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INVESTIGATION OF 2,3'-BIQUINOLYL. 11.* REGIOSELECTIVITY IN THE HYDROXYLATION OF 1-ALKYL-3-(2-QUINOLYL)QUINOLINIUM HALIDES

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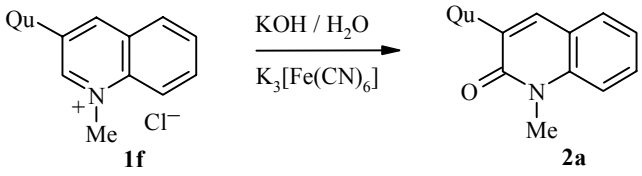
The hydroxylation of 1-alkyl-3-(2-quinolyl)quinolinium halides by an alkaline solution of $K_3[Fe(CN)_6]$ in aqueous 1,4-dioxane leads to a mixture of 1-alkyl-3-(2-quinolyl)-1,2-dihydro-2-quinolones and 1-alkyl-3-(2-quinolyl)-1,4-dihydro-4-quinolones with predominance of the former. The use of the system of $K_3[Fe(CN)_6]/Mg(OH)_2$ in aqueous 1,4-dioxane leads to the regiospecific formation of 1-alkyl-3-(2-quinolyl)-1,4-dihydro-4-quinolones.

Keywords: 2,3'-biquinolyls, 1-alkyl-3-(2-quinolyl)quinolinium halides, 1-alkyl-3-(2-quinolyl)-1,2-dihydro-2-quinolones, 1-alkyl-3-(2-quinolyl)-1,4-dihydro-4-quinolones, hydroxylation, oxidation, nucleophilic addition, regioselectivity.

Derivatives of 2,3'-biquinolyl, in particular, its 1'-quaternization products, 1-alkyl-3-(2-quinolyl)quinolinium halides (**1**) [3], have become available with the development of a convenient synthesis of 2,3'-biquinolyl [2]. The hydroxylation for 2,3'-biquinolyl derivatives was studied within an investigation of nucleophilic addition in these compounds.

This reaction was described by Kröhnke [4] for 1-methyl-3-(2-quinolyl)quinolinium chloride (**1f**). The oxidation of **1f** by the $K_3[Fe(CN)_6]/KOH/H_2O$ system gives 1-methyl-3-(2-quinolyl)-1,2-dihydro-2-quinolone (**2a**) as indicated by IR spectroscopy in 50% yield. Water-soluble chloride **1f** was obtained by two-fold exchange of the counter-ion.



1f **2a**

Qu = 2-quinolyl

The products of the quaternization of 2,3'-biquinolyl by alkyl iodides and bromides are the most available as starting compounds for developing a general method for the synthesis of **2**. The low solubility of **1a-e** in water led us to use 50% aqueous dioxide. The yield of **2a-e** after recrystallization was 40-60%.

* Communication 10, see ref. [1].

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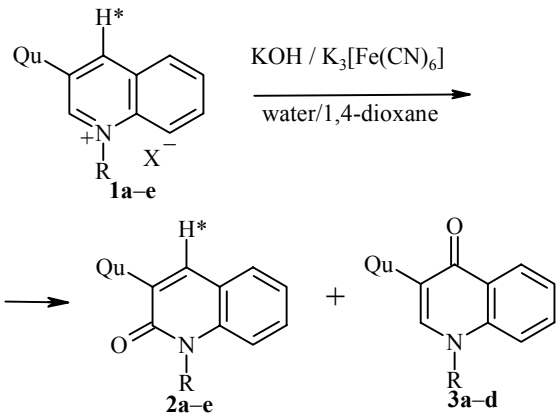

1, 2 a H* = D; **1**, **2**, **3 a** R = Me, **b** R = Et, **c** R = Bu, **d** R = CH_2Ph;
1, **2 e** R = $CH_2CH{=}CH_2$; **1**a–d X = I, **e** X = Br

4-Quinolones were formed in the oxidation reaction. The structure of methylquinolones **2a** and **3a** was demonstrated experimentally with the 4-D salt of **1a**. The isomer ratio is given in Table 1 and depends on steric hindrance at $C_{(2)}$ created by the substituent at $N_{(1)}$.

The addition of the hydroxide ion to $C_{(4)}$ in the 3-nitroquinolinium cation is thermodynamically controlled [5]. We assumed that 4-quinolones **3** are the thermodynamic control products. Indeed, products **3b** and **3c** were isolated in about 40% yield upon heating the reaction mixture at reflux. However, thin-layer chromatography showed the formation of side-products, namely, 1,2- and 1,4-dihydro systems, as in the reaction without oxidizing agent. We also showed that replacement of the counter-ion by thiocyanate ion in salts **1a** and **1b** (as the result of an attempt to effect nucleophilic addition) leads to an increased fraction of 4-quinolones but poor reproducibility of the oxidation results hindered the development of this method.

On the other hand, the corresponding 4-quinolone was obtained in an attempt to effect the cyanomethylation of **1a** in KOH/CH_3CN. Since addition at $C_{(4)}$ in azinium salts is attributed to softness of the nucleophile [6], we assumed that crystalline KOH is a softer reagent than the solvated hydroxide ion. In order to reduce the hydroxide ion concentration in solution, which also required suppression of the competing cyanomethylation, we dried the reaction mixture with $Mg(ClO_4)_2$. Indeed, heating salts **1a-c** in the $Mg(ClO_4)_2/CH_3CN/KOH$ system gave 4-quinolones but in low yield.

Alternative hypotheses for addition at $C_{(4)}$ appeared in addition to the presumably critical role of the softness of crystalline alkali, namely, the replacement of the counter-ion in the salt by ClO_4^- and formation of $Mg(OH)_2$. The oxidation of quinolinium perchlorates **1a-c** by the $K_3[Fe(CN)_6]/KOH/1,4$-dioxane/H_2O system upon heating at reflux led to a complex product mixture.

The use of $K_3[Fe(CN)_6/Mg(OH)_2$ in aqueous 1,4-dioxane proved most efficient. In the resultant procedure, $Mg(OH)_2$ was obtained in one pot from KOH and $Mg(ClO_4)_2$. The yields of **3a-c** were 50-70%.

TABLE 1. Ratio of the 2- and 4-Hydroxylation Products of 1-Alkyl-3-(2-quinolyl)quinolinium Iodides **1a-d**

Compounds **2**, **3**	R	Ratio **2** : **3**	Total yield, %
a	Me	90.8 : 9.2	9.4
b	Et	87.3 : 13.3	98.5
c	Bu	82.5 : 17.5	98.0
d	$PhCH_2$	90.2 : 9.8	94.0

EXPERIMENTAL

The IR spectra were taken on a Pye Unicam 9512 spectrometer for KBr pellets. The NMR spectra were registered on a Bruker WP-200 spectrometer at 200 MHz and Bruker AM-300 spectrometer at 300 MHz using TMS as the internal standard. The elemental analysis of **2e** was carried out on a CHN-1 analyzer. The reaction course and purity of the products were monitored by thin-layer chromatography on Silufol UV-254 plates using 1:1 ethyl acetate–hexane as the eluent. The mass spectra were taken on a Varian CH7 mass spectrometer.

A sample of 2,3'-biquinolyl for the preparation of salts **1a-e** was prepared according to our procedure [1], while 4'-D-2,3'-biquinolyl was prepared according to our reported procedure [7]. Salts **1a** and **1b** were prepared according to Romanenko [8], while salts **1c-e** were prepared according to our previous procedure [2].

1-Alkyl-3-(2-quinolyl)-1,2-dihydro-2-quinolones (2a-e). A. A mixture of finely ground 1-alkyl-3-(2-quinolyl)quinolinium halide **1a-e** (2.5 mmol), KOH (0.62 g, 11 mmol), and $K_3[Fe(CN)_6]$ (1.81 g, 5.5 mmol) in 50% aqueous 1,4-dioxane (40 ml) was stirred vigorously for 2 h at room temperature. The reaction mixture was heated until the precipitate dissolved, cooled to room temperature, and extracted with benzene. The extract was washed with water. The organic layer was evaporated in vacuum and the crystalline precipitate was recrystallized from ethanol to give 2-quinolones **2a-e** in 40-60% yield. The residue after evaporation was dissolved in 10 ml benzene and subjected to flash chromatography on a dry column packed with silica gel L5/40 (h = 25 mm, d = 23 mm) [9]. The first fraction was eluted with benzene (**2a-d**) and the second fraction was eluted with ethyl acetate (**3a-d**). The solvent was evaporated and the yield determined. When necessary, the products were recrystallized from ethanol.

B. A mixture of KOH (0.62 g, 11 mmol) and $Mg(ClO_4)_2$ (1.22 g, 5.5 mmol) in 50% aqueous 1,4-dioxane (40 ml) was heated at reflux. Then, finely ground 1-alkyl-3-(2-quinolyl)quinolinium halide **1a-d** (2.5 mmol) with $K_3[Fe(CN)_6]$ (1.81 g, 5.5 mmol) was added and the mixture was heated at reflux for 2 h. The reaction mixture was cooled to room temperature and extracted with benzene. The extract was washed with water and filtered. The organic layer was evaporated in vacuum and the crystalline precipitate was recrystallized from ethanol to give the products in 50-70% yield.

1-Methyl-3-(2-quinolyl)-1,2-dihydro-2-quinolone (2a, $C_{19}H_{14}N_2O$) was obtained by procedure A. Yield 0.450 g (62.9%); mp 174-175°C (ethanol) (mp 174-175°C [3]), R_f 0.62 (1;2 ethyl acetate–hexane). IR spectrum: 1631 cm^{-1} (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, J, Hz: 3.86 (3H, s, 1-CH_3); 7.30 (1H, dd, J_{56} = 7.78, J_{67} = 7.44, 6-H); 7.43 (1H, d, $J_{5'6'}$ = 7.94, 5'-H); 7.55 (1H, dd, $J_{5'6'}$ = 7.94, $J_{6'7'}$ = 7.71, 6'-H); 7.63 (1H, dd, J_{67} = 7.44, J_{78} = 8.25, 7-H); 7.74 (1H, dd, $J_{6'7'}$ = 7.71, $J_{7'8'}$ = 8.31, 7'-H); 7.78 (1H, d, J_{56} = 7.78, 5-H); 7.86 (1H, d, J_{78} = 8.25, 8-H); 8.17 (1H, d, $J_{7'8'}$ = 8.31, 8'-H); 8.22 (1H, d, $J_{3'4'}$ = 8.85, 4'-H); 8.44 (1H, d, $J_{3'4'}$ = 8.85, 3'-H); 8.69 (1H, s, 4-H). Mass spectrum, m/z (I_{rel}, %): 286 (100) $[M]^+$, 271 (98) $[M - CH_3]^+$, 257 (90) $[M - CHO]^+$, 242 (11), 230 (8), 143 (22), 135 (8), 128 (71), 115 (6), 101 (16), 89 (6), 76 (15), 63 (5), 58 (11), 51 (15), 46 (31), 44 (37).

4-D-1-Methyl-3-(2-quinolyl)-1,2-dihydro-2-quinolone (2a, $C_{19}H_{13}DN_2O$) was prepared according to procedure A. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, J, Hz: 3.78 (3H, s, 1-CH_3); 7.35 (1H, dd, J_{56} = 7.67, J_{67} = 7.54, 6-H); 7.61 (1H, d, $J_{5'6'}$ = 8.09, 5'-H); 7.63 (1H, dd, $J_{5'6'}$ = 8.09, $J_{6'7'}$ = 7.36, 6'-H); 7.71 (1H, dd, J_{67} = 7.54, J_{78} = 7.95, 7-H); 7.79 (1H, dd, $J_{6'7'}$ = 7.36, $J_{7'8'}$ = 8.43, 7'-H); 7.96 (1H, d, J_{56} = 7.67, 5-H); 8.00 (1H, d, J_{78} = 7.95, 8-H); 8.11 (1H, d, $J_{7'8'}$ = 8.43, 8'-H); 8.22 (1H, d, $J_{3'4'}$ = 8.52, 4'-H); 8.44 (1H, d, $J_{3'4'}$ = 8.52, 3'-H); 8.72 (1H(D), w. s, 4-H).

1-Ethyl-3-(2-quinolyl)-1,2-dihydro-2-quinolone (2b, $C_{20}H_{16}N_2O$). A. Yield 0.443 g (59%); mp 146-147°C (ethanol), R_f 0.76 (1:2 ethyl acetate–hexane). IR spectrum: 1641 cm^{-1} (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, J, Hz: 1.32 (3H, t, J = 7.05, 1-CH_2CH_3); 4.45 (2H, q, J = 7.05, 1-$C\underline{H}_2CH_3$); 7.34 (1H, dd, J_{56} = 7.89, J_{67} = 7.41, 6-H); 7.61 (1H, d, $J_{5'6'}$ = 7.40, 5'-H); 7.66 (1H, dd, $J_{5'6'}$ = 7.40, $J_{6'7'}$ = 7.75, 6'-H); 7.71 (1H, dd, J_{67} = 7.41, J_{78} = 7.61, 7-H); 7.79 (1H, dd, $J_{6'7'}$ = 7.75, $J_{7'8'}$ = 8.43, 7'-H); 7.97 (1H, d, J_{56} = 7.89, 5-H); 8.00 (1H, d, J_{78} = 7.61, 8-H); 8.11 (1H, d, $J_{7'8'}$ = 8.43, 8'-H); 8.22 (1H, d, $J_{3'4'}$ = 8.55, 4'-H); 8.44 (1H, d, $J_{3'4'}$ = 8.55, 3'-H); 8.72 (1H, s, 4-H). Mass spectrum, m/z (I_{rel}, %): 300 (90) $[M]^+$, 286 (100) $[M - CH_2]^+$, 272 (88)

$[M - C_2H_5]^+$, 257 (61), 244 (90), 228 (6), 218 (11), 202 (7), 128 (83), 114 (6), 101 (21), 90 (6), 76 (23), 63 (5), 58 (13), 51 (8), 44 (24).

1-Butyl-3-(2-quinolyl)-1,2-dihydro-2-quinolone (2c, $C_{22}H_{20}N_2O$) was obtained according to procedure A. Yield 0.492 g (60%); mp 113-114°C (ethanol), R_f 0.91 (1:2 ethyl acetate–hexane). IR spectrum: 1641 cm^{-1} (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm, *J*, Hz: 0.98 (3H, t, *J* = 6.77, 1-$CH_2CH_2CH_2C\underline{H}_3$); 1.47 (2H, m, 1-$CH_2CH_2C\underline{H}_2CH_3$); 1.72 (2H, m, $CH_2C\underline{H}_2CH_2CH_3$); 4.39 (2H, t, *J* = 6.79, 1-$C\underline{H}_2CH_2CH_2CH_3$); 7.33 (1H, dd, J_{56} = 7.92, J_{67} = 7.32, 6-H); 7.63 (1H, d, $J_{5'6'}$ = 7.52, 5'-H); 7.64 (1H, dd, $J_{5'6'}$ = 7.52, $J_{6'7'}$ = 7.12, 6'-H); 7.71 (1H, dd, J_{67} = 7.32, J_{78} = 8.21, 7-H); 7.80 (1H, dd, J_{67} = 7.12, $J_{7'8'}$ = 8.36, 7'-H); 7.96 (1H, d, J_{56} = 7.92, 5-H); 8.01 (1H, d, J_{78} = 8.21, 8-H); 8.11 (1H, d, $J_{7'8'}$ = 8.36, 8'-H); 8.22 (1H, d, $J_{3'4'}$ = 8.54, 4'-H); 8.44 (1H, d, $J_{3'4'}$ = 8.54, 3'-H); 8.71 (1H, s, 4-H). Mass spectrum, *m/z* (I_{rel}, %): 328 (90) $[M]^+$, 313 (14) $[M - CH_2]^+$, 299 (69) $[M - C_2H_5]^+$, 286 (100) $[M - C_3H_6]^+$, 727 (88) $[M - C_4H_8]^+$, 257 (61) $[M - C_3H_7CO]^+$, 244 (90), 228 (6), 218 (11), 202 (7), 128 (83), 114 (6), 101 (21), 90 (6), 76 (23), 63 (5), 58 (13), 51 (8), 44 (24).

1-Benzyl-3-(2-quinolyl)-1,2-dihydro-2-quinolone (2d, $C_{25}H_{18}N_2O$) was obtained according to procedure A. Yield 0.335 g (37%); mp 167-168°C (ethanol), R_f 0.84 (1:2 ethyl acetate–hexane). IR spectrum: 1640 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm, *J*, Hz: 5.69 (2H, s, 1-$C\underline{H}_2Ph$); 7.25 (5H, m, 1-$CH_2\underline{Ph}$); 7.32 (1H, dd, J_{56} = 7.76, J_{67} = 7.51, 6-H); 7.49 (1H, d, $J_{5'6'}$ = 7.85, 5'-H); 7.56 (1H, dd, $J_{5'6'}$ = 7.85, $J_{6'7'}$ = 7.78, 6'-H); 7.65 (1H, dd, J_{67} = 7.51, J_{78} = 8.32, 7-H); 7.74 (1H, dd, $J_{6'7'}$ = 7.78, $J_{7'8'}$ = 8.45, 7'-H); 7.78 (1H, d, J_{56} = 7.76, 5-H); 7.86 (1H, d, J_{78} = 8.32, 8-H); 8.19 (1H, d, $J_{7'8'}$ = 8.45, 8'-H); 8.23 (1H, d, $J_{3'4'}$ = 8.90, 4'-H); 8.50 (1H, d, $J_{3'4'}$ = 8.90, 3'-H); 8.76 (1H, s, 4-H). Mass spectrum, *m/z* (I_{rel}, %): 362 (100) $[M]^+$, 333 (15) $[M - CHO]^+$, 286 (6) $[M - C_6H_4]^+$, 271 (14) $[M - C_6H_5CH_2]^+$, 257 (34) $[M - C_6H_5CO]^+$, 244 (7), 230 (9), 216 (8), 206 (7), 166 (8), 128 (31), 101 (4), 91 (39), 44 (70).

1-Allyl-3-(2-quinolyl)-1,2-dihydro-2-quinolone (2e, $C_{21}H_{16}N_2O$) was obtained according to procedure A. Yield 0.312 g (40%); mp 94-95°C (benzene–petroleum ether). ^1H NMR spectrum (acetone-d_6), δ, ppm, *J*, Hz: 5.12 (2H, m, J_{vic} = 5.13, J_{gem} = 1.71, 1-$C\underline{H}_2CH{=}CH_2$); 5.20 (1H, dd, J_{trans} = 15.37, J_{gem} = 3.84, 1-$CH_2CH{=}C\underline{H}^AH^B$); 5.23 (1H, dd, J_{cis} = 10.24, J_{gem} = 3.84, 1-$CH_2CH{=}CH^AC\underline{H}^B$) 6.07 (1H, m, 1-$CH_2C\underline{H}{=}CH_2$); 7.33 (1H, dd, J_{56} = 7.90, J_{67} = 7.05, 6-H); 7.55 (1H, d, $J_{5'6'}$ = 7.81, 5'-H); 7.60 (1H, dd, $J_{5'6'}$ = 7.81, $J_{6'7'}$ = 7.68, 6'-H); 7.67 (1H, dd, J_{67} = 7.05, J_{78} = 8.11, 7-H); 7.78 (1H, dd, $J_{6'7'}$ = 8.96, $J_{7'8'}$ = 8.96, 7'-H); 7.94 (1H, d, J_{56} = 7.90, 5-H); 7.98 (1H, d, J_{78} = 8.11, 8-H); 8.12 (1H, d, $J_{7'8'}$ = 8.96, 8'-H); 8.34 (1H, d, $J_{3'4'}$ = 8.54, 4'-H); 8.58 (1H, d, $J_{3'4'}$ = 8.54, 3'-H); 8.85 (1H, s, 4-H). Found, %: C 80.86; H 5.02; N 9.03. $C_{21}H_{16}N_2O$. Calculated, %: C 80.75; H 5.16; N 8.97.

1-Methyl-3-(2-quinolyl)-1,4-dihydro-4-quinolone (3a, $C_{19}H_{14}N_2O$) was obtained according to procedure B. Yield 0.402 g (56.5%); mp 193-194°C (benzene) (mp 193-194°C [3]), R_f 0.05 (1:2 ethyl acetate–hexane). IR spectrum: 1619 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm, *J*, Hz: 4.00 (3H, s, 1-CH_3); 7.48 (1H, dd, J_{56} = 7.86, J_{67} = 7.34, 6-H); 7.49 (1H, dd, $J_{5'6'}$ = 7.53, $J_{6'7'}$ = 7.12, 6'-H); 7.51 (1H, d, J_{78} = 8.20, 8-H); 7.69 (1H, dd, J_{67} = 7.34, J_{78} = 8.20, 7-H); 7.73 (1H, dd, $J_{6'7'}$ = 7.12, $J_{7'8'}$ = 8.35, 7'-H); 7.83 (1H, d, $J_{5'6'}$ = 7.53, 5'-H); 8.06 (1H, d, $J_{7'8'}$ = 8.35, 8'-H); 8.20 (1H, d, $J_{3'4'}$ = 8.40, 4'-H); 8.64 (1H, d, J_{56} = 7.86, 5-H); 8.84 (1H, d, $J_{3'4'}$ = 8.40, 3'-H); 8.91 (1H, s, 2-H). Mass spectrum, *m/z* (I_{rel}, %): 286 (88) $[M]^+$, 271 (100) $[M - CH_3]^+$, 257 (43) $[M - CHO]^+$, 242 (14), 230 (11), 215 (6), 154 (6), 143 (37), 128 (6), 115 (28), 102 (15), 80 (7), 76 (13), 69 (6), 63 (6), 58 (11), 51 (5), 44 (69).

1-Ethyl-3-(2-quinolyl)-1,4-dihydro-4-quinolone (3b, $C_{20}H_{16}N_2O$) was obtained according to procedure B. Yield 0.518 g (69%); mp 131-132°C (benzene), R_f 0.19 (1:2 ethyl acetate–hexane). IR spectrum: 1618 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm, *J*, Hz: 1.62 (3H, t, *J* = 7.26, 1-$CH_2C\underline{H}_3$); 4.42 (2H, q, *J* = 7.26, 1-$C\underline{H}_2CH_3$); 7.47 (1H, dd, J_{56} = 7.80, J_{67} = 7.39, 6-H); 7.50 (1H, dd, $J_{5'6'}$ = 7.56, $J_{6'5'}$ = 7.10, 6'-H); 7.54 (1H, d, J_{78} = 8.18, 8-H); 7.70 (1H, dd, J_{67} = 7.39, J_{78} = 8.18, 7-H); 7.73 (1H, dd, $J_{6'7'}$ = 7.10, $J_{7'8'}$ = 8.25, 7'-H); 7.83 (1H, d, $J_{5'6'}$ = 7.56, 5'-H); 8.08 (1H, d, $J_{7'8'}$ = 8'-H); 8.21 (1H, d, $J_{3'4'}$ = 8.54, 4'-H); 8.66 (1H, d, J_{56} = 7.80, 5-H); 8.85 (1H, d, $J_{3'4'}$ = 8.54, 3'-H); 8.95 (1H, s, 2-H). Mass spectrum, *m/z* (I_{rel}, %): 300 (50) $[M]^+$, 272 (100) $[M - C_2H_4]^+$, 242 (15), 216 (11), 154 (18), 150 (14), 140 (16), 128 (27), 114 (6), 76 (23), 63 (7), 58 (32), 51 (14), 44 (38).

1-Butyl-3-(2-quinolyl)-1,4-dihydro-4-quinolone (3c, $C_{22}H_{20}N_2O$) was obtained according to procedure B. Yield 0.410 g (50.0%); mp 121-122°C (benzene), R_f 0.47 (1:2 ethyl acetate–hexane). IR spectrum: 1618 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm, *J*, Hz: 1.20 (3H, t, *J* = 7.26, 1-$CH_2CH_2CH_2C\underline{H}_3$); 1.51 (2H, m, 1-$CH_2CH_2C\underline{H}_2CH_3$); 1.96 (2H, m, 1-$CH_2C\underline{H}_2CH_2CH_3$); 4.32 (2H, t, *J* = 7.68, 1-$C\underline{H}_2CH_2CH_2CH_3$); 7.46 (1H, dd, J_{56} = 7.88, J_{67} = 7.30, 6-H); 7.49 (1H, dd, $J_{5'6'}$ = 7.50, $J_{6'7'}$ = 7.15, 6'-H); 7.51 (1H, d, J_{78} = 8.21, 8-H); 7.69 (1H, dd, J_{67} = 7.30, J_{78} = 8.23, 7-H); 7.71 (1H, dd, $J_{6'7'}$ = 7.15, $J_{7'8'}$ = 8.30, 7'-H); 7.83 (1H, d, $J_{5'6'}$ = 7.50, 5'-H); 8.08 (1H, dd, $J_{7'8'}$ = 8.30, $J_{4'8'}$ = 0.61, 8'-H); 8.20 (1H, dd, $J_{3'4'}$ = 8.85, $J_{4'8'}$ = 0.61, 4'-H); 8.66 (1H, d, J_{56} = 7.88, 5-H); 8.86 (1H, d, $J_{3'4'}$ = 8.85, 3'-H); 8.93 (1H, s, 2-H). Mass spectrum, *m/z* (I_{rel}, %): 328 (58) $[M]^+$, 300 (11) $[M - C_2H_4]^+$, 286 (59) $[M - C_3H_6]^+$, 272 (98) $[M - C_4H_8]^+$, 257 (21) $[M - C_3H_7CHO]^+$, 244 (38), 229 (6), 216 (9), 168 (6), 154 (17), 130 (14), 128 (49), 121 (6), 113 (6), 108 (8), 102 (12), 95 (9), 76 (24), 63 (10), 58 (29), 44 (100).

1-Benzyl-3-(2-quinolyl)-1,4-dihydro-4-quinolone (3d, $C_{25}H_{18}N_2O$) was obtained according to procedure A. Yield 0.335 g (37%); mp 202-203°C (benzene), R_f 0.30 (1:2 ethyl acetate–hexane). IR spectrum: 1617 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, *J*, Hz: 5.69 (2H, s, 1-$C\underline{H}_2Ph$); 7.30 (5H, m, 1-$CH_2\underline{Ph}$); 7.33 (1H, d, J_{78} = 8.21, 8-H); 7.35 (1H, dd, J_{56} = 7.88, J_{67} = 7.30, 6-H); 7.48 (1H, dd, J_{67} = 7.30, J_{78} = 8.23, 7-H); 7.55 (1H, ddd, $J_{5'6'}$ = 8.09, $J_{6'7'}$ = 7.68, $J_{6'8'}$ = 0.96, 6'-H); 7.74 (1H, ddd, $J_{6'7'}$ = 7.68, $J_{7'8'}$ = 8.53, $J_{5'7'}$ = 1.28, 7'-H); 7.79 (1H, d, J_{56} = 7.88, 5-H); 7.86 (1H, dd, $J_{5'6'}$ = 8.09, $J_{5'7'}$ = 1.28, 5'-H); 8.19 (1H, dd, $J_{7'8'}$ = 8.53, $J_{6'8'}$ = 0.96, 8'-H); 8.23 (1H, d, $J_{3'4'}$ = 8.96, 4'-H); 8.50 (1H, d, $J_{3'4'}$ = 8.96, 3'-H); 8.77 (1H, s, 2-H). Mass spectrum, *m/z* (I_{rel}, %): 362 (71) $[M]^+$, 361 (100) $[M - H]^+$, 345 (6), 271 (32) $[M - C_6H_5CH_2]^+$, 256 (15), 242 (18), 234 (5), 216 (13), 189 (5), 154 (4), 140 (6), 128 (20), 113 (7), 101 (9), 91 (86), 76 (15), 65 (48), 58 (11), 51 (13), 44 (19).

REFERENCES

1. A. V. Aksenov and O. N. Nadein, *Khim. Geterotsikl. Soedin.*, 1527 (2000).
2. A. V. Aksenov, I. V. Magedov, and Yu. I. Smushkevich, *J. Chem. Soc., Perkin Trans., 1*, 759 (1992).
3. A. V. Aksenov, O. N. Nadein, I. V. Borovlev, and Yu. I. Smushkevich, *Khim. Geterotsikl. Soedin.*, 1218 (1998).
4. F. Kröhnke and H. Dickhäuser, and I. Vogt, *Liebigs Ann. Chem.*, **644**, 93 (1961).
5. J. W. Bunting and W. G. Meathrel, *Canad. J. Chem.*, **52**, 303 (1974).
6. I. S. Poddubnyi, *Khim. Geterotsikl. Soedin.*, 774 (1995).
7. A. V. Aksenov, I. V. Aksenova, I. V. Borovlev, A. A. Bumber, A. F. Pozharskii, and Yu. I. Smushkevich, *Khim. Geterotsikl. Soedin.*, 1391 (1996).
8. I. V. Romanenko, N. A. Klyuev, and A. K. Sheinkman, *Voprosy Khimii i Khimicheskoi Tekhnologii*, No. 57, 78 (1979).
9. J. Sharp, I. Gosin, and A. Rolley, *Organic Chemistry Laboratory Textbook* [Russian translation], Mir, Moscow (1993), p. 193.