Russian Journal of Organic Chemistry, Vol. 40, No. 9, 2004, pp. 1322–1328. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 9, 2004, pp. 1369–1375.

Oxidation of 4,7-Phenanthroline Derivatives

K. N. Gusak, N. G. Kozlov, and A. B. Tereshko

Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus,
ul. Surganova 13, Minsk, 220072 Belarus
e-mail: loc@ifoch.bas-net.by

Received March 23, 2004

Abstract—Oxidation of 1,3-diphenyl-4,7-phenanthroline with potassium permanganate in alkaline medium results in transformation of the 4,7-phenanthroline ring system into 1,8-diaazafluorenone. Oxidation of 12-aryl- and 12-aryl-9,9-dimethyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-ones (condensation products of 6-arylmethylene-aminoquinolines with 1,3-cyclohexanedione and dimedone) with sodium nitrite in acetic acid leads to 12-aryl-9,10-dihydro-8*H*-benzo[*b*][4,7]phenanthrolin-11-ones. 13-Aryl-7,13-dihydro-12*H*-indeno-[2,1-*b*][4,7]phenanthrolin-12-ones obtained by reaction of 6-arylmethyleneaminoquinolines with 1,3-indandione are oxidized to 13-aryl-12*H*-indeno[2,1-*b*][4,7]phenanthrolin-12-ones on heating in nitrobenzene.

Among chemical transformations of 4,7-phenanthroline derivatives, oxidation of these compounds attracts specific attention. Formerly, 4,7-phenanthroline was oxidized with the goal of proving the angular structure of the compound obtained from *p*-phenylenediamine or 6-aminoquinoline according to Skraup [1, 2]. The subsequent interest in oxidation of 4,7-phenanthrolines arose from search for efficient methods of synthesis of 4,7-phenanthroline-5,6-dione and its analogs which exhibit a high antibacterial activity and are used for treatment of gastrointestinal diseases [3–8]. It was shown that 5- or 6-hydroxy-, methoxy-, or amino-substituted 4,7-phenanthrolines are oxidized to 4,7-phenanthroline-5,6-dione more readily than unsubstituted 4,7-phenanthroline [6–8].

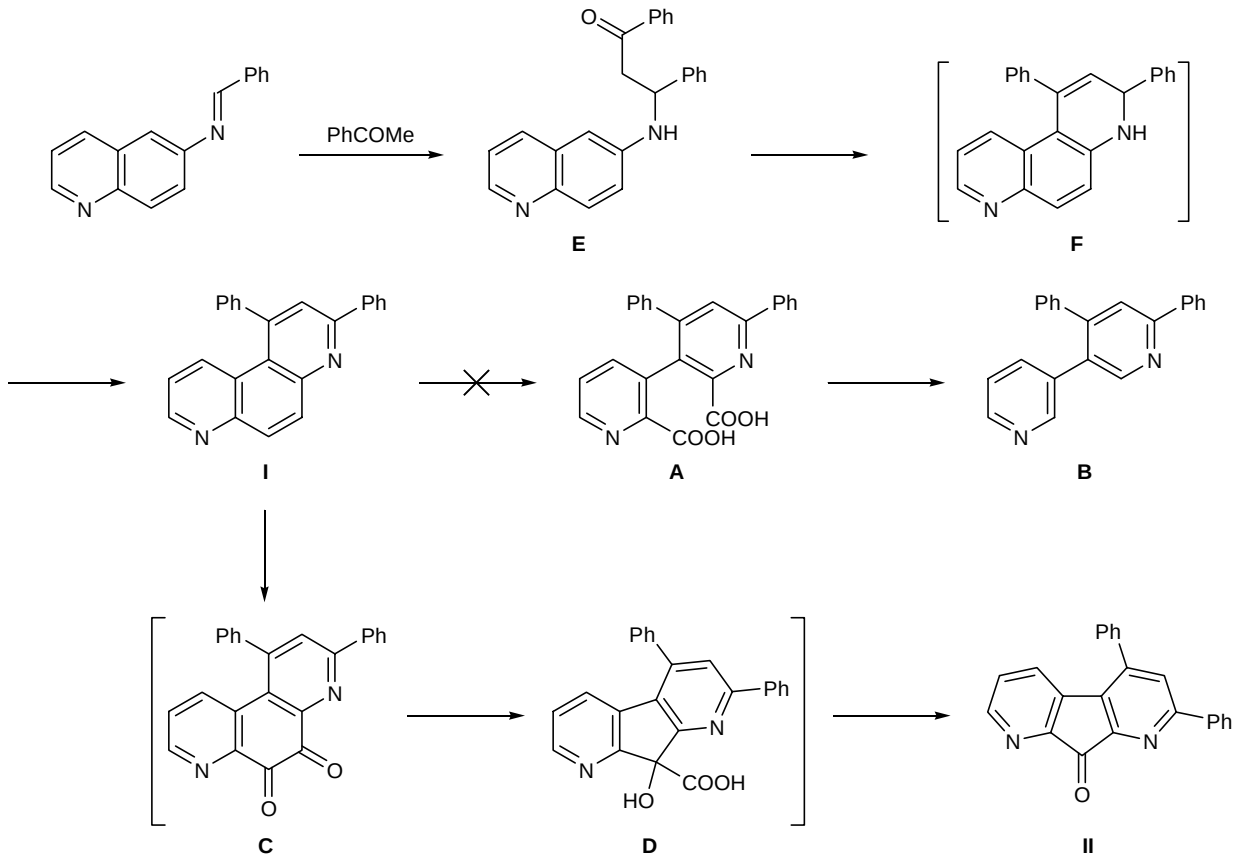
In the present work we were the first to study oxidation of 1,3-diphenyl-4,7-phenanthroline (**I**) with potassium permanganate in alkaline medium. Phenanthroline **I** was prepared by condensation of 6-benzylideneaminoquinoline with acetophenone in butyl alcohol in the presence of concentrated hydrochloric acid [9]. The oxidation was carried out by heating a suspension of phenanthroline **I** in an aqueous solution of $KMnO_4$ and KOH. By analogy with the data of [1, 2], we anticipated that the oxidation product will be 4,6-diphenyl-3,3'-bipyridine-2,2'-dicarboxylic acid **A**. Its decarboxylation should give rise to the corresponding 3,3'-bipyridine **B**. However, instead of acid **A**, the only oxidation product was 2,4-diphenyl-1,8-diazafluoren-9-one (**II**) (yeld 36%).

The formation of an analogous compound, 4,5-diazafluoren-9-one, as an impurity to 3,3'-bipyridinedicarboxylic acid was observed previously in the oxidation of 1,10-phenanthroline with an alkaline solution of $KMnO_4$ [10]. This fact has attracted interest from the viewpoint of possible synthesis of difficultly accessible compounds of the diazafluorenone series. A procedure was developed for the preparation of isomeric diazafluoren-9-ones by oxidation of 1,7-, 1,8-, 1,9-, 1,10-, and 2,8-phenanthrolines with potassium permanganate; however, the yield of 1,8-diazafluoren-9-one from 4,7-phenanthroline did not exceed 2% [11]. Therefore, 1,8-diazafluoren-9-one was obtained by oxidation of 5-methoxy-4,7-phenanthroline to 4,7-phenanthroline-5,6-dione and subsequent thermal treatment of the latter with alkali [11].

Taking into account the above data, as well as the data on transformations of phenanthrene- and diazaphenanthrenequinones in alkaline medium [12, 13], we presumed that the primary oxidation product of phenanthroline **I** is 1,3-diphenyl-4,7-phenanthroline-5,6-dione **C** which undergoes rearrangement (by analogy with benzilic acid rearrangenent [14]) into unstable α-hydroxy acid **D**. Decarboxylation of the latter yields 2,4-diphenyl-1,8-diazafluoren-9-one (**II**) (Scheme 1).

The IR spectrum of diazafluorenone **II** contained a strong absorption band at 1740 cm^{-1} due to stretching vibrations of the carbonyl group. The molecular ion $[M]^+$, *m*/*z* 334, was the most abundant (I_{rel} = 100%) in

Scheme 1.



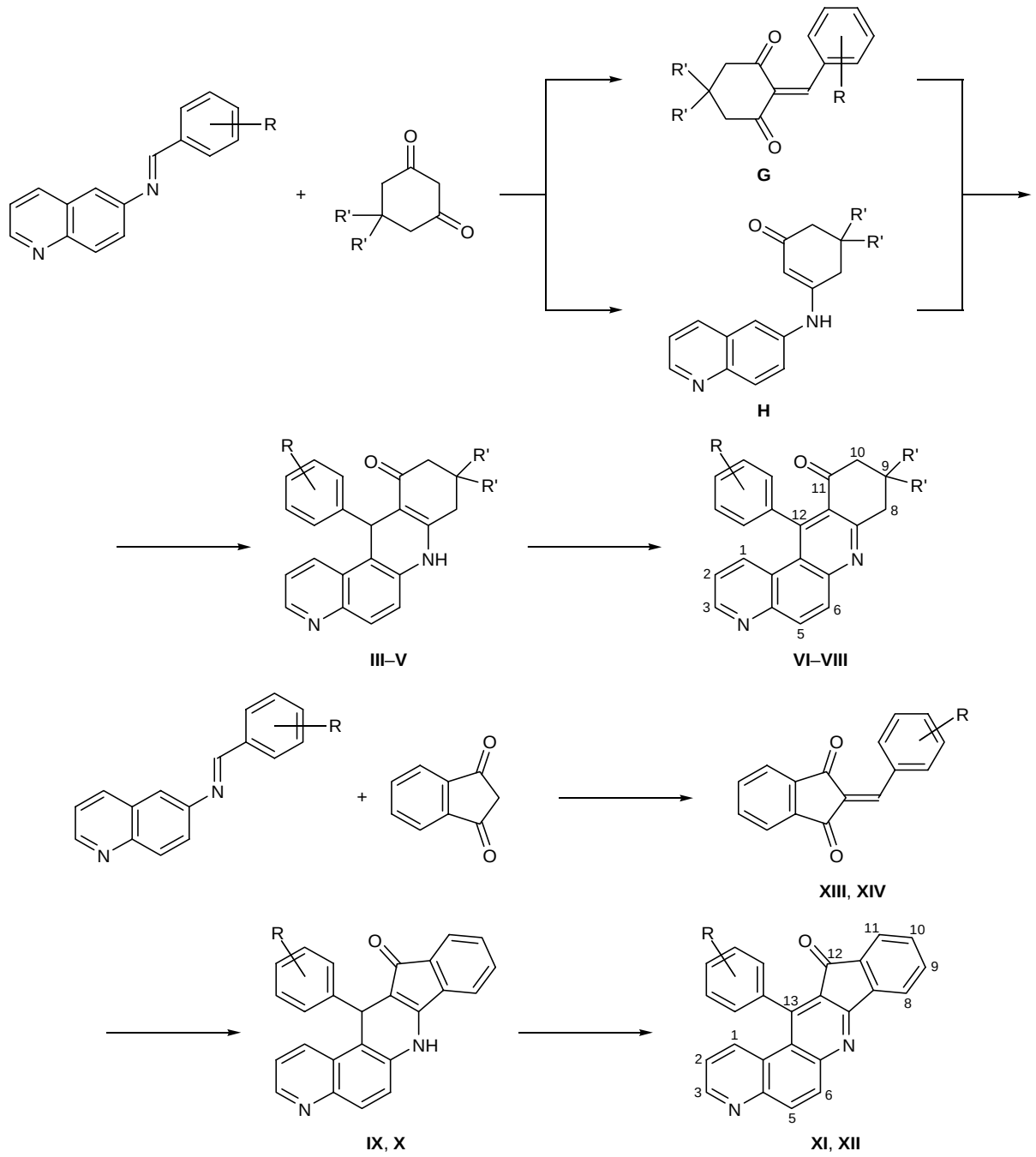
the mass spectrum of **II**; in addition, the following fragment ion peaks were present in the mass spectrum, *m*/*z* (I_{rel}, %): 305 (31) $[M - 1 - CO]^+$, 281 (19) $[M - 2 - CO - HCN]^+$, 254 (20) $[M - 2 - CO - 2HCN]^+$. The UV spectrum of **II**, as well as of isomeric 4,5-diazafluoren-9-one [10], consists of three absorption bands with their maxima at 207 ($\log\varepsilon$ = 4.48), 255 ($\log\varepsilon$ = 4.26), and 320 nm ($\log\varepsilon$ = 4.18). Unlike the 4,5-diaza analog, the long-wave absorption band in the spectrum of 1,8-diazafluoren-9-one (**II**), which originates from the presence of a carbonyl group, lacks vibrational structure; presumably, the reason is that both nitrogen atoms are located close to the carbonyl group. In the ^{1}H NMR spectrum of diazafluorenone **II** we observed no one-proton doublets at δ 8.22 and 8.33 ppm, which are typical of initial 1,3-diphenyl-4,7-phenanthroline (5-H and 6-H, respectively).

Insofar as 2,4-diphenyl-1,8-diazafluoren-9-one (**II**) was the only product, the oxidation of 1,3-diaryl-4,7-phenanthrolines with potassium permanganate can be regarded as a method for preparation of new derivatives of the 1,8-diazafluoren-9-one series. It should be noted that redox processes also occur during the synthesis of initial 1,3-diaryl-4,7-phenanthrolines by reaction of CH acids with Schiff bases derived from 6-aminoquinoline, in particular in the synthesis of 1,3-diphenyl-4,7-phenanthroline (**I**). In the first stage, CH acid (acetophenone) adds at the C=N bond of 6-benzylideneaminoquinoline to give 1,3-diphenyl-3-(6-quinolylamino)propanone **E** which undergoes intramolecular ring closure to 1,3-diphenyl-3,4-dihydro-4,7-phenanthroline **F** with elimination of water. The subsequent oxidation (or dehydrogenation) of **F** yields 1,3-diphenyl-4,7-phenanthroline (**I**) (Scheme 1).

By analogy with Skraup's procedure, where an oxidant is added to the reaction medium in order to effect dehydrogenation of intermediate dihydro derivative [1, 2], we performed condensation of 6-benzylideneaminoquinoline with acetophenone in the presence of nitrobenzene. We also tried to isolate intermediate dihydrophenanthroline by carrying out the reaction in the absence of nitrobenzene. However, in the absence of an oxidant at room temperature, the product was aminoketone **E**, while at elevated temperature 1,3-diphenyl-4,7-phenanthroline (**I**) was obtained. These data indicate ready oxidation of the

1,2-dihydropyridine ring in the 4,7-phenanthroline molecule. Furthermore, no appreciable affect of an oxidant on the yield of phenanthroline **I** was observed; therefore, further condensations of 6-arylmethyleneaminoquinolines with acetophenone were performed in the absence of nitrobenzene. The reactions of halo- and hydroxy-substituted Schiff bases with acetophenone (in the absence of nitrobenzene), apart from the target 1,3-diaryl-4,7-phenanthrolines, afforded the corresponding 6-benzylaminoquinolines which were likely to be formed by reduction of the initial Schiff bases with hydrogen liberated during aromatization (dehydrogenation or oxidation) of the 3,4-dihydro-4,7-phenanthroline ring [9].

Scheme 2.



III, **VI**, R = 3-OH; **IV**, **VII**, R = 2,4-Cl_2; **V**, **VIII**, R = 3,4-OCH_2O; **IX**, **XI**, **XIII**, R = 4-Br; **X**, **XII**, **XIV**, R = 3-NO_2; **III**, **IV**, **VI**, **VII**, R' = H; **V**, **VIII**, R' = Me.

The condensation of 6-arylmethyleneaminoquinolines with cyclic β-dicarbonyl compounds, 1,3-cyclohexanedione, dimedone, and 1,3-indandione takes a different pathway. Due to high reactivity of the methylene group in position *2* of cyclic 1,3-diketone (CH acid) and the carbonyl groups, 1,3-cyclohexanedione and dimedone are capable of reacting with each precursor of the Schiff base which undergoes hydrolysis in alcoholic medium, i.e., with aromatic aldehyde and 6-aminoquinoline to give, respectively, enedione **G** and enamine **H**. Cyclocondensation of intermediate **G** with 6-aminoquinoline and of enamine **H** with aromatic aldehyde leads to formation of the same product, 4,7-phenanthroline incorporating a 1,4-dihydropyridine ring fused to a cyclohexane ring, 12-aryl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one **III** or **IV** or 9,9-dimethyl derivative **V** (Scheme 2).

Unlike 3,4-dihydrophenanthrolines **F**, the dihydropyridine ring in **III**–**V** is stable to oxidation. Aromatization of the 4,7-phenanthroline system occurs neither during the synthesis of **III**–**V** nor on prolonged heating with excess nitrobenzene. We were the first to effect oxidation of phenanthrolines **III**–**V** by the action of sodium nitrite in acetic acid.

In contrast to initial compounds **III**–**V**, the IR spectra of their oxidation products, 12-aryl- and 12-aryl-9,9-dimethyl-9,10-dihydro-8*H*-benzo[*b*][4,7]phenanthrolin-11-ones **VI**–**VIII** lacked absorption band at 3290–3280 cm^{-1}, which is typical of amino group stretching vibrations. Instead of strong bands at 1580 and 1525 cm^{-1} due to vinylogous amide fragment in the spectra of **III**–**V** [14], oxidation products **VI**–**VIII** give rise to one carbonyl stretching vibration band at 1680–1675 cm^{-1}.

The mass spectra of **VI**–**VIII** contain the molecular ion peak $[M]^+$ which has the maximal intensity (I_{rel} 100%), $[M - C_6H_4R]^+$ ion peak ($[M - C_6H_3R]^+$ for compound **VII)** with *m*/*z* 247 (phenanthrolines **VI** and **VII**, I_{rel} 15–18%) or 275 (dimethyl derivative **VIII**, I_{rel} 24%), and ion peak with *m*/*z* 191 (I_{rel} 10–17%) which corresponds to elimination of the CH_2CH_2CO fragment (Me_2CCH_2CO for compound **VIII**) from $[M - C_6H_4R]^+$.

The UV spectra of compounds **VI**–**VIII** having an extended conjugated bond system differ from the spectra of initial tetrahydro derivatives **III**–**V** which possess three independent chromophores (quinoline ring, aryl substituent, and carbonyl group) (see Experimental). Aromatization of the heterocyclic system leads to appearance of a highly intense absorption band at λ 295–296 nm (log ε 4.78–4.85) and less intense bands at λ 253–255 (log ε 4.49–4.52) and 337–345 nm (log ε 3.98–4.00); the presence of these bands makes the UV spectra of **VI**–**VIII** similar to those of 1,3-diaryl-4,7-phenanthrolines [9], and they can be identified as *p*-, β-, and α-bands according to Clar. As compared to 1,3-diarylphenanthrolines, the vibrational structure of the α-band in the spectra of **VI**–**VIII** is smoothed, presumably due to the presence of a fused cyclohexane ring [15].

The ^1H NMR spectra of **VI**–**VIII** contain no signals at δ 9.57–9.60 and 5.78–5.80 ppm, which are observed in the spectra of initial phenanthrolines **III**–**V** (NH and 12-H in the 1,4-dihydropyridine ring, respectively). Aromatization of the 4,7-phenanthroline ring system in **VI**–**VIII** makes the substituted benzene ring on C^{12} acoplanar to the tricyclic system, and the 1-H proton appears in the cone affected by the ring current of the aryl substituent; as a result, the 1-H signal shifts considerably upfield relative to the corresponding signal of initial phenanthrolines **III**–**V** and is located at δ 7.59–7.80 ppm. The 5-H and 6-H signals in the spectra of **VI**–**VIII** are displaced to a weaker field due to effect of the electronegative pyridine-like nitrogen atom.

Condensation products of 6-arylmethyleneaminoquinolines with 1,3-indandiones, 13-aryl-7,13-dihydro-12*H*-indeno[2,1-*b*][4,7]phenanthrolin-12-ones **IX** and **X**, are oxidized more readily than their cyclohexene analogs **III**–**V**. On heating in boiling nitrobenzene for 3–4 h, intensely red dihydro derivatives **IX** and **X** are converted into aromatic 13-arylindeno[2,1-*b*][4,7]-phenanthrolin-12-ones **XI** and **XII** which precipitate from the reaction solution (after cooling) as greenish–yellow crystals. While preparing initial dihydrophenanthrolines **IX** and **X**, we have found that the reaction mixtures contained 2-arylmethylene-1,3-indandiones **XIII** and **XIV** before formation of the target products. Therefore, we presumed that dihydroindenophenanthrolinones **IX** and **X** are formed via reaction of 1,3-indandione with aromatic aldehydes (which are products of hydrolysis of the initial Schiff bases), followed by condensation of 2-arylmethylene-1,3-indandiones **XIII** and **XIV** with 6-aminoquinoline. This reaction scheme was confirmed by the synthesis of dihydrophenanthrolinones **IX** and **X** by condensation of 6-aminoquinoline with 2-arylmethylene-1,3-indandiones **XIII** and **XIV** which were prepared in turn by reaction of 1,3-indandione with substituted benzaldehydes.

It should be noted that dihydroindenophenanthrolinones **IX** and **X** undergo partial oxidation on melting; however, we failed to attain the complete conversion of **IX** and **X** into aromatic compounds **XI** and **XII** in this way. In order to isolate pure oxidation products, mixtures **IX**/**XI** and **X**/**XII** should be heated in boiling nitrobenzene for an additional 3 h.

The IR spectra of indenophenanthrolines **XI** and **XII** contain no NH stretching vibration band at 3260–3230 cm^{-1}, which is present in the spectra of initial compounds **IX** and **X**. The carbonyl absorption band in the spectra of **XI** and **XII** is displaced toward higher frequencies, as compared to **IX** and **X** (νCO 1710 against 1670–1660 cm^{-1}, respectively). The mass spectra of **XI** and **XII** contain the molecular ion peaks $[M]^+$ (I_{rel} 100%) and fragment ion peaks $[M - C_6H_4R]^+$ with *m*/*z* 281 (I_{rel} 47–50%). In addition, $[M - Br]^+$ ion peak with *m*/*z* 357 (I_{rel} 66%) was observed in the mass spectrum of **XI**, and $[M - NO]^+$ (*m*/*z* 373, I_{rel} 26%) and $[M - NO_2]^+$ ion peaks (*m*/*z* 357, I_{rel} 20%), in the spectrum of **XII**. As a result of aromatization of the dihydropyridine ring, the ^1H NMR spectra of **XI** and **XII** lack signals at δ 5.92–6.20 and 9.95–9.98 ppm which belong to the 13-H and NH protons in the spectra of dihydro derivatives **IX** and **X**. The 1-H signal in the spectra of **XI** and **XII** is displaced upfield, as was observed for cyclohexene analogs **VI**–**VIII**.

Aromatization of the 4,7-phenanthroline ring system also leads to transformation of the UV spectra where intense absorption bands appear at λ 225, 253–258 (*p*-band), and 298–299 nm (β-band). The result is that the UV spectra of indenophenanthrolines **XI** and **XII** become typical of those observed for compounds of the azaphenanthrene series, specifically for 1,3-diaryl-4,7-phenanthrolines [9]. An exception is the long-wave α-band. This band is fairly intense in the spectra of azaphenanthrenes and is generally characterized by vibrational structure [9, 16]. The corresponding band in the spectra of **XI** and **XII** appears as a weak shoulder at λ 334–337 nm.

Thus, oxidation of 4,7-phenanthrolines having a dihydropyridine ring leads to formation of new compounds of the 4,7-phenanthroline series, which possess an extended conjugation system and are promising as luminescent and light-sensitive materials.

EXPERIMENTAL

The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS 50 instrument. The IR spectra were recorded on a Nicolet Protégé-460 spectrometer. The NMR spectra were measured on Bruker AC-500 (500 MHz, Bruker) and Tesla BS-567 (100 MHz) spectrometers using DMSO-d_6 as solvent and TMS as internal reference. The UV spectra were recorded from solutions in ethanol ($c = 10^{-4}$ M) on a Specord UV-Vis spectrometer. The melting points were recorded on a Kofler device.

1,3-Diphenyl-4,7-phenanthroline (**I**) was synthesized by the procedure reported in [9]. 2-Arylmethylene-1,3-indandiones **XIII** and **XIV** were obtained and identified as described in [17, 18].

Oxidation of 1,3-diphenyl-4,7-phenanthroline (I). Potassium hydroxide, 1.0 g, and powdered potassium permanganate, 2.0 g, were added with stirring to a suspension of 1.1 g (3 mmol) of phenanthroline (**I**) in 300 ml of water. The mixture was heated for 12 h at 100°C under vigorous stirring, cooled, and filtered from MnO_2. The filtrate was evaporated by half and extracted with chloroform. The extract was evaporated, the solid residue was treated with boiling benzene to remove traces of unreacted phenanthroline **I**, and the undissolved material was recrystallized from DMF. Yield of 2,4-diphenyl-1,8-diazafluoren-9-one (**II**) 0.4 g (36%), mp 312–313°C. ^1H NMR spectrum, δ, ppm: 7.18 d.d (6-H) (^3J = 8.2, ^4J = 4.1 Hz), 7.68 s (3-H), 7.90 d (5-H, ^3J = 8.0 Hz), 8.33 d.d (7-H, ^3J = 4.1, ^4J = 2.0 Hz), 7.43 m and 8.22 m (10H, H_{arom}). Found, %: C 82.53; H 4.02; N 8.14. $C_{23}H_{14}N_2O$. Calculated, %: C 82.63; H 4.19; N 8.38.

12-Aryl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin-11-ones III and IV. A solution of 5 mmol of 1,3-cyclohexanedione and 5 mmol of the corresponding Schiff base in 20 ml of 1-butanol was heated for 3 h under reflux. The precipitate was filtered off and recrystallized from ethanol–benzene (2:1).

12-(3-Hydroxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (III). Yield 75%, mp 323–324°C. ^1H NMR spectrum, δ, ppm: 1.92 m (2H, 9-H), 2.25 m (2H, 8-H), 2.66 m (2H, 10-H), 5.75 s (12-H), 6.32–7.00 m (4H, H_{arom}), 7.36 d (2-H, ^3J = 8.1 Hz), 7.52 d and 7.87 d (5-H, 6-H, ^3J = 8.5 Hz), 8.29 d (1-H, ^3J = 8.4 Hz), 8.67 d (3-H, ^3J = 4.8 Hz), 9.06 s (OH), 9.85 s (NH). UV spectrum, λ_{max}, nm (log ε): 219 (4.63), 254 (4.26), 299 (4.12), 336 (3.99), 382 (3.90). Found, %: C 76.81; H 5.29; N 7.96. $C_{22}H_{18}N_2O_2$. Calculated, %: C 77.19; H 5.26; N 8.19.

12-(2,4-Dichlorophenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IV). Yield 80%, mp 307–308°C. ^1H NMR spectrum, δ, ppm: 1.90 m (2H, 9-H), 2.21 m (2H, 8-H), 2.63 m (2H,

10-H), 6.00 s (12-H), 7.18 m (3H, H_{arom}), 7.33 d (2-H, ^3J = 8.4 Hz), 7.50 d and 7.86 d (5-H, 6-H, ^3J = 8.8 Hz), 8.29 d (1-H, ^3J = 8.4 Hz), 8.67 d (3-H, ^3J = 4.8 Hz), 9.90 s (NH). UV spectrum, λ_{max}, nm (logε): 219 (4.60), 248 (4.29), 2.97 (4.10), 335 (4.12), 383 (3.91). Found, %: C 66.78; H 3.81; Cl 17.52; N 7.29. $C_{22}H_{16}Cl_2N_2O$. Calculated, %: C 67.00; H 4.06; Cl 17.77; N 7.11.

9,9-Dimethyl-12-(3,4-methylenedioxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (V) was synthesized from dimedone and 6-(3,4-methylenedioxyphenylmethyleneamino)quinoline following the procedure described above for compounds **III** and **IV**. Yield 61%, mp 321–322°C. ^{1}H NMR spectrum, δ, ppm: 0.89 s (Me), 1.10 s (Me), 2.10 d.d (2H, 10-H, ^2J = 16.0 Hz), 2.48 m (2H, 8-H), 5.67 s (12-H), 5.84 m (OCH_2O), 6.59 s and 6.78 s (3H, H_{arom}), 7.27 d.d (2-H, ^3J = 8.4, ^4J = 2.8 Hz), 7.49 d and 7.80 d (5-H, 6-H, ^3J = 8.6 Hz), 8.28 d (1-H, ^3J = 8.4 Hz), 8.60 d (3-H, ^3J = 4.6 Hz), 9.59 s (NH). UV spectrum, λ_{max}, nm (logε): 214 (4.58), 243 (4.23), 291 (4.08), 333 (4.10), 380 (3.98). Found, %: C 75.40; H 5.31; N 7.11. $C_{25}H_{22}N_2O_3$. Calculated, %: C 75.38; H 5.53; N 7.04.

Oxidation of 12-aryl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-ones III and IV and 9,9-dimethyl-12-(3,4-methylenedioxyphenyl)-8,9,-10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (V). A solution of 10 mmol of $NaNO_2$ in 5 ml of water was added with stirring at 3–5°C to a solution of 5 mmol of tetrahydrophenanthrolinone **III**–**V** in 15 ml of acetic acid, and the mixture was stirred for 30 min at that temperature. The mixture was neutralized with aqueous ammonia, and the precipitate of **VI**–**VIII** was filtered off and recrystallized from ethanol–benzene (3:1) (**VI**, **VII**) or ethanol (**VIII**).

12-(3-Hydroxyphenyl)-9,10-dihydro-8*H*-benzo-[*b*][4,7]phenanthrolin-11-one (VI). Yield 79%, mp 307–308°C. ^{1}H NMR spectrum, δ, ppm: 1.90 m (2H, 9-H), 2.21 m (2H, 8-H), 2.60 m (2H, 10-H), 6.41–6.96 m (4H, H_{arom}), 7.28 d (2-H, ^3J = 8.0 Hz), 7.65 d (1-H, ^3J = 8.0 Hz), 8.06 d and 8.18 d (5-H, 6-H, ^3J = 8.8 Hz), 8.78 d.d (3-H, ^3J = 4.9, ^4J = 2.8 Hz), 9.00 s (OH). Found, %: C 77.34; H 4.69; N 7.93. $C_{22}H_{16}N_2O_2$. Calculated, %: C 77.65; H 4.71; N 8.24.

12-(2,4-Dichlorophenyl)-9,10-dihydro-8*H*-benzo-[*b*][4,7]phenanthrolin-11-one (VII). Yield 75%, mp 304–305°C. ^{1}H NMR spectrum, δ, ppm: 1.89 m (2H, 9-H), 2.24 m (2H, 8-H), 2.61 m (2H, 10-H), 7.15–7.24 m (3H, H_{arom}), 7.30 d (2-H, ^3J = 7.8 Hz), 7.68 d (1-H, ^3J = 7.8 Hz), 8.02 d and 8.14 d (5-H, 6-H, ^3J = 8.9 Hz), 8.76 d.d (3-H, ^3J = 4.2, ^4J = 2.1 Hz). Found, %: C 67.03; H 3.58; Cl 17.84; N 6.96. $C_{22}H_{14}Cl_2N_2O$. Calculated, %: C 67.18; H 3.56; Cl 18.07; N 7.12.

9,9-Dimethyl-12-(3,4-methylenedioxyphenyl)-9,10-dihydro-8*H*-benzo[*b*][4,7]phenanthrolin-11-one (VIII). Yield 71%, mp 233–234°C. ^{1}H NMR spectrum, δ, ppm: 1.10 s (6H, Me); 2.40–2.60 m (4H, 8-H, 10-H); 6.08 m (OCH_2O); 6.62 d, 6.83 s, and 7.00 d (3H, H_{arom}, ^3J = 7.2 Hz); 7.28 d.d (2-H, ^3J = 8.1, ^4J = 2.8 Hz); 7.52 d (1-H, ^3J = 8.1 Hz); 8.09 d and 8.19 d (5-H, 6-H, ^3J = 8.9 Hz); 8.80 d.d (3-H, ^3J = 4.6, ^4J = 2.2 Hz). Found, %: C 75.48; H 4.98; N 7.03. $C_{25}H_{20}N_2O_3$. Calculated, %: C 75.76; H 5.05; N 7.07.

13-Aryl-7,13-dihydro-12*H*-indeno[2,1-*b*][4,7]-phenanthrolin-12-ones IX and X. *a*. A solution of 5 mmol of 6-arylmethyleneaminoquinoline and 5 mmol of 1,3-indandione in 30 ml of 2-propanol was heated for 16 h under reflux. During that period, 1 mmol of 6-aminoquinoline was added in 2, 4, and 6 h. The red precipitate was filtered off and recrystallized from nitrobenzene–toluene (2:1).

b. A solution of 5 mmol of 2-arylmethylene-1,3-indandione **XIII** or **XIV** and 7.5 mmol of 6-aminoquinoline in 30 ml of 2-propanol was heated for 8–10 h under reflux. The products were isolated as described above in *a*.

13-(4-Bromophenyl)-7,13-dihydro-12*H*-indeno-[2,1-*b*][4,7]phenanthrolin-12-one (IX). Yield 54% (*a*), 61% (*b*); mp 315–316°C. ^{1}H NMR spectrum, δ, ppm: 5.92 s (13-H), 7.29–7.48 m and 7.68 d (9H, 2-H, 8-H, 9-H, 10-H, 11-H, H_{arom}, ^3J = 7.1 Hz), 7.83 d and 8.04 d (5-H, 6-H, ^3J = 9.0 Hz), 8.36 d (1-H, ^3J = 7.4 Hz), 8.77 d (3-H, ^3J = 4.9 Hz), 9.95 s (NH). UV spectrum, λ_{max}, nm (logε): 200 (4.81), 236 (4.80), 269 (4.76), 353 (4.09), 480 (3.80). Found, %: C 68.14; H 3.29; Br 17.93; N 6.17. $C_{25}H_{15}BrN_2O$. Calculated, %: C 68.43; H 3.42; Br 18.22; N 6.38.

13-(3-Nitrophenyl)-7,13-dihydro-12*H*-indeno-[2,1-*b*][4,7]phenanthrolin-12-one (X). Yield 69% (*a*), 72% (*b*); mp 370–371°C. ^{1}H NMR spectrum, δ, ppm: 6.20 s (13-H); 7.32–7.50 m, 7.56 t, 7.70 d, 7.80 d, 7.88 d, and 8.28 s (9H, 2-H, 8-H, 9-H, 10-H, 11-H, H_{arom}, ^3J = 7.4 Hz); 8.04 d and 8.10 d (5-H, 6-H, ^3J = 8.9 Hz); 8.44 d (1-H, ^3J = 7.6 Hz); 8.76 d (3-H, ^3J = 4.7 Hz); 9.91 s (NH). UV spectrum, λ_{max}, nm (logε): 202 (4.61), 238 (4.51), 268 (4.56), 350 (3.87), 475 (3.68). Found, %: C 73.78; H 3.61; N 10.11. $C_{25}H_{15}N_3O_3$. Calculated, %: C 74.07; H 3.70; N 10.37.

Oxidation of 13-aryl-7,13-dihydro-12*H*-indeno-[2,1-*b*][4,7]phenanthrolin-12-ones IX and X. A mix-

ture of 1 mmol of dihydro derivative **IX** or **X** and 10 ml of nitrobenzene was heated for 3–4 h under reflux. The precipitate was filtered off and recrystallized from nitrobenzene–toluene (2:1).

13-(4-Bromophenyl)-12*H*-indeno[2,1-*b*][4,7]-phenanthrolin-12-one (XI). Yield 85%, mp 379–380°C. ^{1}H NMR spectrum, δ, ppm: 7.24–7.62 m (9H, 2-H, 8-H, 9-H, 10-H, 11-H, H_{arom}), 7.74 d (1-H, ^3J = 7.6 Hz), 7.92 d and 8.09 d (5-H, 6-H, ^3J = 8.8 Hz), 8.73 d (3-H, ^3J = 4.7 Hz). Found, %: C 68.55; H 3.02; Br 18.15; N 6.27. $C_{25}H_{13}BrN_2O$. Calculated, %: C 68.65; H 2.97; Br 18.31; N 6.41.

13-(3-Nitrophenyl)-12*H*-indeno[2,1-*b*][4,7]-phenanthrolin-12-one (XII). Yield 92%, mp 339–340°C. ^{1}H NMR spectrum, δ, ppm: 7.26–7.44 m and 7.52 d (5H, 2-H, 8-H, 9-H, 10-H, 11-H, ^3J = 7.3 Hz); 7.71 d, 7.84 d, and 8.28 s (4H, H_{arom}, ^3J = 7.6 Hz), 7.79 d (1-H, ^3J = 7.7 Hz); 8.00 d and 8.08 d (5-H, 6-H, ^3J = 8.5 Hz); 8.69 d (3-H, ^3J = 4.4 Hz). Found, %: C 74.19; H 3.34; N 10,23. $C_{25}H_{13}N_3O_3$. Calculated, %: C 74.44; H 3.23; N 10.42.

REFERENCES

1. Smith, C.R., *J. Am. Chem. Soc*., 1930, vol. 52, p. 397.
2. Kabachnik, M.I. and Rezon, V.V., *Zh. Prikl. Khim*., 1936, vol. 9, p. 2026.
3. Husseini, R. and Stretton, R.J., *Microbios*, 1981, vol. 30, p. 7.
4. Bailenger, J., *Therapie*, 1961, vol. 16, p. 287; *Chem. Abstr*., 1964, vol. 60, p. 2222z.
5. Mashkovskii, M.D., *Lekarstvennye veshchestva* (Drugs), Khar'kov: Torsing, 1998, vol. 2, p. 313.
6. FRG Patent no. 1232156, 1967; *Chem. Abstr*., 1967, vol. 66, p. 115700b.
7. Fr. Patent no. 1369625, 1964; *Chem. Abstr*., 1965, vol. 62, p. 1664i.
8. Fr. Patent no. 1382542, 1964; *Chem. Abstr*., 1965, vol. 63, p. 7912a.
9. Kozlov, N.S., Gusak, K.N., Serzhanina, V.A., and Krot, N.A., *Khim. Geterotsikl. Soedin*., 1985, p. 1398.
10. Eckhard, J.F. and Summers, L.A., *Aust. J. Chem*., 1973, vol. 26, p. 2727.
11. Klock, K., Mlochowski, J., and Szulc, Z., *J. Prakt. Chem*., 1977, vol. 319, p. 959.
12. Diesveld, J.W., Borkent, J.H., and Laarhoven, W.H., *Tetrahedron*, 1982, vol. 38, p. 1803.
13. Mlochowski, J. and Skrowarczewska, Z., *Roczn. Chem*., 1973, vol. 47, p. 2255.
14. Martinez, R., Cortes, E., and Toscano, R.A., *J. Heterocycl. Chem*., 1990, vol. 27, p. 363.
15. Kozlov, N.S., Gusak, K.N., and Serzhanina, V.A., *Dokl. Akad. Nauk SSSR*, 1986, vol. 287, p. 1142.
16. Kozlov, N.S., *5,6-Benzokhinoliny* (5,6-Benzoquinolines), Minsk: Nauka i Tekhnika, 1970, p. 96.
17. Neiland, O., *Tsiklicheskie β-diketony* (Cyclic β-Diketones), Riga: Akad. Nauk Latv. SSR, 1961, p. 155.
18. Kozlov, N.S., Pak, V.D., and Nugumanov, Z.Z., *Khim. Geterotsikl. Soedin*., 1970, p. 194.