Russian Journal of Organic Chemistry, Vol. 37, No. 10, 2001, pp. 1495–1502. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 10, 2001, pp. 1564–1571.

Synthesis of Fused Derivatives of 4,7-Phenanthroline by Condensation of 6-Aminoquinoline with Aromatic Aldehydes and Dimedone

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Received December 27, 2000

Abstract—8-Aryl-11,11-dimethyl-7,8,9,10,11,12-hexahydrobenzo[*a*]phenanthrolin-9-ones were obtained by condensation of 6-aminoquinoline with aromatic aldehydes and dimedone.

Compounds of 4,7-phenanthroline series possess high and versatile biological activity. Proceeding from 4,7-phenanthroline-5,6-dione were developed very efficient bactericidal pharmaceuticals "Entobex" and "Mexaform" [1]. Among the derivatives of 4,7-phenanthroline were found compounds of anti-allergic and antitumor activity, enzymes inhibitors, and fungicides [2–6]. The main trend in the building up of 4,7-phenanthroline skeleton is a construction of additional pyridine ring on the carbocyclic core of 6-aminoquinoline. It was formerly shown [7] that in reaction with 6-aminoquinoline with aromatic aldehydes and 1,3-cyclohexanedione the building up of the pyridine cycle was accompanied with fusion of cyclohexanone ring affording 8-aryl-7,8,9,10,11,12-hexahydrobenzo[*a*]phenanthrolin-9-ones. These compounds because of the presence in the molecule of partly hydrogenated pyridine and benzene rings are interesting as analogs of ergoalkaloids whose main structural fragment is azaphenanthrene skeleton [8].

In order to prepare new compounds of this class were brought into reaction dimedone (**I**), 6-aminoquinoline (**II**), and aromatic aldehydes. The reaction was carried out by boiling in 1-butanol of equimolar reagents amounts with no catalyst.

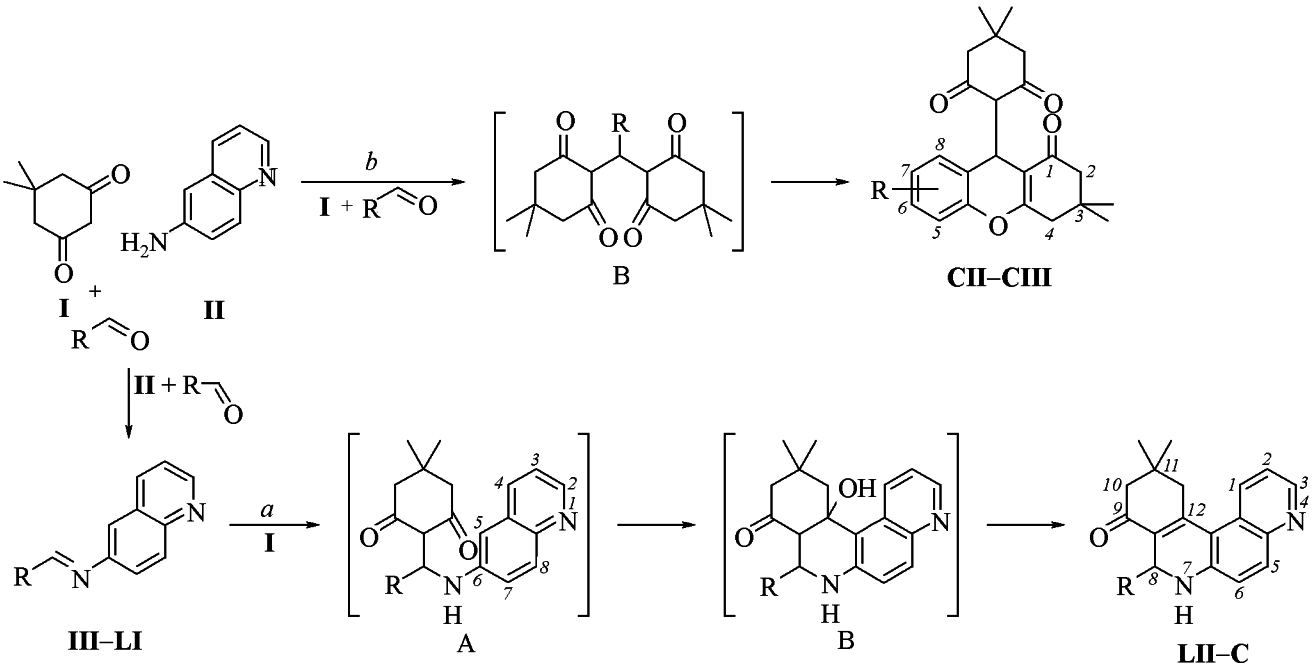
It was shown before [7] that three-component condensation of diketone **I**, amine **II**, and aromatic aldehyde can take either of two routes. The most probable for the majority of aldehydes is a primary reaction with amine **II** providing azomethines **III–LI** that further undergo condensation with dimedone (**I**) yielding fused derivatives of 4,7-phenanthroline, 8-aryl-11,11-dimethyl-7,8,9,10,11,12-hexahydrobenzo[*a*]phenanthrolin-9-ones (**LII–C**).

The mechanism of reaction between Schiff's bases and CH-acids, in particular, with the cyclic 1,3-diones, is considered in detail in [7, 9, 10]. The reaction proceeds through intermediate formation of 2-[(aryl)(6-quinolylamino)methyl]-5,5-dimethyl-1,3-cyclohexanedione (A) and its cyclization product, hydroxyketone (B) (route *a*). Neither aminodiketone (A) nor cyclic alcohol (B) were isolated in the reaction under study. Apparently due to high reactivity of carbonyl group and of methylene group located between them intermediate (A) quickly transforms into aminoalcohol (B) that is stabilized by water elimination to afford benzo[*a*]-4,7-phenanthrolines **LII–C**.

To confirm the assumed three-component condensation route we synthesized azomethines of 6-aminoquinoline series **III–LI** by reaction of 6-aminoquinoline with aromatic aldehydes, isolated them as individual compounds, and brought them into reaction with diketone **I** under conditions used in one-pot condensation of the latter with amine **II** and aromatic aldehydes. The target compounds, phenanthrolines **LII–C**, formed in approximately same yield as in the three-component condensation.

The substituent in the aromatic ring of aldehyde R affects to a certain degree the yield of the target reaction products **LII–C** (Table 1). The presence in the phenyl ring of the aldehyde of a hydroxy group in *meta*- and *para*-position, of halogen atom, nitro, alkoxy, alkoxycarbonyl group activates aldehyde molecule by *–I*-effect or by *–I*- and *–M*-effect during its reaction with amine **II**. In the next stage these groups activate the azomethine molecule during condensation with diketone **I**. Therefore the yield of compounds **LVII–LXIII**, **LXVII–LXXXII**, **LXXXVII–XCI** is higher than that of alkyl- and alkylamino-substituted phenanthrolines **LIII–LVI**, **LXXXIII–LXXXV**. The increased yield of reaction

1070-4280/01/3710-1495$25.00



R = H (**III, LII, CI**), 4-MeC_6H_4 (**IV, LIII**), 2-MeC_6H_4 (**V, LIV**), 4-EtC_6H_4 (**VI, LV**), 4-(*i*-Pr)C_6H_4 (**VII, LVI**), 4-FC_6H_4 (**VIII, LVII**), 2-FC_6H_4 (**IX, LVIII**), 4-ClC_6H_4 (**X, LIX**), 2-ClC_6H_4 (**XI, LX**), 4-BrC_6H_4 (**XII, LXI**), 3-BrC_6H_4 (**XIII, LXII**), 2,3-$Cl_2C_6H_3$ (**XIV, LXIII**), 2,4-$Cl_2C_6H_3$ (**XV, LXIV**), 2,3-$Cl_2C_6H_3$ (**XVI, LXV**), 2-Cl, 6-FC_6H_3 (**XVII, LXVI**), 4-HOC_6H_4 (**XVIII, LXVII**), 3-HOC_6H_4 (**XIX, LXVIII**), 3,4-$(HO)_2C_6H_3$ (**XX, LXIX**), 4-$MeOC_6H_4$ (**XXI, LXX**), 2-$MeOC_6H_4$ (**XXII, LXXI**), 4-$EtOC_6H_4$ (**XXIII, LXXII**), 4-$PrOC_6H_4$ (**XXIV, LXXIII**), 2,4-$(MeO)_2C_6H_3$ (**XXV, LXXIV**), 2,5-$(MeO)_2C_6H_3$ (**XXVI, LXXV**), 3,4-$(MeO)_2C_6H_3$ (**XXVII, LXXVI**), 3,4,5-$(MeO)_3C_6H_2$ (**XXVIII, LXXVII**), 4-HO, 3,5-$(MeO)_2C_6H_2$ (**XXIX, LXXVIII**), 3-EtO, 4-HOC_6H_3 (**XXX, LXXIX**), 2-MeO, 5-BrC_6H_3 (**XXXI, LXXX**), 4-$MeO_2CC_6H_4$ (**XXXII, LXXXI**), 3-MeO, 4-$MeO_2CC_6H_3$ (**XXXIII, LXXXII**), 4-$Me_2NC_6H_4$ (**XXXIV, LXXXIII**), 4-$Et_2NC_6H_4$ (**XXXV, LXXXIV**), 4-$(CH_2CH_2Cl)_2NC_6H_4$ (**XXXVI, LXXXV**), 3,4-$CH_2O_2C_6H_3$ (**XXXVII, LXXXVI**), 4-$NO_2C_6H_4$ (**XXXVIII, LXXXVII**), 3-$NO_2C_6H_4$ (**XXXIX, LXXXVIII**), 2-$NO_2C_6H_4$(XL, LXXXIX), 4-PhC_6H_4(XLI, XC), 4-$PhCH_2OC_6H_4$(XLII, XCI), 3-MeO, 4-$PhCH_2OC_6H_3$ (**XLIII, XCII**), 2-$CF_3C_6H_4$ (**XLIV, XCIII**), cyclohexen-4-yl (**XLV, XCIV**), 4-$MeSC_6H_4$ (**XLVI, XCV**), 2-thienyl (**XLVII, XCVI**), 3-methyl-2-thienyl (**XLVIII, XCVII**), 2-pyridyl (**XLIX, XCVIII**), 3-pyridyl (**L, XCIX**), 1-naphthyl (**LI, C**), 6-OH (**CII**), 7,8-benzo (**CIII**).

products **XCVI–XCIX** is caused by the replacement of the phenyl ring by pyridine or thiophene one. In this case the increase in polarization and reactivity of C=O and C=N bonds in the molecules of aldehyde and azomethine is due to the *–I*-effect of the nitrogen or sulfur atom of the heterocyclic ring.

We believe that the observed yield reduction for phenanthrolines **LXXXIII–LXXXV** is due to deceleration of the reaction at the stage of Schiff's base **XXXIV–XXXVI** condensation with diketone **I** caused by stabilization of a protonated form of the azomethine through mesomeric transformations as it is known for *para*-dialkylamino-substituted benzalanilines and benzal-2-naphthylamines [10, 11].

The quaternization of azomethine is provided by a proton cleaved from diketone **I** (for brevity on the scheme are not shown the enol and enolate-anion forms present in the proton-acceptor solvent, alcohol [10]).

The replacement of the phenyl ring in the azomethine molecule by naphthyl results in reduced yield of reaction product C due to steric hindrances from the bulky substituent. The considerably smaller yields of phenanthrolines **LXV**, **LXVI** are caused apparently by steric hindrances from two *ortho*-substituents.

The condensation of salicylaldehyde, resorcylaldehyde, and also of 2-hydroxy-1-naphthalenecarbaldehyde with diketone **I** and amine **II** does not afford the expected 4,7-phenanthroline derivatives. The reaction provides products that do not contain nitro-

Table 1. Yields, melting points, and elemental analyses of aryl(heteryl)methylene-6-aminoquinolines **V, XIV, XVI, XXII**–**XXIV, XXVI, XXX, XXXI, XXXIII, XLIII**–**XLIX, LI** and 8-aryl-11,11-dimethyl-7,8,9,10,11,12-hexahydrobenzo[*a*]-4,7-phenanthrolin-9-ones **LII**–**C**

Compd. no.	Yield, %	mp, °C	Found, %[a]			Formula	Calculated, %[b]		
			C	H	N		C	H	N
V	78	44–45	82.90	5.74	11.69	$C_{17}H_{14}N_2$	82.92	5.69	12.07
XIV	75	43–144	63.51	3.18	9.26	$C_{16}H_{10}Cl_2N_2$	63.79	3.32	9.30
XVI	69	115–116	63.80	3.07	9.11	$C_{16}H_{10}Cl_2N_2$	63.79	3.32	9.30
XXII	76	140–141	77.53	5.36	10.54	$C_{17}H_{14}N_2O$	77.86	5.34	10.69
XXIII	82	92–93	77.96	5.53	9.87	$C_{18}H_{16}N_2O$	78.26	5.80	10.14
XXIV	79	73–75	78.51	6.24	9.27	$C_{19}H_{18}N_2O$	78.62	6.21	9.66
XXVI	74	88–89	74.09	5.56	9.31	$C_{18}H_{16}N_2O_2$	73.93	5.48	9.59
XXX	81	144–145	73.62	5.36	9.23	$C_{18}H_{16}N_2O_2$	73.93	5.48	9.59
XXXI	78	118–119	59.77	3.67	8.03	$C_{17}H_{13}BrN_2O$	59.82	3.81	8.21
XXXIII	83	121–122	71.29	4.83	8.45	$C_{19}H_{16}N_2O_3$	71.25	5.00	8.75
XLIII	80	153–154	78.17	5.25	7.73	$C_{24}H_{20}N_2O_2$	78.26	5.43	7.61
XLIV	84	71–72	–	–	9.26	$C_{17}H_{11}F_3N_2$	–	–	9.33
XLV	75	48–49	81.49	6.41	11.63	$C_{16}H_{15}N_2$	81.70	6.38	11.91
XLVI	83	114–115	74.12	5.29	9.34	$C_{18}H_{16}N_2S$	73.97	5.48	9.59
XLVII	77	88–89	70.51	4.26	11.53	$C_{14}H_{10}N_2S$	70.59	4.20	11.76
XLVIII	72	62–63	71.28	4.53	10.92	$C_{15}H_{12}N_2S$	71.43	4.76	11.11
XLIX	68	51–52	76.94	4.70	18.15	$C_{15}H_{11}N_3$	77.25	4.72	18.03
LI	76	43–44	84.89	4.71	9.76	$C_{20}H_{14}N_2$	85.11	4.96	9.93
LII	65	321–322	81.12	6.23	7.69	$C_{24}H_{22}N_2O$	81.36	6.21	7.91
LIII	55	319–320	81.43	6.28	7.81	$C_{25}H_{24}N_2O$	81.52	6.52	7.61
LIV	59	329–330	81.64	6.50	7.33	$C_{25}H_{24}N_2O$	81.52	6.52	7.61
LV	58	310–311	81.73	6.90	7.29	$C_{26}H_{26}N_2O$	81.68	6.81	7.33
LVI	51	319–320	81.59	7.28	7.04	$C_{27}H_{28}N_2O$	81.82	7.07	7.07
LVII	73	307–308	–	–	7.36	$C_{24}H_{21}FN_2O$	–	–	7.53
LVIII	75	308–309	–	–	7.19	$C_{24}H_{21}FN_2O$	–	–	7.53
LIX	69	314–315	73.92	5.29	6.88	$C_{24}H_{21}ClN_2O$	74.13	5.41	7.21
LX	72	340–341	74.01	5.52	7.14	$C_{24}H_{21}ClN_2O$	74.13	5.41	7.21
LXI	68	320–321	66.47	4.79	6.28	$C_{24}H_{21}BrN_2O$	66.51	4.85	6.47
LXII	69	323–324	66.32	4.69	6.11	$C_{24}H_{21}BrN_2O$	66.51	4.85	6.47
LXIII	83	345–346	67.75	4.52	6.71	$C_{24}H_{20}Cl_2N_2O$	68.09	4.73	6.62
LXIV	58	335–336	68.10	4.84	6.29	$C_{24}H_{20}Cl_2N_2O$	68.09	4.73	6.62
LXV	48	287–288	67.93	4.59	6.39	$C_{24}H_{20}Cl_2N_2O$	68.09	4.73	6.62
LXVI	30	294–295	–	–	7.01	$C_{24}H_{20}ClFN_2O$	–	–	6.89
LXVII	78	334–335	77.92	6.04	7.63	$C_{24}H_{22}N_2O_2$	77.84	5.95	7.57
LXVIII	71	342–343	78.01	6.11	7.42	$C_{24}H_{22}N_2O_2$	77.84	5.95	7.57
LXIX	66	322–324	74.59	5.73	7.12	$C_{24}H_{22}N_2O_3$	74.61	5.70	7.25
LXX	70	310–311	77.76	6.14	7.33	$C_{25}H_{24}N_2O_2$	78.13	6.25	7.29
LXXI	78	299–300	78.08	6.31	7.08	$C_{25}H_{24}N_2O_2$	78.13	6.25	7.29
LXXII	66	305–306	78.24	6.59	6.87	$C_{26}H_{26}N_2O_2$	78.39	6.53	7.04
LXXIII	78	248–249	78.41	6.52	6.94	$C_{27}H_{28}N_2O_2$	78.64	6.80	6.80
LXXIV	81	323–324	75.51	6.39	6.41	$C_{26}H_{26}N_2O_3$	75.36	6.28	6.76
LXXV	80	309–310	75.30	6.44	6.67	$C_{26}H_{26}N_2O_3$	75.36	6.28	6.76
LXXVI	69	265–266	75.10	6.16	6.84	$C_{26}H_{26}N_2O_3$	75.36	6.28	6.76
LXXVII	78	263–264	73.00	6.39	5.97	$C_{27}H_{28}N_2O_4$	72.97	6.31	6.31
LXXVIII	75	273–274	72.46	5.91	6.73	$C_{26}H_{26}N_2O_4$	72.56	6.05	6.51

Table 1 (Contd.)

Compd. no.	Yield, %	mp, °C	Found, %[a]			Formula	Calculated, %[b]		
			C	H	N		C	H	N
LXXIX	82	318–319	75.13	6.22	6.59	$C_{26}H_{26}N_2O_3$	75.36	6.28	6.76
LXXX	81	335–336	64.58	5.23	5.77	$C_{25}H_{24}BrN_2O_2$	64.66	5.17	6.03
LXXXI	82	311–312	75.46	5.80	6.84	$C_{26}H_{24}N_2O_3$	75.73	5.83	6.80
LXXXII	78	282–283	73.18	6.01	5.97	$C_{27}H_{26}N_2O_4$	73.30	5.88	6.33
LXXXIII	39	299–300	78.63	6.82	10.36	$C_{26}H_{27}N_3O$	78.59	6.80	10.58
LXXXIV	34	294–295	78.74	7.19	10.01	$C_{28}H_{31}N_3O$	79.06	7.29	9.88
LXXXV	40	276–277	67.68	5.94	8.33	$C_{28}H_{29}Cl_2N_3O$	68.02	5.87	8.50
LXXXVI	59	321–322	75.40	5.31	7.11	$C_{25}H_{22}N_2O_3$	75.38	5.53	7.04
LXXXVII	75	344–345	71.93	5.06	10.24	$C_{24}H_{21}N_3O_3$	72.18	5.26	10.53
LXXXVIII	74	304–305	72.16	5.21	10.64	$C_{24}H_{21}N_3O_3$	72.18	5.26	10.53
LXXXIX	70	305–306	72.04	5.29	10.31	$C_{24}H_{21}N_3O_3$	72.18	5.26	10.53
XC	71	306–308	83.59	5.94	6.50	$C_{30}H_{26}N_2O$	83.72	6.05	6.51
XCI	72	283–284	83.77	6.39	5.98	$C_{31}H_{28}N_2O$	83.78	6.31	6.31
XCII	64	254–255	78.21	6.03	5.76	$C_{32}H_{30}N_2O_3$	78.37	6.12	5.71
XCIII	68	314–315	–	–	7.03	$C_{25}H_{21}FN_2O$	–	–	7.29
XCIV	65	272–273	80.44	7.07	7.65	$C_{24}H_{25}N_2O$	80.67	7.00	7.84
XCV	65	307–308	74.83	6.02	6.69	$C_{25}H_{24}N_2OS$	75.00	6.00	7.00
XCVI	72	333–334	73.20	5.61	7.54	$C_{22}H_{20}N_2OS$	73.33	5.56	7.78
XCVII	78	328–329	74.00	5.92	7.31	$C_{23}H_{22}N_2OS$	73.80	5.88	7.49
XCVIII	71	292–293	77.55	5.90	11.65	$C_{23}H_{21}N_3O$	77.75	5.92	11.83
XCIX	78	322–323	77.80	5.83	11.84	$C_{23}H_{21}N_3O$	77.75	5.92	11.83
C	52	320–321	82.78	6.00	6.64	$C_{28}H_{24}N_2O$	83.17	5.94	6.93

[a] Found, %: Br 23.09 (**XXXI**), 18.22 (**LXI**), 18.50 (**LXII**), 17.19 (**LXXX**); **Cl 23.22 (XIV**), 23.19 (**XVI**), 8.93 (**LIX**), 8.86 (**LX**), 16.53 (**LXIII**), 16.34 (**LXIV**), 16.80 (**LXV**), 14.28 (**LXXXV**); **S 10.52 (XLVI**), 13.12 (**XLII**), 12.58 (**XLVIII**), 7.78 (**XCV**), 8.63 (**XCVI**), 8.24 (**XCVII**).

[b] **Calculated, %: Br 23.46 (XXXI**), 18.48 (**LXI, LXII**), 17.24 (**LXXX**); **Cl 23.59 (XIV, XVI**), 9.14 (**LIX, LX**), 16.78 (**LXIII**–**LXV**), 14.37 (**LXXXV**); **S 10.96 (XLVI**), 13.45 (**XLVII**), 12.70 (**XLVIII**), 8.00 (**XCV**), 8.89 (**XCVI**), 8.56 (**XCVII**).

gen, 2,5-dioxo-1-cyclohexyl derivatives of tetrahydroxanthene **CI**–**CIII**.

Obviously the three-component condensation with the above aldehydes takes the route *b* where the molecule of the aromatic aldehyde reacts with two dimedone (**I**) molecules yielding intermediate compound **C** followed by dehydration of the latter with participation of hydroxy group attached to benzene or naphthalene ring that affords exclusively tetrahydroxanthenes **CI**–**CIII**.

Demethylated analogs of xanthenes **CI, CII** were previously obtained by condensation of 6-aminoquinoline with salicylaldehyde, resorcylaldehyde, and 1,3-cyclohexadiene. With this diketone and the other aldehydes were isolated intermediate bisdiketones (B) that at heating with excess amine **II** afforded derivatives of 4,7-phenanthroline. We failed to obtain bisdiketones (**C**) in reaction of dimedone (**I**) with aromatic aldehydes and amine **II**. Thus with dimedone the second condensation route is limited to aldehydes containing ortho- or para-hydroxy group. The latter provided efficient transformation of bisdiketone (**C**) into partially hydrogenated xanthene derivatives.

Synthesized fused derivatives of 4,7-phenanthroline **LII**–**C** are colorless or yellow high-melting crystalline compounds. In their IR spectra appear characteristic absorption bands of stretching vibrations of NH and CO groups at 3290–3210 and 1620–1585 cm^{-1} respectively. The shift of the bands to lower frequencies is due to an intramolecular hydrogen bond [12], and also to conjugation of the carbonyl group with the quinoline ring. The stretching vibrations of alkyl groups and cycloaliphatic C–H bonds are observed in the region 2960–2870 cm^{-1}, of aromatic C–H bonds at 3060–3030 cm^{-1}. In the IR

Table 2. ^{1}H NMR spectrum of 8-aryl-l 1,1 I-dimethyl -7,8,9,10,ll,12-hexahydrobenzo[*a*]4,7-phenanthroline-9-enes (**LII**–**C**), δ, ppm[a]

Compd. no.	H[1], d (^3J4.6 Hz)	H[2], d.d (^3J8.2, ^4J 2.8 Hz)	H[3], d (^3J8.2 Hz)	H[5], H[6], 2d (^3J 8.6 Hz)	H[8], s	H[10], m	H[12], d.d (^{2}J 16.0 Hz)	Aromatic protons (*J*, Hz)	NH, s	Me, s
LII	8.29	7.33	8.61	7.49, 7.80	5.75	2.47	2.10	6.94-7.10 m	9.50	0.88, 1.11
LIII	8.28	7.30	8.60	7.50, 7.81	5.73	2.46	2.10	6.86 d, 7.12 d (^3J 8.2)	9.51	0.90, 1.10
LIV	8.33	7.31	8.59	7.51, 7.80	5.79	2.48	2.13	6.95-7.11 m	9.49	0.89, 1.11
LV	8.30	7.32	8.61	7.50, 7.82	5.76	2.43	2.12	6.90 d, 7.11 d (^3J 8.0)	9.52	0.92, 1.12
LVI	8.32	7.30	8.58	7.49, 7.77	5.81	2.45	2.11	6.94 d, 7.10 d (^3J 8.5)	9.53	0.91, 1.10
LVII	8.32	7.34	8.64	7.51, 7.88	5.80	2.43	2.10	6.91 t (^3J 8.9), 7.18 m	9.80	0.89, 1.03
LVIII	8.29	7.30	8.62	7.49, 7.80	5.77	2.48	2.08	6.99 m (^3J 8.8), 7.19-7.28 m	9.51	0.89, 1.10
LIX	8.33	7.31	8.59	7.50, 7.79	5.73	2.50	2.10	7.14 d, 7.22 d (SJ 8.2)	9.56	0.90, 1.11
LX	8.30	7.33	8.64	7.48, 7.81	5.78	2.47	2.09	6.98-7.17 m	9.53	0.91, 1.10
LXI	8.29	7.29	8.60	7.51, 7.78	5.75	2.51	2.10	7.11 d, 7.39 d (^3J 7.9)	9.60	0.90, 1.12
LXII	8.31	7.30	8.58	7.50, 7.79	5.69	2.50	2.12	7.00 s, 7.11-7.28 m	9.61	0.89, 1.09
LXIII	8.28	7.30	8.61	7.52, 7.79	5.74	2.46	2.11	7.08-7.21 m	9.52	0.90, 1.10
LXIV	8.29	7.31	8.59	7.49, 7.80	5.78	2.49	2.10	7.02-7.11 m, 7.14 s	9.50	0.91, 1.13
LXV	8.30	7.28	8.62	7.50, 7.83	5.75	2.53	2.12	7.06-7.19 m	9.58	0.88, 1.11
LXVI	8.29	7.34	8.66	7.51, 7.80	5.59	2.52	2.11	6.66-6.94 m	9.63	0.89, 1.07
LXVII	8.31	7.36	8.67	7.49, 7.84	5.61	2.50	2.12	6.48 d, 6.99 d (^3J 8.8)	9.74	0.87, 1.02
LXVIII	8.33	7.31	8.64	7.50, 7.86	5.74	2.47	2.10	6.42 d (V 4.0), 6.50-7.00 m	9.71	0.90, 1.09
LXIX	8.32	7.39	8.67	7.51, 7.87	5.63	2.51	2.13	6.48 s, 6.50 s	9.63	0.91, 1.06
LXX	8.29	7.30	8.65	7.49, 7.81	5.79	2.52	2.11	6.60 d, 7.07 d (^3J 8.1)	9.63	0.90, 1.08
LXXI	8.31	7.32	8.64	7.50, 7.77	5.78	2.48	2.10	6.72-7.04 m	9.59	0.89, 1.10
LXXII	8.27	7.30	8.60	7.46, 7.75	5.76	2.50	2.11	6.69 d, 7.10 d (^3J 8.0)	9.60	0.88, 1.10
LXXIII	8.32	7.29	8.66	7.51, 7.87	5.74	2.50	2.15	6.68 d, 7.12 d (^3J 7.9)	9.76	0.86, 1.09
LXXIV	8.27	7.30	8.59	7.48, 7.79	5.70	2.46	2.10	6.31-6.49 m, 7.06 d (^3J 8.2)	9.57	0.91, 1.10
LXXV	8.30	7.31	8.60	7.49, 7.81	5.73	2.49	2.12	6.40-6.50 m, 7.00 s	9.56	0.89, 1.10
LXXVI	8.39	7.39	8.65	7.51, 7.85	5.72	2.50	2.14	6.60 m, 7.01 s	9.51	0.92, 1.12
LXXVII	8.37	7.35	8.61	7.50, 7.82	5.75	2.48	2.12	6.45 s	9.55	0.95, 1.08
LXXVIII	8.36	7.33	8.62	7.48, 7.81	5.71	2.46	2.13	6.42 s	9.49	0.97, 1.11
LXXIX	8.31	7.28	8.60	7.49, 7.80	5.66	2.49	2.12	6.51-6.63 m, 7.00 s	9.50	0.94, 1.10
LXXX	8.28	7.30	8.63	7.50, 7.76	5.70	2.51	2.10	6.64 s, 6.71-6.99 m	9.47	0.91, 1.09
LXXXI	8.29	7.30	8.69	7.49, 7.80	5.78	2.48	2.07	7.36 d, 7.71 d (^3J 8.1)	9.54	0.90, 1.10
LXXXII	8.27	7.26	8.60	7.48, 7.77	5.76	2.49	2.11	7.01 s, 7.11-7.21 m	9.66	0.87, 1.08
LXXXIII	8.30	7.31	8.57	7.49, 7.78	5.73	2.50	2.10	6.46 d, 6.99 d (^3J 8.6)	9.70	0.88, 1.11

Table 2. (Contd.)

Compd. no.	H^1, d (^3J 4.6 Hz)	H^2, d.d (^3J 8.2, ^4J 2.8 Hz)	H^3, d (^3J 8.2 Hz)	H^5, H^6, 2d (^3J 8.6 Hz)	H^8, s	H^{10}, m	H^{12}, d.d (^{2}J 16.0 Hz)	Aromatic protons (*J*, Hz)	NH, s	Me, s
LXXXIV	8.34	7.32	8.64	7.50, 7.77	5.65	2.51	2.12	6.40 d, 7.00 d (^3J 8.5)	9.69	0.88, 1.10
LXXXV	8.30	7.29	8.63	7.51, 7.82	5.74	2.47	2.12	6.52 d, 7.03 d (^3J 8.6)	9.70	0.90, 1.09
LXXXVI	8.28	7.27	8.60	7.48, 7.80	5.67	2.49	2.10	6.59 s, 6.78 s	9.59	0.89, 1.10
LXXXVII	8.30	7.31	8.64	7.53, 7.93	5.84	2.50	2.09	7.45 d, 8.02 d (^3J 8.2)	9.72	0.90, 1.12
LXXXVII	8.29	7.30	8.63	7.55, 7.94	5.89	2.52	2.11	7.60-7.82 m, 8.10 s	9.78	0.90, 1.10
LXXXIX	8.80	7.25	8.70	7.54, 7.90	5.92	2.51	2.10	7.10 d, 7.40 m,	9.80	0.80, 1.03
XC	8.28	7.30	8.62	7.51, 7.83	5.79	2.52	2.13	7.75 d (^3J 8.2) 7.32-7.48 m	9.59	0.94, 1.11
XCI	8.29	7.28	8.63	7.50, 7.81	5.78	2.48	2.11	6.70 d, 7.12 d (^3J 7.8), 7.32 m	9.52	0.95, 1.10
XCII	8.30	7.28	8.60	7.52, 7.80	5.80	2.50	2.10	6.76-6.98 m, 7.07 s	9.51	0.94, 1.12
XCIII	8.33	7.30	8.61	7.53, 7.86	5.88	2.52	2.09	7.36-7.47 m, 8.03-8.19 m	9.73	0.91, 1.11
XCIV	8.37	7.38	8.70	7.50, 7.82	5.49	2.49	2.18	–	9.61	0.99, 1.12
XCV	8.32	7.39	8.56	7.49, 7.83	5.73	2.49	2.11	7.00 d, 7.19 d (^3J 7.9)	9.82	0.88, 1.04
XCVI	8.31	7.30	8.58	7.50, 7.80	6.03	2.50	2.14	6.55 s, 6.70 s, 7.00 s	9.61	0.89, 1.10
XCVII	8.30	7.27	8.60	7.48, 7.80	5.76	2.53	2.18	6.53 d, 6.95 d (^3J 7.9)	9.76	0.90, 1.11
XCVIII	8.32	7.29	8.61	7.50, 7.76	5.79	2.50	2.13	6.96-7.11 m, 8.49 d (^3J 7.8)	9.70	0.91, 1.12
XCIX	8.29	7.32	8.60	7.51, 7.83	5.71	2.49	2.11	6.91-7.06 m, 8.37 s	9.72	0.90, 1.10
C	8.36	7.31	8.58	7.49, 7.81	5.77	2.50	2.13	6.95-7.22 m	9.74	0.89, 1.10

[a] Chemical shifts, δ, ppm: 2.18, s (Me) (**LIV**); 1.15 t, 2.50 q (Et) (**LV**); 1.08 d, 2.70 m ($CHMe_2$) (**LVI**); 9.00 s (OH) (**LXVII**); 9.11 s (OH) (**LVIII**); 8.38 s (OH), 8.47 s (**LXIX**); 3.80 s (OMe) (**LXX**); 3.82 s (OMe) (**LXXI**); 1.20 t, 4.10 q (OEt) (**LXXII**); 0.94 t, 1.60 q, 3.75 t (OCH_2CH_2Me) (**LXXIII**); 3.62 s (OMe), 3.87 s (OMe) (**LXXIV**); 3.60 s (OMe), 3.86 s (OMe) (**LXXV**); 3.14 s (OMe), 3.21 s (OMe) (**LXXVI**); 3.55 s (OMe), (**LXXVII**); 3.66 s [(OMe_2)], 7.90 s (OH) (**LXXVIII**); 1.18 t, 4.13 q (OEt), 8.10 s (OH) (**LXXIX**); 3.76 s (OMe) (**LXXX**); 3.76 s (CO_2Me) (**LXXXI**); 3.70 s (OMe), 3.82 s (CO_2Me) (**LXXXII**); 2.72 s (NMe_2) (**LXXXIII**); 0.98 t, 3.15 q (NEt_2) (**LXXXIV**); 3.12 d 4.58 d [$N(CH_2CH_2Cl)_2$] (**LXXXV**); 5.84 m (OCH_2O) (**LXXXVI**); 4.90 s (OCH_2Ph) (**XCI**); 3.84 s (OMe), 4.87 s (OCH_2Ph) (**XCII**); 1.16–2.00 m (7H cycloaliph.), 4.80 s (CH=CH) (**XCIV**); 2.44 s (Me) (**XCVII**).

spectra of compounds **LXX–LXXXII, LXXXVI, XCI, XCII** appear the bands from the C–O–C fragment in the region 1245–1230 cm^{-1}, in the spectrum of compound **XCV** is observed a strong band of stretching vibrations of C–S bond at 1125 cm^{-1}, and those of phenanthrolines **LXXXI, LXXXII** contain an absorption band of the ester group at 1725–1720 cm^{-1}.

In the mass spectra of benzophenanthrolines **LII–C** the molecular ion $[M]^+$ peaks are of moderate intensity (12–45%). The most abundant (100%) is the ion $[M–R]^+$ (*m/z* 277). In the spectra of compounds **LXXIV, LXXXIII, C** were registered peaks of ions $[R + H]^+$, *m/z* 138 (26%), 121 (83%), 128 (15%) respectively evidencing the relative stability of 1,3-dimethoxybenzene, *N*,*N*-dimethylaniline, and naphthalene ions to electron impact. In all the spectra of phenanthrolines **LII–C** appears a peak of ion with *m/z* 193 (18–52%) corresponding to elimination of a fragment $(CH_3)_2CHCH_2CO$ from ion $[M–R]^+$.

The electron absorption spectra of compounds **LII–C** have bands in the UV region with pronounced vibronic structure. Since in the molecules of benzophenanthrolines **LII–C** the benzene and pyridine rings are partly hydrogenated, the main chromophore is the quinoline core conjugated with a carbonyl group. Therefore the bands with λ_{max} 214–222, 234–258, 288–299 nm may be assigned to the 6-aminoquinoline system [UV spectrum, λ_{max}, nm ($\log\varepsilon$): 206 (4.08), 247 (4.35), 279 (3.59)]. A considerable red shift and greater intensity of the first and third bands in the spectra of phenanthrolines **LII–C** are apparently due to the effect of the carbonyl group and overlapping with the absorption bands of phenyl, heteroaromatic, or naphthalene substituent R unconjugated with the quinoline core. The bands appearing in the longwave spectrum region (333–339, 369–381 nm) are probably due to the presence of the carbonyl group [13]. The substituents in the phenyl ring of compounds **LIII–XCIII, XCIV** virtually do not affect the position and intensity of the absorption bands. It is noteworthy that the UV spectra of compounds **LII–C** are identical to those of the previously studied demethylated analogs, 8-aryl-7,8,9,10,11,12-hexahydrobenzo[*a*]-4,7-phenanthrolin-9-ones [7] that presumably evidences no steric hindrances to conformational lability of cyclohexene and dihydropyridine rings from the of methyl groups; therefore the presence of the methyl groups does not affect the electron transitions in the fused quinoline system and the carbonyl group.

A characteristic feature of ^1H NMR spectra of 4,7-phenanthrolines **LII–C** consists in a downfield shift of the signal from the methine proton in the hydrogenated pyridine ring (H^8) as compared to the usual position of methine proton signals in cyclic compounds. This shift is due to the effect of the adjacent nitrogen atom and of an aromatic ring. The influence of the latter is confirmed by the fact that in the spectrum of phenanthroline **XCIV** where instead of aryl is present a cyclohexenyl substituent the downfield shift of H^8 atom is the least in the phenanthroline series **LII–c**, and the corresponding chemical shift is the smallest (5.49 ppm).

Thus the three-component condensation of 6-aminoquinoline, aromatic aldehyde, and dimedone can serve as a convenient one-pot preparation method for synthesis of diverse hard-to-obtain derivatives of 4,7-phenanthroline. The intermediate compounds in the phenanthrolines synthesis, azomethines of the 6-aminoquinoline series, are of separate interest as potential biologically active substances and synthons for preparation of various nitrogen-containing heterocycles.

EXPERIMENTAL

IR spectra were obtained on UR-20 instrument from KBr pellets. Mass spectra were registered on MKh-1320 device with direct samples input, energy of ionizing electrons 50 eV, evaporation of samples at 180–200°C. UV spectra of solutions in ethanol (c 10^{-4} mol l^{-1}) were measured on spectrophotometer Specord UV-Vis. ^1H NMR spectra were recorded on spectrometers Bruker AC-300 (300 MHz) or Tesla BS-567 (100 MHz) at concentration of solutions 2–5 wt% in deuterochloroform for azomethines **III–LI** and DMSO-d_6 for compounds **LII–C**, internal reference TMS. Melting points were measured on Koeffler heating block.

6-Aminoquinoline (II) was prepared along procedure [14]. Arylmethylene-6-aminoquinolines **III–LI** were synthesized by boiling amine **II** and an appropriate aromatic aldehyde in ethanol or 2-propanol. Preparation procedure and characteristics of azomethines **III,IV, VI–XIII, XV, XVII–XXI, XXV, XXVII–XXIX, XXXII, XXXIV–XLII, L**) were published elsewhere [14]. The yields and analytical data on the azomethines obtained for the first time **V, XIV, XVI, XXII–XXIV, XXVI, XXX, XXXI, XXXIII, XLIII–XLIX, LI** are presented in Table 1.

8-Aryl-11,11-dimethyl-7,8,9,10,11,12-hexahydro[*a*]-4,7-phenanthrolin-9-ones LII–C.

(a) A solution of 5 mmol of dimedone (**I**), 5 mmol of 6-aminoquinoline (**II**), and 5 mmol of an appropriate aldehyde in 20 ml of 1-butanol was refluxed for 5–6 h. The precipitate separated on cooling was filtered off and recrystallized from a mixture ethanol–benzene (3 : 1). (b) A solution of 5 mmol of dimedone (**I**) and 5 mmol of azomethine **III–LI** in 20 ml of 1-butanol was refluxed for 5 h. The reaction products **LII–C** were isolated as described above. Yield of phenanthrolines **LII–C** 40–85%.

9-[1-(1,3-Dioxocyclohexyl)]-3,3,6,6-tetramethyl-1,2,3,4-tetrahydroxanthen-1-ones CI–CIII were obtained from dimedone (**I**), 60 aminoquinoline (**II**), and an appropriate aldehyde along procedure *a*. Reaction products **CI–CIII** were recrystallized from ethanol. Compound **CI**, yield 39%, mp 205–206°C. IR spectrum, ν, cm^{-1}: 1620 (C=O), 1255 (C–O–C), 2960–2870 (CH_3, CH_2). ^1H NMR spectrum, δ, ppm: 0.96 s (6H, CH_3), 1.08 s (3H, CH_3), 1.14 s (3H, CH_3), 2.18–2.60 m (8H, CH_2), 5.08 s (1H, CH), 7.00–7.20 m (4H arom). Mass spectrum, *m/z* (I_{rel}, %): 366 $[M]^+$ (58), 281 (100), 227 (80). Found, %: C 75.25; H 7.02. $C_{23}H_{26}O_4$. Calculated, %: C 75.41; H 7.10. Compound **CII**, yield 66%, mp 242–243°C. IR spectrum, ν, cm^{-1}: 1630 (C=O), 1240 (C–O–C), 2970–2890 (CH_3, CH_2). ^1H NMR spectrum, δ, ppm: 0.98 s (6H, CH_3), 1.08 s (3H, CH_3), 1.16 s (3H, CH_3), 2.20– 2.62 m (8H, CH_2), 5.00 s (1H, CH), 6.38– 6.88 m (3H arom). Mass spectrum, *m/z* (I_{rel}, %): 382 $[M]^+$ (20), 298 (25), 242 (50), 227 (100). Found, %: C 72.02; H 6.88. $C_{23}H_{26}O_5$. Calculated, %: C 72.25; H 6.81. Compound **CIII**, yield 48%, mp 244–245°C. IR spectrum, ν, cm^{-1}: 1650 (C=O), 1240 (C–O–C), 2950–2820 (CH_3, CH_2). ^1H NMR spectrum, δ, ppm: 0.90 s (6H, CH_3), 1.08 s (3H, CH_3), 1.18 s (3H, CH_3), 2.10– 2.68 m (8H, CH_2), 5.62 s (1H, CH), 7.20–8.35 m (6H arom). Mass spectrum, *m/z* (I_{rel}, %): 416 $[M]^+$ (50), 332 (45), 277 (100). Found, %: C 77.49; H 6.49. $C_{27}H_{28}O_4$. Calculated, %: C 77.88; H 6.71.

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