Selected Reactions on the *o*-Aminonitrile System of Substituted Pyrroles [1]

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The synthesis of the difficult to obtain pyrrolo[2,3-*d*]pyrimidine-2,4-diamine (**4**) is reported. Furthermore, some unexpected reactions on the 2-aminopyrrole-3-carbonitrile system are described **15-17**.

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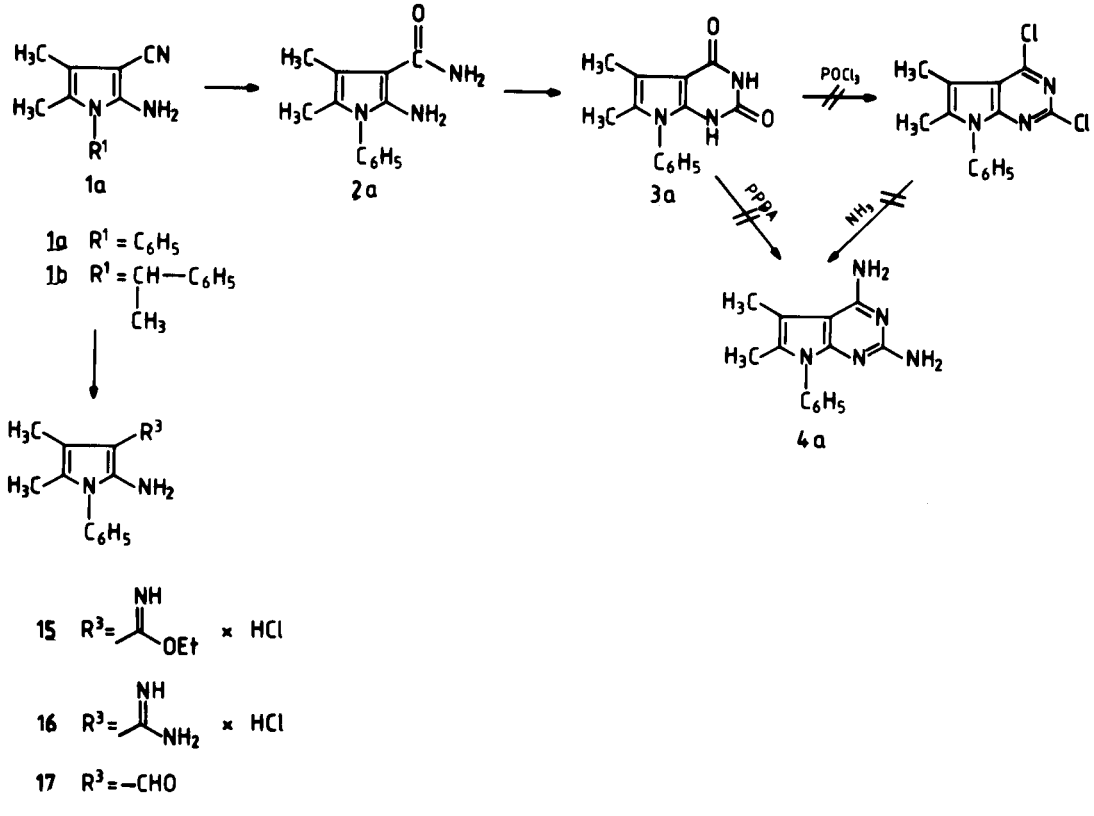
Aromatic and heterocyclic *o*-aminonitriles are widely used building blocks for condensed nitrogen heterocycles. In most cases they are readily available and open a fascinating field of study for chemists [2]. For a long time now the special 2-amino-pyrrole-3-carbonitrile system has been our preferential basis for the synthesis of condensed heterocycles, *e.g.* pyrrolo[2,3-*d*]- and [1,2-*a*]pyrimidines, pyrrolo[2,3-*b*]pyridines, pyrrolo[2,3-*c*]thiadiazines [3a-f]. As one aspect of our ongoing work, we have a special interest in the synthesis of the pyrrolo[2,3-*d*]pyrimidine-2,4-di amines of type **4**. In general, condensed pyrimidine-2,4-diamines can be obtained by the following two methods: 1) Substitution of a suitable pyrimidine derivative with ammonia, 2) appropriate cyclisation directly to the pyrimidine-2,4-diamine system.

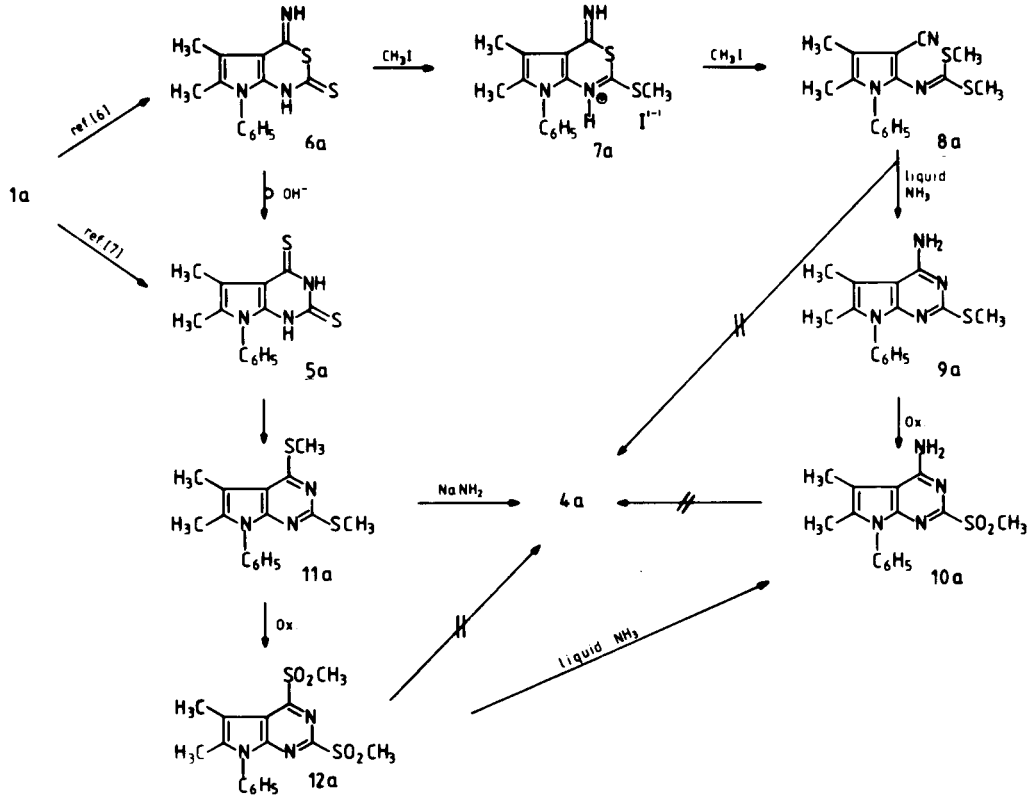
Robins and co-workers have recently failed in the bis-amination of pyrrolopyrimidine derivatives in positions 2 and 4 [4]. Nevertheless, we decided to examine both methods for the synthesis of the above mentioned compounds. The present paper deals with the results of this study.

Using following method 1), we synthesized the pyrrolo-[2,3-*d*]pyrimidine-2,4-dione **3a** by cyclisation of the pyrrolecarbonamide **2a** with urea in dimethylformamide (Scheme 1). The chlorination with phosphorus oxychloride yielded no results. In contrast, the chlorination of a monolactam such as 5,6-dimethylpyrrolo[2,3-*d*]pyrimidin-4-one led to the 4-chloro-compound [3b]. The attempted direct amination procedure of **3a** with phenylphosphorusdiamide (PPDA) was also unsuccessful.

Scheme 1



Scheme II



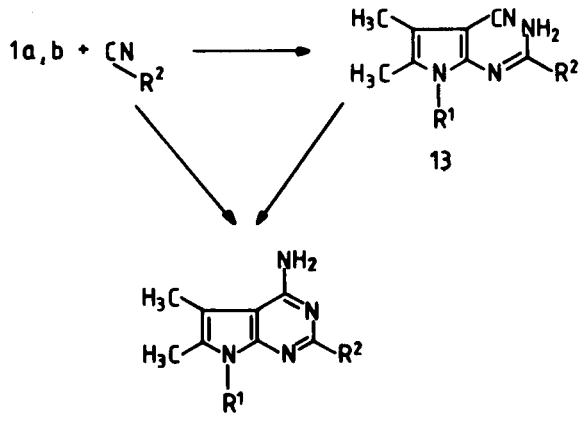
In the following experiment we tried to replace the functional sulfur groups with ammonia. There are two alternatives for the synthesis of pyrrolopyrimidine-2,4,-dithione **5a** and its derivative. Starting from the pyrrolocarbonitrile **1a** [3a] either a) reaction with carbon disulfide in pyridine [6] or b) direct cyclisation with potassium xanthogenate [7] is possible (Scheme II).

Methylation of **6a** yielded the hydroiodide **7a**. A second methylation step resulted in a ring opening reaction and led to **8a**. It was not possible to convert **8a** into **4a** with liquid ammonia under pressure. It was only possible to replace one methylmercapto-group, resulting in **9a**. Oxidation of **9a** with *m*-chloroperoxybenzoic acid led to **10a**. When **10a** was treated with liquid ammonia under pressure, no reaction could be registered. By modifying **5a** by methylation and oxidation, with reaction in the same manner as above, compounds **11a** and **12a** were obtained. Neither of the two, when treated with liquid ammonia, led to the desired compound **4a**. Only **12a** could be induced to react to the monoamine **10a**. The use of a stronger nucleophile than ammonia - *i.e.* sodium amide in toluene - proved to be more successful. Compound **4a** could be synthesized in low yields (20%) *via* the Tschischibabin reaction.

However, because of the less satisfying results, we tried to obtain the desired compound by direct cyclisation of the 2-amino-pyrrole-3-carbonitrile (Method 2). Several methods have been previously described. Most favoured is the ring closure with guanidine or chloroformamidine, although the yields in most cases are low [2,8-11]. With neither reagent, under various conditions, was it possible to obtain the desired compound **4a**. A further possibility exists in the reaction of cyanamide in the presence of pyridine hydrochloride [9]. This method also failed in our case. However, by changing the reaction conditions, we are able to obtain the guanidine derivative **13a** as an intermediate in good yield (Scheme III). In order to achieve this, it was necessary to apply a drastic method, *e.g.* boiling for 27 hours in dioxane in the presence of gaseous hydrogen chloride. The ensuing ring closure in methanol saturated with ammonia was nearly quantitative.

Treatment of **4b** with polyphosphoric acid yielded **4c** [5]. Working according to the general method for synthesis of condensed pyrimidines described by Shishoo and coworkers [13], we found that 2-aminopyrrolo-3-carbonitriles required stronger conditions for ring closure with aliphatic or aromatic nitriles as described in the literature. In 1980 Shishoo [13] suggested that the cyclisation reaction

Scheme III



13a $R^1 = C_6H_5$, $R^2 = NH_2$

13b $R^1 = CH(CH_3)-C_6H_5$, $R^2 = NH_2$

13c $R^1 = CH(CH_3)-C_6H_5$, $R^2 = CH_3$

4a-c, 14a-l (s. Table I)

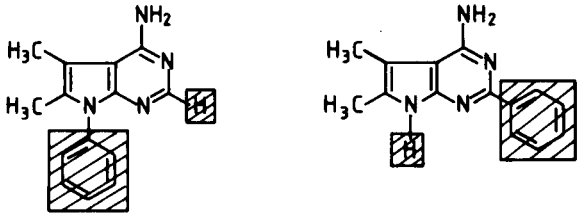
4a $R^1 = C_6H_5$, $R^2 = NH_2$

4b $R^1 = CH(CH_3)-C_6H_5$, $R^2 = NH_2$

4c $R^1 = H$, $R^2 = NH_2$

procedes *via* an amidine intermediate. We can now confirm this, because we are able to successfully isolate this intermediate **13a-c**, by the reaction of **1a,b** respectively with cyanamide or with acetonitrile. Furthermore, we were able to show that it is possible to bring aromatic nitriles with space-filling groups to reaction (Table 1). By treating **14g-i** with polphosphoric acid [5], it is possible to obtain isomers of the 7-substituted pyrrolopyrimidines, with proven antiphlogistic and anticonvulsant properties [14a,b] (Scheme IV).

Scheme IV



It is noteworthy that **14k** showed none of these activities, although it has the same base unit as Zaprinast, a potent inhibitor of reagin-mediated anaphylaxis [14c]. An appropriate study of this research is currently in progress. An interesting phenomenon can be observed in the ^{1}H-nmr spectra of the above-mentioned compounds. For **14k** for example, the aromatic hydrogens exhibit signals with different chemical shifts at different integrations. A signal group of 3 aromatic hydrogens is found at 7.4 ppm, whereas 2 hydrogen signals are detected at 8.4 ppm. Similar effects are revealed in the spectra of the 2-*ortho*-chlorophenyl derivative **14e**. The aromatic region is also split into two different signal groups at 8.1 ppm (1H) and 7.6 ppm (3H). So it is evident that the ortho-hydrogens of the 2-phenyl moiety are shifted downfield under the influence of the lone pairs of the nitrogens at position 1 and 3 respectively. This interpretation is clearly supported by a study from Murrell and co-workers on the steric requirements of phenylsubstituents in nitrogen heterocycles [15].

According to published reports, it should be impossible to synthesize iminoethers using aromatic or heteroaromatic nitriles which are substituted in the ortho position [8,16]. Therefore, it is interesting to note that **1a** reacts in ethanol which is saturated with hydrogen chloride gas to the iminoether derivative **15** in high yield. The reaction in ethanol saturated with ammonia produces the resulted amidine derivative **16** in low yield (Scheme I). Likewise by compound **1a** we can demonstrate its ability to reduce the cyanogroup to the aldehyde function **17**. This reaction requires drastic conditions *i.e.* refluxing with lithium aluminum hydride in dioxane.

EXPERIMENTAL

Melting points (°C) were determined in open capillaries and are uncorrected. Infrared spectra were recorded in potassium bromide on a Beckmann spectrometer IR 33, The ^{1}H-nmr spectra were taken on a Varian T 60, with TMS as the internal reference. The pyrrolecarboni-

triles **1a** and **1b** were prepared according to [3a,5].

2-Amino-4,5-dimethyl-1-phenyl-1*H*-pyrrole-3-carbonamide (**2a**).

Compound **1a** (6.3 g, 30 mmoles) was stirred in a mixture of polyphosphoric acid (60.0 g)/phosphoric acid (75.0 g) and heated for 5 hours. The temperature was held constant at 110-120°. After cooling, crushed ice and ammonia (25%) was added until *p*H 7 obtained. The precipitate was collected and recrystallized from ethanol, yield 1.4 g (66%), mp 198-200°.

Anal. Calcd. for $C_{13}H_{15}N_3O$: C, 68.13; H, 6.56; N, 18.35. Found: C, 68.08; H, 6.60; N, 18.47.

5,6-Dimethyl-7-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (**3a**).

Compound **2a** (4.3 g, 20 mmoles) and urea (25.0 g) were dissolved in 50.0 g of dimethylformamide and refluxed for 4 hours. After cooling, the white crystals were collected and recrystallized from dimethylformamide, yield 1.65 g (65%), mp 320-325°.

Anal. Calcd. for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.72; H, 5.20; N, 16.96.

5,6-Dimethyl-7-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine-2,4-diamine (**4a**).

a) Compound **11a** (2.52 g, 8 mmoles) was dissolved in 20 ml of dry toluene. After addition of a suspension of sodiumamide (10 ml) the mixture was refluxed for 30 minutes. After cooling, the reaction mixture was stirred with care in a cold solution of sodium hydroxide (5%). The resulting precipitate from both phases was collected by filtration and recrystallized from ethanol, yield 0.5 g (20%).

b) Compound **13a** (6.50 g, 26 mmoles) was dissolved in a solution of sodium (2.6 g, 0.1 mole) in 100 ml of methanol. After stirring for 12 hours at room temperature, the precipitate was collected by filtration and recrystallized, yield 5.45 g (84%).

c) Compound **13a** (6.50 g, 26 mmoles) was dissolved in methanol (60.0 ml), saturated with ammonia gas, and stirred for 12 hours at room temperature, yield 5.84 g (90%), mp 278-280°; ^{1}H-nmr (DMSO-d_6): δ (ppm) 2.05 (s, 3H, H_6); 2.15 (s, 3H, H_5), 5.45 (s, 2H, NH_2), 6.1 (s, 2H, NH_2) 7.45 (m, 5H, C_6H_5).

Anal. Calcd. for $C_{14}H_{15}N_5$: C, 66.38; H, 5.97; N, 27.65. Found: C, 66.51; H, 6.01; N, 27.28.

5,6-Dimethyl-7-(DL-1-phenylethyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine-2,4-diamine (**4b**).

d) Compound **13b** (4.2 g, 15 mmoles) was dissolved in a solution of sodium methylate (2.0 g) in methanol (100 ml). The precipitate was collected by filtration and recrystallized from ethanol, yield 3.7 g (88%), mp 177°.

Anal. Calcd. for $C_{16}H_{19}N_5$: C, 68.30; H, 6.82; N, 21.04. Found: C, 68.23; H, 6.77; N, 20.79.

5,6-Dimethyl-7*H*-pyrrolo[2,3-*d*]pyrimidine-2,4-diamine (**4c**) see ref [5].

5,6-Dimethyl-7-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine-2,4(1H,3H)-dithione (**5a**).

According to ref [7], **1a** (14.5 g, 0.70 mmoles) was refluxed in a mixture of potassium xanthogenate (16.0 g, 0.1 mole) in l-butanol (115.0 g) for 3.5 hours. After cooling, the solid mass was collected by filtration, dissolved in dimethylformamide/water (40 ml/60 ml) and acidified with acetic acid (~50%). The precipitate was collected and recrystallized from methanol, yield 19.3 g (98%), mp 278°.

Anal. Calcd. for $C_{14}H_{13}N_3S_2$: C, 58.54; H, 4.53; N, 14.63. Found: C, 58.09; H, 4.60; N, 14.99.

4-Imino-5,6-dimethyl-7-phenyl-4,7-dihydropyrrolo[2,3-*d*][1,3]thiazine-2(1*H*)-thione (**6a**).

According to ref [6], **1a** (5.0 g, 24 mmoles) was refluxed for 2 hours in a mixture of 50 ml of carbon disulfide and 40 ml of pyridine. After cooling the crystals were collected by filtration and recrystallized from ethanol, yield 7.2 g (74%), mp 313-316°.

Anal. Calcd. for $C_{14}H_{13}N_3S_2$: C, 58.54; H, 4.53; N, 14.63. Found: C, 58.58; H, 4.49; N, 14.51.

4-Imino-5,6-dimethyl-2-methylthio-7-phenyl-4,7-dihydropyrrolo-[2,3-*d*][1,3]thiazine Hydroiodide (**7a**).

A solution of **6a** (3.0 g, 10 mmoles) in methanol (100 ml) was added with methyl iodide (15.0 g). The mixture was refluxed for one hour. The excess methanol was removed *in vacuo*. The resulting oily residue was mixed with diethylether. The precipitate was collected by filtration, yield 4.0 g (96%), mp 208°.

Anal. Calcd. for $C_{15}H_{16}IN_3S_2$: C, 41.96; H, 3.73; N, 9.80. Found: C, 41.87; H, 3.68; N, 9.99.

3-Cyano-4,5-dimethyl-1-phenyl-1*H*-pyrrole-2-imiddimethyldithiocarbnate (**8a**).

Compound **7a** (2.0 g, 5 mmoles) was stirred at room temperature for one hour in a mixture of potassium hydroxide (5%) and methyl iodide (4.0 g). The resulting precipitate was collected by filtration and recrystallized from ethanol, yield 0.9 g (57%), mp 140-142°; ^{1}H-nmr (DMSO-d_6): δ (ppm) 1.95 (s, 3H, H_5), 2.1 (s, 3H, H_4), 2.4 (s, 6H, 2 x SCH_3), 7.4 (m, 5H, C_6H_5).

Anal. Calcd. for $C_{16}H_{17}N_3S_2$: C, 60.94; H, 5.43; N, 13.33. Found: C, 60.81; H, 5.37; N, 13.66.

5,6-Dimethyl-2-methylthio-7-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine-4-amine (**9a**).

Compound **8a** (3.0 g, 9.5 mmoles) was suspended in liquid ammonia (100 ml), and immediately sealed in a steel vessel and heated at 100° for 3 hours. After cooling the vessel in an ice bath, the pressure in the vessel was carefully released. The resulting solid was recrystallized from ethanol, yield 2.8 g (100%), mp 192°; ^{1}H-nmr (DMSO-d_6): δ (ppm) 2.1 (s, 3H, H_6), 2.35 (s, 6H, H_5, SCH_3), 6.6 (s, 2H, NH_2), 7.5 (m, 5H, C_6H_5).

Anal. Calcd. for $C_{15}H_{16}N_4S$: C, 63.26; H, 5.67; N, 19.71. Found: C, 62.92; H, 5.72; N, 19.55.

4-Amino-5,6-dimethyl-7-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine-2-methylsulfone (**10a**).

a) Compound **9a** (2.0 g, 7 mmoles) was dissolved in 100.0 ml of ethanol, after addition of *m*-chloroperoxybenzoic acid (3.6 g, 40 mmoles) the mixture was stirred at room temperature for 12 hours. The yellowish crystals were collected by filtration and recrystallized from ethanol, yield 1.9 g (96%), mp 237-240°; ^{1}H-nmr (DMSO-d_6): δ (ppm) 2.15 (s, 3H, H_6), 2.4 (s, 3H, H_5), 3.2 (s, 3H, SO_2CH_3), 7.2 (s, 2H, NH_2), 7.5 (s, 5H, C_6H_5).

Anal. Calcd. for $C_{15}H_{16}N_4O_2S$: C, 56.96; H, 5.10; N, 17.71. Found: C, 56.91; H, 5.05; N, 17.98.

b) Compound **12a** (1.2 g, 3.2 mmoles) was suspended in liquid ammonia (50 ml), and treated in an analogous manner to that described for **9a**.

5,6-Dimethyl-2,4-bis(methylthio)-7-phenyl-7*H*-pyrrolo[2,3-*d*]pyrimidine (**11a**).

Compound **5a** (4.05 g, 15 mmoles) was added to ammonium hydroxide (100 ml, 0.75%) and methyl iodide (20.8 g). After refluxing for 30 minutes, the reaction mixture was evaporated *in vacuo*. The residue was acidified with acetic acid (20%) and extracted with methylene chloride (3 x 40 ml). The organic layer was removed on a rotary evaporator. The residue was recrystallized from methanol, yield 3.1 g (66%), mp 149°; ^{1}H-nmr (DMSO-d_6): δ (ppm) 2.1 (s, 3H, H_6), 2.4 (s, 3H, H_5), 2.5 (s, 3H, C_2-SCH_3), 2.65 (s, 3H, C_4-SCH_3), 7.5 (m, 5H, C_6H_5).

Anal. Calcd. for $C_{16}H_{17}N_3S_2$: C, 60.94; H, 5.43; N, 13.33. Found: C, 60.84; H, 5.34; N, 13.48.

5,6-Dimethyl-7-phenyl-2,4-bis(methylsulfonyl)-7*H*-pyrrolo[2,3-*d*]pyrimidine (**12a**).

Compound **11a** (2.0 g, 7 mmoles) was dissolved in ethanol (90.0 ml), *m*-chloroperoxybenzoic acid (3.6 g, 40 mmoles) was added. The mixture was stirred at room temperature for 12 hours. The resulting crystals were

collected by filtration and recrystallized from ethanol, yield 1.8 g (75%), mp 174°.

Anal. Calcd. for $C_{16}H_{17}N_3O_4S_2$: C, 50.66; H, 4.52; N, 11.08. Found: C, 50.78; H, 4.60; N, 11.30.

3-Cyano-4,5-dimethyl-1*H*-pyrrole-2-amidines **13a-c**.

Compound **13a**.

Compound **1a** (5.25 g, 25 mmoles) and cyanamide (1.16 g, 27 mmoles) were dissolved in *p*-dioxane (50.0 ml). The solution was continuously saturated with hydrogen chloride gas at room temperature for 5 hours, and subsequently for 2 hours at 80°. After this time the mixture was refluxed for 20 hours. The solvent was removed on a rotary evaporator. Ice-water was added to the residue, following alkalisation with ammonium hydroxide (10%). The solid was collected by filtration and recrystallized from benzene, yield 4.1 g (65%), mp 267-269°; ^{1}H-nmr (DMSO-d_6): δ (ppm) 1.9 (s, 3H, H_5), 2.05 (s, 3H, H_4), 5.55 (s broad, 4H, 2 x NH_2), 7.4 (m, 5H, C_6H_5).

Anal. Calcd. for $C_{14}H_{15}N_5$: C, 66.38; H, 5.97; N, 27.65. Found: C, 66.05; H, 6.05; N, 27.90.

Compound **13b**.

Compound **1b** (5.76 g, 20 mmoles) brought to reaction in an analogous manner as described for compound **13a**, yield 5.0 g (74%); mp 168-170°.

Anal. Calcd. for $C_{16}H_{19}N_5$: C, 68.30; H, 6.81; N, 24.89. Found: C, 68.36; H, 6.76; N, 24.97.

Compound **13c**.

Compound **13c** was isolated in low yield (20%) from the filtrate of **14g** after the filtrate had been allowed to stand at 0° for 24 hours. The white crystals were collected by filtration and recrystallized from ethanol, mp 232-234°.

Anal. Calcd. for $C_{17}H_{20}N_4$: C, 72.82; H, 7.19; N, 19.99. Found: C, 72.90; H, 7.25; N, 20.13.

General Method for the Synthesis of the 2,7-Disubstituted-5,6-dimethylpyrrolo[2,3-*d*]pyrimidine-4-amines **14a-l**.

The pyrrole **1a** or **1b** (20 mmoles) was dissolved in 2-propanol (40 ml). Sodium methylate (2.72 g, 40 mmoles) and acetonitrile (or another nitrile, according to the compound to be prepared) (20 mmoles) were added to the solution. The solution was refluxed for several hours (see Table I).

2-Amino-4,5-dimethyl-1-phenyl-1*H*-pyrrol-3-ylimino Ethyl Ether Hydrochloride (**15**).

Compound **1a** (4.22 g, 20 mmoles) was dissolved in ethanol (100.0 ml), saturated with hydrogen chloride gas and stirred at room temperature for 3 days. The solid was collected by filtration and recrystallized from ethanol, yield 4.6 g (78%), mp 257°.

Anal. Calcd. for $C_{15}H_{20}ClN_3O$: C, 61.33; H 6.87; N, 14.31. Found: C, 61.43; H, 6.84; N, 14.19.

2-Amino-4,5-dimethyl-1-phenyl-1*H*-pyrrol-3-ylcarbamidine Hydrochloride (**16**).

Compound **15** (2.93 g, 10 mmoles) was added to a solution of ethanol, saturated with ammonia gas (40 ml). The mixture was stirred for 12 days at room temperature. The solvent was removed on a rotary evaporator. The residue was suspended in methylene chloride, and **16** was isolated by filtration, yield 0.7 g (27%); mp 280°.

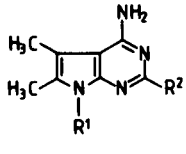
Anal. Calcd. for $C_{13}H_{17}ClN_4$: C, 58.97; H, 6.49; N, 21.17. Found: C, 58.91; H, 6.44; N, 21.34.

2-Amino-4,5-dimethyl-1-phenyl-1*H*-pyrrol-3-ylcarbaldehyde (**17**).

Compound **1a** (4.22 g, 20 mmoles) was dissolved in dry dioxane (50.0 ml). The mixture was added to a stirred suspension of lithium aluminium hydride (0.78 g, 20 mmoles) in dry dioxane (30.0 ml). The temperature was slowly raised in order to reflux for 30 minutes (caution). After cooling, first ice-water (75 ml) was added dropwise, then sulfuric acid (3*N*, 30 ml). The solvent was removed with an evaporator to 50 ml. Subsequently

Table I

2 - Substituted Pyrrolo [2,3 - d] pyrimidine - 4 - amines



Compound No	R^1	R^2	reaction time	Mp °C	% yield	Molecular Formula	Molecular Weight	Microanalysis Calcd. / Found % C	% H	% N
14 a	C_6H_5	H_3C—	20 h	239	59.0	$C_{15}H_{16}N_4$	252.31	71.40 71.20	6.39 6.36	22.21 22.24
b	C_6H_5	C_6H_5	24 h	212–15	20.7	$C_{20}H_{18}N_4$	314.38	76.40 76.11	5.77 5.75	17.82 17.68
c	C_6H_5	[1] naphthyl—CH_2—	18 h	191	50.4	$C_{25}H_{22}N_4$	378.46	79.33 79.44	5.86 5.91	14.81 14.99
d	C_6H_5	benzhydryl	62 h	176–78	67.5	$C_{24}H_{24}N_4$	368.46	78.23 78.13	6.57 6.51	15.21 15.38
e	C_6H_5	o—Cl—C_6H_4	30 h	215	57.4	$C_{20}H_{18}ClN_4$	349.87	68.67 68.58	5.19 5.13	16.02 16.52
f	C_6H_5	p—Cl—C_6H_4	18 h	212	64.5	$C_{20}H_{18}ClN_4$	349.87	68.67 68.72	5.19 5.23	16.02 16.44
g	C_6H_5—CH(CH$_3$)—	H_3C—	44 h	292	51.8	$C_{17}H_{20}N_4$	280.36	72.82 72.78	7.19 7.37	19.99 19.85
h	C_6H_5—CH(CH$_3$)—	C_6H_5	30 h	175	38.1	$C_{22}H_{22}N_4$	342.43	77.16 77.26	6.48 6.42	16.36 16.06
i	C_6H_5—CH(CH$_3$)—	p—Cl—C_6H_4	20 h	181	33.5	$C_{22}H_{20}ClN_4$	375.88	70.30 70.43	5.37 5.31	14.91 14.86
j	H	H_3C—	20 h	347	33.8	$C_9H_{12}N_4$	176.22	61.34 61.45	6.86 6.92	31.80 31.71
k	H	C_6H_5	20 h	259	76.4	$C_{14}H_{14}N_4$	238.28	70.56 70.34	5.92 6.02	23.51 23.64
l	H	p—Cl—C_6H_4	24 h	290	98.2	$C_{13}H_{14}ClN_4$	272.74	59.66 59.56	5.40 5.45	21.61 21.49

the residue was alkalized with potassium hydroxide (3*N*), and extracted with diethyl ether. The organic solvent was separated and removed on a rotary evaporator. The residue was recrystallized from ethanol, yield 2.1 g (49%), mp 147-149°; ^{1}H-nmr (DMSO-d_6): δ (ppm) 1.83 (s, 3H, H_5), 2.1 (s, 3H, H_4), 6.35 (s, 2H, NH_2), 7.5 (s, 5H, C_6H_5), 9.45 (s, 1H, CHO).

Anal. Calcd. for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.08. Found: C, 72.78; H, 6.52; N, 12.95.

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