and a mixture of disubstitution products **4d** which is difficult to separate is obtained in trace amounts.



4d

Using ^{31}P NMR spectroscopy, we studied the effect of solvents on phosphorylation of dipyrrolopyrazines **1**. In addition to benzene, the reactions were conducted in pyridine and methylene chloride. In pyridine, the reactions occur nonselectively: as in the reaction of dimethyldipyrrolopyrazines **1b,d** with phosphorus tribromide (substrate:reagent, 1:1), in the spectra we observed three intense signals in the +96 ppm to +101 ppm region which may be assigned to different monophosphorus-substituted dipyrrolopyrazines, and also signals in the +33 ppm to +52 ppm region corresponding to phosphorus-containing polymers. We should note that the intensity of the latter signals increases significantly over time. When the reaction is carried out with a five-fold excess of phosphorus tribromide, the number of signals increases, suggesting an increase in the number of phosphorylation products.

TABLE 5. Physical and Chemical Characteristics of Synthesized Compounds

Compound	Empirical formula	mp, °C	M calc.	*m/z* (I_{rel}, %)
3a	$C_{19}H_{25}N_4O_2PS$	127-128	404	M^+ 404 (63), 318 (20), 286 (50), 233 (38), 201 (56), 170 (100), 118 (10), 85 (4), 56 (3)
3b	$C_{20}H_{27}N_4O_2PS$	170-171	418	M^+ 418 (53), 332 (11), 300 (26), 247 (32), 215 (51), 185 (27), 184 (100), 118 (14), 86 (10), 55 (16)
3c	$C_{19}H_{27}N_4O_2PS$	122-123	406	M^+ 406 (25), 320 (10), 288 (19), 235 (15), 234 (20), 203 (51), 172 (100), 118 (21), 86 (11), 56 (13)
3d	$C_{20}H_{29}N_4O_2PS$	163-164	420	M^+ 420 (59), 334 (12), 302 (17), 249 (13), 248 (22), 247 (13), 217 (44), 187 (15), 186 (100), 185 (25)
3e	$C_{20}H_{27}N_4O_2PS$	179-180	418	M^+ 418 (14), 300 (22), 246 (31), 245 (44), 184 (46), 183 (41), 87 (72), 86 (41), 64 (17), 57 (100), 40 (83)
4a	$C_{27}H_{40}N_6O_4P_2S_2$	Mixture	638	M^+ 638 (65), 520 (45), 466 (16), 404 (61), 286 (38), 233 (28), 232 (43), 231 (25), 203 (82), 201 (50), 170 (100), 118 (73), 86 (98)
4b	$C_{28}H_{42}N_6O_4P_2S_2$	145-146	652	M^+ 652 (47), 534 (57), 480 (60), 479 (39), 418 (29), 277 (21), 246 (86), 245 (100), 215 (47), 184 (57), 118 (40), 86 (61), 56 (51)
4c	$C_{27}H_{42}N_6O_4P_2S_2$	Mixture	640	M^+ 640 (15), 460 (23), 288 (13), 235 (21), 234 (19), 203 (100), 172 (50), 149 (12), 118 (52), 86 (86), 57 (54)

Phosphorylation occurs similarly in methylene chloride, where the content of polymer products increases. Thus the best results for phosphorylation of dipyrrolopyrazines are obtained when using benzene as the solvent. The structure of the synthesized compounds was confirmed by ^{1}H, ^{13}C, ^{31}P NMR spectroscopy and mass spectroscopy.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-400 spectrometer (400 MHz) in $CDCl_3$ solution at a temperature of 28°C, internal standard TMS. The signals in the proton spectra were assigned using a series of H–{^{1}H} double resonance experiments and comparison with literature data. The ^{13}C NMR spectra (100 MHz) were recorded with ^{13}C–{^{1}H} proton decoupling. To assign the signals in the spectrum of the starting 2,8-dimethyl-5,6-dihydrodipyrrolo[1,2-*a*;2',1'-*c*]pyrazine **1c**, we recorded the ^{13}C spectrum without proton decoupling, and also spectra with selective decoupling from H(9) protons and protons of the CH_3(2) and CH_3(8) groups. The ^{31}P NMR spectra (160 MHz) were recorded relative to H_3PO_4 as an external standard. The mass spectra of the compounds were recorded on a Kratos MS-90 with ionization energy 70 eV. The course of the reaction was monitored using TLC on Silufol UV-254 plates.

2-Methyldipyrrolo[1,2-*a*;2',1'-*c*]pyrazine (1a), 2,8-Dimethyldipyrrolo[1,2-*a*;2',1'-*c*]pyrazine (1b), 2-Methyl-5,6-dihydrodipyrrolo[1,2-*a*;2',1'-*c*]pyrazine (1c), 2,8-Dimethyl-5,6-dihydrodipyrrolo-[1,2-*a*;2',1'-*c*]pyrazine (1d) were synthesized according to the procedure in [3].

2-Methyldipyrrolo[1,2-*a*;2',1'-*c*]pyrazin-3-yl(dimorpholino)phosphine Sulfide (3a), 2,8-Dimethyl-dipyrrolo[1,2-*a*;2',1'-*c*]pyrazin-3-yl(dimorpholino)phosphine Sulfide (3b), 2-Methyl-5,6-dihydro-dipyrrolo[1,2-*a*;2',1'-*c*]pyrazin-3-yl(dimorpholino)phosphine Sulfide (3c), 2,8-Dimethyl-5,6-dihydro-dipyrrolo[1,2-*a*;2',1'-*c*]pyrazin-3-yl(dimorpholino)phosphine Sulfide (3d), 3,9-Dimethyldipyrrolo-[1,2-*a*;2',1'-*c*]pyrazin-1-yl(dimorpholino)phosphine Sulfide (3e)*, 2-Methyldipyrrolo[1,2-*a*;2',1'-*c*]-pyrazine-3,8-diylbis[(dimorpholino)phosphine sulfide] (4a), 3,9-Dimethyldipyrrolo[1,2-*a*;2',1'-*c*]pyrazine-1,8-diylbis[(dimorpholino)phosphine Sulfide] (4b)*, 2-Methyl-5,6-dihydrodipyrrolo[1,2-*a*;2',1'-*c*]-pyrazine-3,8-diylbis[(dimorpholino)phosphine Sulfide] (4c) were synthesized by procedure A or B. The yields and constants for the synthesized compounds are given in Tables 1, 2, and 5; the spectral characteristics of the studied compounds are given in Tables 3, 4, and 5. We could not do elemental analysis because of the instability of the phosphorylated derivatives of dipyrrolo[1,2-*a*;2',1'-*c*]pyrazines **3a-e, 4a-c**.

A. A solution of phosphorus tribromide in benzene (2 ml) was added to a solution of dipyrrolopyrazine (1 mmol) and pyridine (1 mmol) in benzene (2 ml), with stirring and cooling with ice. The mixture was held for 1 h at that temperature. Heptane (5 ml) was added and the precipitate was filtered out. A solution of morpholine (2 mmol) and triethylamine (3 mmol) in heptane (5 ml) was added to the filtrate with cooling. This was held at room temperature for 2 h. The precipitate was filtered out, sulfur (1 mmol) was added to the filtrate, and the mixture was heated for 1 h at 80°C. The solution was evaporated down to dryness, the dry residue was chromatographed (ethylacetate–petroleum ether (70-100°C), 1:3) on silica gel (100/160). The product was recrystallized from heptane.

B (reverse addition). A solution of dipyrrolopyrazine (1 mmol) and pyridine (1 mmol) in benzene (2 ml) was added to a solution of phosphorus tribromide in benzene (2 ml), with stirring and cooling by ice. This was held for 1 h at this temperature. Heptane (5 ml) was added and the precipitate was filtered out. A solution of morpholine (2 mmol) and triethylamine (3 mmol) in heptane (5 ml) was added to the filtrate with cooling. The mixture was held for 2 h at room temperature. The precipitate was filtered out, sulfur (1 mmol) was added to the

* Substitution products of 2,8-dimethyldipyrrolo[1,2-*a*;2',1'-*c*]pyrazine.

filtrate, and the mixture was heated for 1 h at 80°C. The solution was evaporated down to dryness, the dry residue was chromatographed (ethylacetate–petroleum ether (70-100°C), 1:3) on silica gel (100/160). The product was recrystallized from heptane.

REFERENCES

1. V. I. Terenin, A. V. Borisov, E. L. Ruchkina, and A. P. Pleshkova, *Khim. Geterotsikl. Soedin.*, 236 (1999).
2. A. A. Tolmachev, S. P. Ivonin, A. V. Kharchenko, and E. S. Kozlov, *Zh. Obshch. Khim.*, **62**, 465 (1992).
3. A. A. Tolmachev, S. P. Ivonin, A. A. Chaikovskaya, T. E. Terikovskaya, *Zh. Obshch. Khim.*, **65**, 2059 (1995).
4. A. A. Tolmachev, A. A. Chaikovskaja, T. E. Terikovskaja, S. P. Ivonin, and A. M. Pinchuk, *Heteroatom. Chem.* **7**, 525 (1996).
5. A. A. Tolmachev, S. P. Ivonin, and A. M. Pinchuk, *Heteroatom. Chem.*, **6**, 407 (1995).
6. A. A. Tolmachev, G. V. Oshovskii, A. S. Merkulov, and A. M. Pinchuk, *Khim. Geterotsikl. Soedin.*, 1288 (1996).
7. V. I. Terenin, E. L. Ruchkina, I. F. Leshcheva, A. P. Pleshkova, and Yu. G. Bundel', *Khim. Geterotsikl. Soedin.*, 52 (1997).
8. E. L. Ruchkina, Dissertation for degree of Candidate of Chemical Sciences, Moscow (1998).