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# 1-Methyl-2-(1'-methyl-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]-imidazole. Synthesis and Electrophilic Substitution Reactions

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**Abstract**—2-(1'-Methyl-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]imidazole was synthesized by heating 9,10-phenanthrenequinone and 1-methyl-2-pyrrolecarboxaldehyde in glacial acetic acid in the presence of ammonium acetate. The reactions of electrophilic substitution (nitration, bromination, sulfonation, formylation, acylation) were studied for the product of its N-methylation in the KOH–DMSO medium. The electrophilic attack was found to affect exclusively the pyrrole ring.

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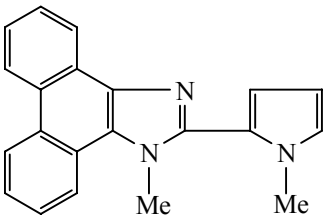
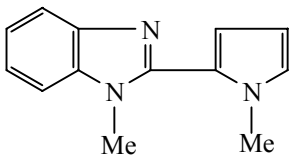
In extention of the search for new biologically active compounds and luminophores in a series of fused derivatives of 2-hetarylimidazoles, we set a goal to develop or find a convenient synthesis method, to study the relative reactivity of 1-methyl-2-(1'-methyl-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]imidazole **Ia**, and to compare it with the benzimidazole analog **II**.



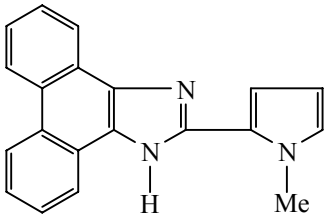

**Ia**



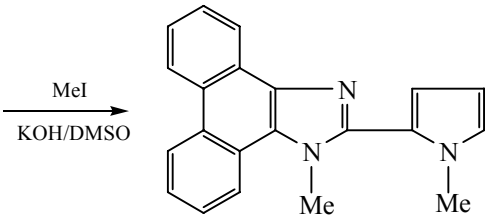

**II**

It was shown earlier [1] that in contrast to other methods [2, 3] the synthesis of 2-(2'-furyl)-1*H*-and 2-(2'-thienyl)-1*H*-phenanthro[9,10-*d*]imidazole gives the best results in the case of condensation of 9,10-phenantrenequinone and the corresponding aldehydes in the presence of ammonium acetate in glacial acetic acid [4]. Our studies confirm that the method of Steck and Day is also appropriate to produce 2-(1'-methyl-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]imidazole **I**, but *n*-propanol should be used instead of acetic acid due to the high acidophobicity of 1-methyl-2-pyrrolecarboxaldehyde. The yield of **I** does not exceed 60%.

The methylation reaction of compound **I** was carried out in a KOH–DMSO system using equivalent amount of methyl iodide to produce the target product in high yield [5]. The product **Ia** was subjected to the action of electrophilic reagents like acetyl nitrate, bromine in dichloroethane, pyridine sulfotrioxide in dichloroethane, the Vilsmeier reagent, urotropine in polyphosphoric acid, acetic anhydride in the presence of perchloric acid, benzoic acid in polyphosphoric acid.



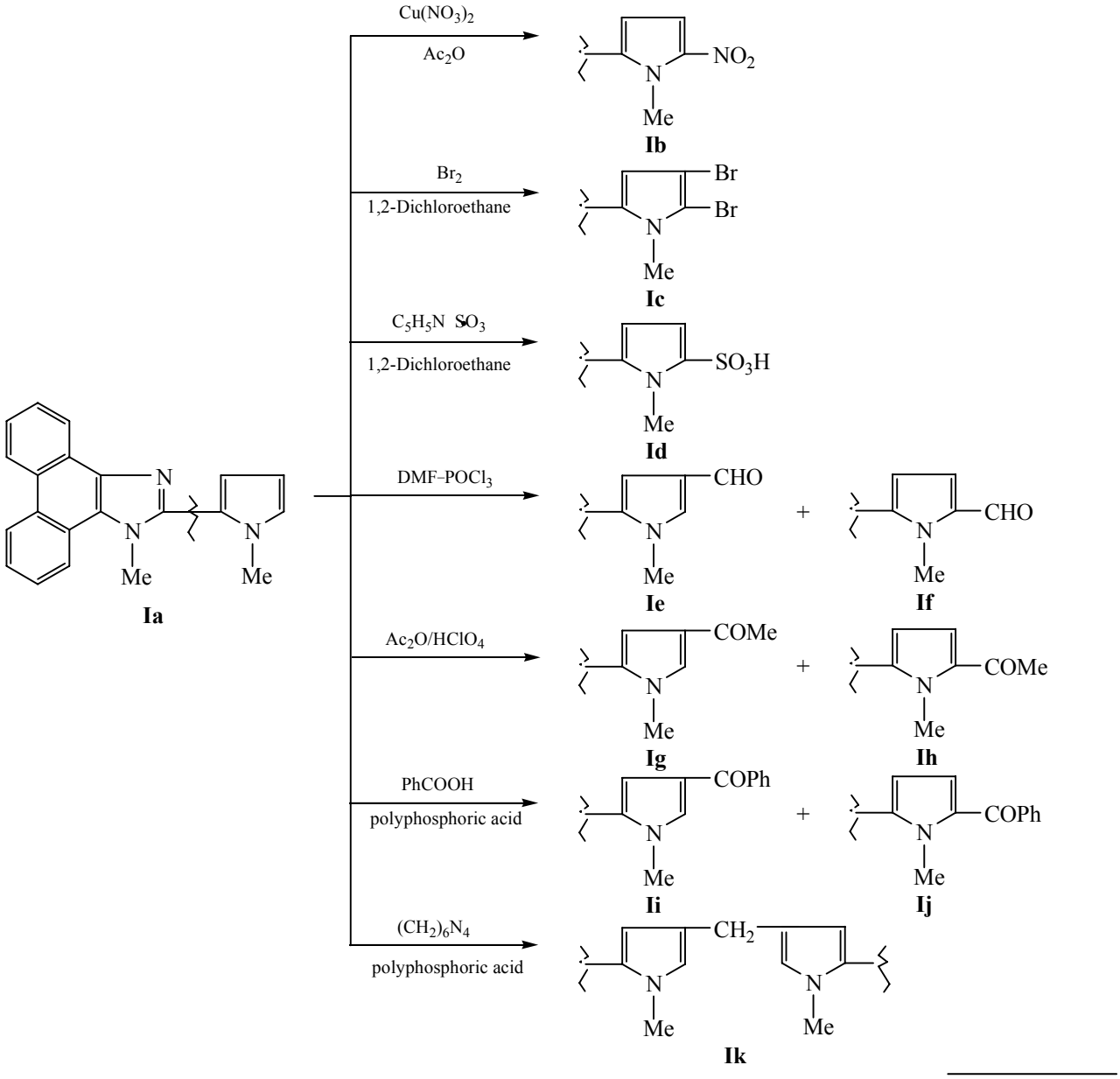

**I**




**Ia**

In previous studies [6, 7] we have shown that various systems of 2-hetarylimidazoles stabilize in their composition five-membered π-excessive heterocycles. Obviously, this is due to the electron-withdrawing nature of the 2-imidazolyl moiety, which increases at the protonation. It was of interest to

determine the degree of electron-withdrawing effect of phenanthro[9,10-*d*]imidazol-2-yl and benzimidazol-2-yl groups on the pyrrole ring on the basis of the $^1$H NMR spectroscopy. Analysis of the downfield shifts of the pyrrole protons $H^3$ of compounds **Ia** (6.53 ppm) and **II** (6.68 ppm) caused primarily by the electron-withdrawing effect clearly indicates that the electron-acceptor properties of the phenanthro[9,10-*d*]imidazol-2-yl group are relatively low. This is due to the low aromaticity of the central benzene ring of the phenanthrene system that reduces its electron-withdrawing effect. In this connection we should expect a higher reactivity of the pyrrole ring in compound **Ia**.




The reactions performed confirm this assumption. The yields and physicochemical constants of the compounds obtained are given in Table 1.

The nitration of compound **II** have been shown [7] to occur at the action of a fuming nitric acid ($d$ 1.5 g cm$^{-3}$) in acetic anhydride at 0°C of the β-position of the pyrrole ring. Under these conditions the similar reaction of compound **Ia** proceeds nonselectively due to its high reactivity with respect to acetyl nitrate. Therefore in this case we used the method of thiophenes nitration [8] by a combination of copper

**Table 1.** Yields, melting points and elemental analysis data for compounds **I**

| Comp. no. | Yield, % | mp, °C | Found, % | | | Formula | Calculated, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | | C | H | N |
| **I** | 60 | 131–132 | 80.93 | 4.88 | 13.91 | $C_{20}H_{15}N_3$ | 80.78 | 5.05 | 14.13 |
| **Ia** | 64 | 149–150 | 81.23 | 5.37 | 13.17 | $C_{21}H_{17}N_3$ | 81.00 | 5.50 | 13.49 |
| **Ib** | 84 | 273–274 | 71.03 | 4.22 | 15.95 | $C_{21}H_{16}N_4O_2$ | 70.78 | 4.53 | 15.72 |
| **Ic** | 87 | 272–273 | 53.87 | 3.49 | 9.14 | $C_{21}H_{15}Br_2N_3$ | 53.76 | 3.22 | 8.96 |
| **Id** | 46 | 258–259 | 64.78 | 4.12 | 10.55 | $C_{21}H_{17}N_3O_3S$ | 64.44 | 4.38 | 10.73 |
| **Ie** | 65 | 227–228 | 78.12 | 4.88 | 12.49 | $C_{22}H_{17}N_3O$ | 77.86 | 5.05 | 12.38 |
| **If** | 17 | 215–216 | 77.68 | 5.17 | 12.66 | $C_{22}H_{17}N_3O$ | 77.86 | 5.05 | 12.38 |
| **Ig** | 69 | 198–199 | 77.93 | 5.62 | 12.11 | $C_{23}H_{19}N_3O$ | 78.16 | 5.42 | 11.89 |
| **Ih** | 12 | 206–207 | 78.44 | 5.75 | 11.64 | $C_{23}H_{19}N_3O$ | 78.16 | 5.42 | 11.89 |
| **Ii** | 42 | 144–145 | 81.27 | 5.17 | 9.88 | $C_{28}H_{21}N_3O$ | 80.94 | 5.09 | 10.11 |
| **Ij** | 12 | 151–152 | 81.15 | 4.88 | 10.37 | $C_{28}H_{21}N_3O$ | 80.94 | 5.09 | 10.11 |
| **Ik** | 44 | 175–176 | 81.25 | 5.53 | 13.10 | $C_{43}H_{34}N_6$ | 81.36 | 5.40 | 13.24 |

nitrate and acetic anhydride. In contrast to compound **II**, the substitution in this case occurs at the position 5' of the pyrrole ring to give **Ib** in yield of 84%.

The bromination of compound **Ia** was carried out by the action of bromine in dichloroethane at –10°C. According to the $^1$H NMR spectrum under these conditions the formation of 4',5'-dibromo-derivative **Ic** actually occurs. A characteristic signal of the spectrum is a singlet of the proton $^3$CH at 6.75 ppm (Table 2). A similar transformation of compound **II** takes place in acetic acid at 20°C.

According to [7], 2-(1'-methyl-2'-pyrrolyl)benzimidazole **II** is sulfonated with sulfuric acid ($d$ 1.84 g cm$^{-3}$) in acetic anhydride on the 4'-position of pyrrole moiety. The compound **Ia** is tarred in such rigid conditions. Therefore it was sulfonated with pyridine sulfotrioxide in the boiling dichloroethane to give 5'-sulfonic acid **Id** in a yield of 46%. The difference in the direction of sulfonation of compounds **II** and **Ia** with sulfuric acid and pyridine sulfotrioxide is obviously due to the fact that in the first case reacts the benzimidazole cation, while in the second case reacts the neutral form of the substrate.

The study of the formylation of compound **Ia** with the Vilsmeier reagent gave the unexpected result. Unlike pyrrolylbenzimidazole **II**, which gives under these conditions exclusively 4'-formyl pyrrole derivative, compound **Ia** is formylated not only in the position 4', but also in the position 5'. The yield of isomeric aldehydes **Ie** and **If** is 65 and 17%, respectively. Obviously, the formation of aldehyde **If** indicates a decrease in the electron-withdrawing effect of phenanthro[9,10-*d*]imidazole moiety on the pyrrole ring in comparison with benzimidazole.

Previously, for the formylation of furyl- and thienylphenantro[9,10-*d*]imidazoles hexamethylenetetramine in polyphosphoric acid medium was used [9]. We attempted to apply this method to compound **Ia**. As a result, as in the case of pyrrolylbenzimidazole **II**, dipyrrolylmethane derivative **Il** was formed in 47% yield.

According to [10], the acetylation of compound **II** with a mixture of acetic and polyphosphoric acid at 110°C occurs at the position 4' of the pyrrole. We succeeded in acetylating compound **Ia** by heating in acetic anhydride in the presence of catalytic amounts of perchloric acid, i. e., in mild conditions of the Dorofeenko reaction. Like the formylation, the acylation proceeds with the formation of a mixture of 4'- and 5'-acetyl derivatives **Ig** and **Ih** in 75% yield. Both isomers are easily separated by the column chromatography. In their $^1$H NMR spectra the signals of pyrrole protons appear at 7.00 and 7.50 ppm ($J_{3,5}$ 1.4 Hz) (**Ig**) and at 6.62 and 7.08 ppm ($J_3$, 4 4.0 Hz) (**Ih**). The coupling constants values indicate clearly the 4'- and 5'-substitution of the pyrrole ring.

The direction of the benzoylation of compound **II** in polyphosphoric acid at 140–150°C is not different from that of the acetylation of the same substrate. Compound **Ia** is benzoylated most smoothly. In

**Table 2.** The IR and $^1$H NMR ($CDCl_3$)[a] spectral data for compounds **Ia**–**Il**

| Comp. no. | IR spectrum ν, $cm^{-1}$ | $^1$H NMR spectrim ($CDCl_3$)[a], δ, ppm |
|---|---|---|
| **Ia** | – | 3.95 s (3H, $NCH_3$), 4.35 s (3H, $NCH_3$), 6.28 d (1H, $CH_{Ht}$, *J* 3.2 Hz), 6.54 d (1H, $CH_{Ht}$, *J* 3.2 Hz), 7.60 m (4H, $CH_{Ar}$), 7.86 d (1H, $CH_{Ht}$, *J* 2.1 Hz), 8.50 d (1H, $CH_{Ht}$, *J* 8.2 Hz), 8.68 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.72 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.82 d (1H, $CH_{Ar}$, *J* 7.7 Hz) |
| **Ib** | 1360 sym. ($NO_2$) 1545 assym. ($NO_2$) | 4.15 s (3H, $NCH_3$), 4.28 s (3H, $NCH_3$), 6.54 d (1H, $CH_{Ht}$, *J* 4.0 Hz), 7.38 d (1H, $CH_{Ht}$, *J* 4.0 Hz), 7.65 m (4H, $CH_{Ar}$), 8.45 d (1H, $CH_{Ar}$, *J* 8.2 Hz), 8.68 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.70 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.82 d (1H, $CH_{Ar}$, *J* 7.7 Hz) |
| **Ic**[a] | – | 3.60 s (3H, $NCH_3$), 4.20 s (3H, $NCH_3$), 6.75 d (1H, $CH_{Ht}$), 7.70 m (4H, $CH_{Ar}$), 8.53 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.65 d (1H, $CH_{Ar}$, *J* 8.2 Hz), 8.82 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.92 d (1H, $CH_{Ar}$, *J* 7.7 Hz) |
| **Id**[b] | 1260 ($SO_2$) | 4.05 s (3H, $NCH_3$), 4.40 s (3H, $NCH_3$), 6.45 d (1H, $CH_{Ht}$, *J* 4.1Hz), 7.32 d (1H, $CH_{Ht}$, *J* 4.1 Hz), 7.60 m (4H, $CH_{Ar}$), 8.42 d (1H, $CH_{Ar}$, *J* 8.2 Hz), 8.63 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.72 d (1H, $CH_{Ar}$, *J* 7.8 Hz), 8.84 d (1H, $CH_{Ar}$, *J* 7.7 Hz) |
| **Ie** | 1660 (C=O) | 4.05 s (3H, $NCH_3$), 4.32 s (3H, $NCH_3$), 7.00 d (1H, $CH_{Ht}$, *J* 1.5 Hz), 7.51 d (1H, $CH_{Ht}$, *J* 1.5 Hz), 7.65 m (4H, $CH_{Ar}$), 8.50 d (1H, $CH_{Ar}$, *J* 8.2 Hz), 8.68 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.72 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.82 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 9.83 s (1H, CHO) |
| **If** | 1680 (C=O) | 4.16 s (3H, $NCH_3$), 4.30 s (3H, $NCH_3$), 6.62 d (1H, $CH_{Ht}$, *J* 4.1 Hz), 7.08 d (1H, $CH_{Ht}$, *J* 4.1 Hz), 7.68 m (4H, $CH_{Ar}$), 8.55 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.68 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.72 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.82 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 9.70 s (1H, CHO) |
| **Ig** | 1660 (C=O) | 2.65 s (3H, $CH_3$), 4.05 s (3H, $NCH_3$),4.32 s (3H, $NCH_3$), 7.00 d (1H, $CH_{Ht}$, *J* 1.4 Hz), 7.50 d (1H, $CH_{Ht}$, *J* 1.4 Hz), 7.64 m (4H, $CH_{Ar}$), 8.50 d (1H, $CH_{Ar}$, *J* 8.2 Hz), 8.68 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.72 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.80 d (1H, $CH_{Ar}$, *J* 7.7 Hz) |
| **Ih** | 1670 (C=O) | 2.53 s (3H, $CH_3$), 4.16 s (3H, $NCH_3$), 4.33 s (3H, $NCH_3$), 6.62 d (1H, $CH_{Ht}$, *J* 4.0 Hz), 7.08 d (1H, $CH_{Ht}$, *J* 4.0 Hz), 7.68 m (4H, $CH_{Ar}$), 8.55 d (1H, $CH_{Ar}$, *J* 8.2 Hz), 8.68 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.72 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.85 d (1H, $CH_{Ar}$, *J* 7.7 Hz) |
| **Ii** | 1650 (C=O) | 4.02 s (3H, $NCH_3$), 4.28 s (3H, $NCH_3$), 6.96 d (1H, $CH_{Ht}$, *J* 1.2 Hz), 7.48 d (1H, $CH_{Ht}$, *J* 1.2 Hz), 7.53 t (3H, $CH_{Ar}$, *J* 7.5 Hz), 7.65 m (4H, $CH_{Ar}$), 7.91 d (2H, $CH_{Ar}$, *J* 7.2 Hz), 8.50 d (1H, $CH_{Ar}$, *J* 8.2 Hz), 8.68 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.75 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.84 d (1H, $CH_{Ar}$, *J* 7.7 Hz) |
| **Ij** | 1660 (C=O) | 4.10 s (3H, $NCH_3$), 4.30 s (3H, $NCH_3$), 6.60 d (1H, $CH_{Ht}$, *J* 4.0 Hz), 7.10 d (1H, $CH_{Ht}$, *J* 4.0 Hz), 7.48 t (3H, $CH_{Ar}$, *J* 7.5 Hz), 7.63 m (4H, $CH_{Ar}$), 7.88 d (2H, $CH_{Ar}$, *J* 7.2 Hz), 8.48 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.65 d (1H, $CH_{Ar}$, *J* 7.7 Hz), 8.72 d (1H, $CH_{Ar}$, *J* 8.0 Hz), 8.82 d (1H, $CH_{Ar}$, *J* 7.7 Hz) |
| **Ik** | – | 3.98 s (6H, $2NCH_3$), 4.33 s (6H, $2NCH_3$), 4.40 s (2H, $CH_2$), 6.47 d (2H, $CH_{Ht}$, *J* 1.5 Hz),7.60 m (8H, $CH_{Ar}$), 7.75 d (2H, $CH_{Ht}$, *J* 1.5 Hz), 8.48 d (2H, $CH_{Ar}$, *J* 8.2 Hz), 8.68 d (2H, $CH_{Ar}$, *J* 7.7 Hz), 8.72 d (2H, $CH_{Ar}$, *J* 8.0 Hz), 8.80 d (2H, $CH_{Ar}$, *J* 7.7 Hz) |

[a] The $^1$H NMR spectrum was recorded in DMSO-$d_6$ + $CCl_4$. [b] The $^1$H NMR spectrum was recorded in DMSO-$d_6$.

the above conditions, after 1 h heating, a mixture of 4'- (**Ii**) and 5'-benzoyl derivatives (**Ik**) was obtained in 42 and 12% yields respectively.

## EXPERIMENTAL

The IR spectra were recorded on a Specord 75 IR spectrophotometer from the mulls in mineral oil. The $^1$H NMR spectra were recorded on a Varian Unity 300 instrument (300 MHz, $CDCl_3$) with internal reference TMS. The reaction was monitored by TLC on the plates covered with $Al_2O_3$ of II degree of Brockmann activity detecting with iodine vapor (eluents $CH_2Cl_2$, $CHCl_3$). The elemental analysis was performed on a Perkin Elmer 2400 analyzer. Melting points were determined by capillary method.

**2-(1'-Methyl-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*] imidazole (I).** To a boiling solution of 4.10 g (0.05 mol) of 9,10-phenanthrenequinone in 300 ml of *n*-propanol 7.7 g (0.1 mol) of ammonium acetate and 6.54 g (0.06 M.) of 1-methyl-2-pyrrolecarboxaldehyde in 50 ml of *n*-propanol was added. The mixture was refluxed for 2 h and kept at room temperature for

2–3 h. The precipitate formed was filtered off and washed with 50 ml of alcohol. The filtrate was diluted with 200 ml of cold water and neutralized with ammonia solution to pH 8–9. The precipitate was separated, dried, and recrystallized from alcohol. The yield, melting point, elemental analysis data of **I** are shown in Table. 1.

**1-Methyl-2-(1'-methyl-2'-pyrrolyl)-1*H*-phenanthro-[9,10-*d*]imidazole (Ia).** To a solution of 2.97 g (0.01 mol) of **I** in 10 ml of DMSO was added 0.62 g (0.011 mol) of KOH powder, and then 1.42 g (0.01 mol) of methyl iodide was added dropwise. The mixture was stirred at room temperature for 2 h and diluted with 200 ml of water. The precipitate was separated, dried and crystallized from *n*-heptane.

**1-Methyl-2-(1'-methyl-5'-nitro-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]imidazole (Ib).** *Preparation of the nitrating mixture.* To an Erlenmeyer flask (100 ml) charged with 16.9 g (0.07 mol) of $Cu(NO_3)_2 \cdot 3H_2O$ was poured in small portions 40 ml of acetic anhydride under strong cooling, maintaining the temperature of the reaction mixture below 30–40°C. As the exothermic reaction completed, the mixture was allowed to stand at room temperature for 24 h. Then the precipitate of copper(II) acetate was filtered off. The resulting mixture was stored no longer than 10 days at 5–10°C.

To a solution of 1.56 g (0.005 mol) of compound **Ia** in 5 ml of the freshly distilled acetic anhydride under vigorous stirring was added in small portions 1.4 ml of nitrating mixture at room temperature. The reaction time was 30–40 min. Then the mixture was diluted with 25 ml of cold water and neutralized with 23% solution of ammonia until the slightly alkaline reaction. The precipitate was filtered off, thoroughly washed with water, and chromatographed on a column with $Al_2O_3$, eluting with dichloromethane. The reaction product was crystallized from alcohol. The yield, melting point, elemental analysis data, and spectral characteristics are shown in Table 1, 2.

**1-Methyl-2-(1'-methyl-4',5'-dibromo-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]imidazole (Ic).** To a solution of 1.76 g (0.011 mol) of bromine in 30 ml of dichloroethane cooled to –10°C was added with stirring a cooled solution of 1.56 g (0.005 mol) of **Ia** in 10 ml of dichloroethane within 30 min. The stirring was continued at the same temperature for 1.5 h, and then **Ic** hydrobromide was filtered off, washed with dichloroethane (15 ml), dried, and neutralized with 25% solution of ammonia. Compound **Ib** was crystallized from alcohol.

**1-Methyl-2-(1'-methyl-5'-sulfo-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]imidazole (Id).** A mixture of 1.56 g (0.005 mol) of compound **Ia** and 1.6 g (0.01 mol) of pyridine sulfotrioxide in 25 ml of dichloroethane was refluxed for 10 h. The reaction mixture was treated with barium carbonate; the sulfonate salt was separated, dissolved by the heating in 100 ml of water, mixed with 5 ml of 10% hydrochloric acid, and cooled. The formed crystals were recrystallized from the aqueous alcohol.

**1-Methyl-2-(1'-methyl-4(5)'-formyl-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]imidazoles (Ie, If).** To a cooled (0°C) solution of 1.56 g (0.005 mol) of compound **Ia** in 7.3 g (0.1 mol) of dimethylformamide was gradually added 1.54 g (0.01 mol) of phosphorus oxychloride, maintaining the temperature of the reaction mixture below 10–15°C. The mixture was stirred at this temperature for 30 min and 1 h at 80°C. The reaction mixture was poured into 50 ml of water and neutralized with ammonia. The released oil was extracted with chloroform and chromatographed on alumina column. The isolated compounds **Ie** and **If** were crystallized from *n*-octane.

**1-Methyl-2-(1'-methyl-4(5)'-acetyl-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]imidazoles (Ig, Ih).** A solution of 1.56 g (0.005 mol) of compound **Ia**, 7 g of acetic anhydride and 0.05 g of perchloric acid was heated on a boiling water bath for 6 h. The reaction mixture was cooled, diluted with 50 ml of water, and neutralized with aqueous ammonia. The products were extracted with 25 ml of chloroform. The extract was dried, concentrated, and fractionally chromatographed on a column (*h* 20 cm, *d* 2.5 cm) with aluminum oxide, eluting with chloroform. The isolated compounds **Ig** and **Ih** were crystallized from *n*-octane.

**1-Methyl-2-(1'-methyl-4(5)'-benzoyl-2'-pyrrolyl)-1*H*-phenanthro[9,10-*d*]imidazoles (Ii, Ik).** A mixture of 1.56 g (0.005 mol) of compound **Ia** and 1.22 g (0.01 mol) of benzoic acid in 20 g of polyphosphoric acid was heated at 140–150°C for 1 h under vigorous stirring. The reaction mixture was cooled, diluted with 100 ml of water, and carefully neutralized with ammonia. Next, the compounds **Ii** and **Ik** were isolated similar to the compounds **Ig** and **Ih** and crystallized from *n*-octane.

**2',2''-Di-(1-methyl-2-phenanthro[9,10-*d*]imidazolyl)-1',1''-dimethyl-4',4''-dipyrrolylmethane (Il).**

A mixture of 1.56 g (0.005 mol) of compound **Ia**, 1.4 g (0.01 mol) of hexamine and 20 g of polyphosphoric acid was stirred at 70–80°C for 2 h. The reaction product was isolated similar to compounds **Ig** and **Ih** and crystallized from xylene.

## REFERENCES


1. Oleinikova, L.Ya. and Pozharskii, F.T., *Khim. Geterotsikl. Soedin.,* no. 11, p. 1014.
2. Weidenhagen, R., *Chem. Ber*., 1936, vol. 69, no. 6, p. 2263.
3. Phillips, M.A., *J. Chem. Soc*., 1928, vol. 80, no. 12, p. 2393.
4. Steck, I.L. and Day, N.S., *J. Am. Chem. Soc*., 1943, vol. 65, no. 6, p. 452.
5. Kinugawa, Y., *Synthesis,* 1981, vol. 12, no. 2, p. 124.
6. Yel'chaninov, M.M., Oleinikova, L.Ya., Simonov, A.M., *Khim. Geterotsikl. Soedin.,* 1979, no. 8, p. 1047.
7. Yel'chaninov, M.M., Simonov A.M., Oleinikova, L.Ya., *Khim. Geterotsikl. Soedin.,* 1980, no. 1, p. 71.
8. Churkin, Yu.D. and Savin, V.I., *Khim. Geterotsikl. Soedin.,* 1968, no. 2, p. 369.
9. Pechkin, A.A., Yel'chaninov, M.M., Stoyanov, V.M., *Zh. Org. Khim.,* 2002, vol. 38, no. 5, p. 763.
10. Yel'chaninov, M.M., Stoyanov, V.M., Kagan, E.Sh., *Zh. Org. Khim.,* 2000, vol. 36, no. 11, p. 1733.