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# INVESTIGATIONS IN THE REGION OF 2,3′-BIQUINOLYL

## 5.* INVESTIGATION OF THE REACTION OF STABILIZED C-NUCLEOPHILES WITH 1-ALKYL-3-(2-QUINOLYL)-QUINOLINIUM HALIDES

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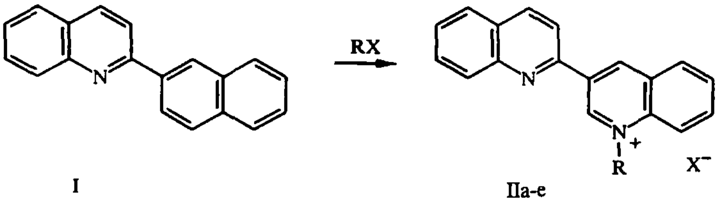
*The regioselectivity of the nucleophilic addition of stabilized C-nucleophiles to 1-alkyl-3-(2-quinolyl)quinolinium halides was investigated. The reaction of the latter with enolates, indolesodium, and cyanide ion leads to 4′-substituted 1′-alkyl-1′,4′-dihydro-2,3′-biquinolyls.*

In a continuation of research into the nucleophilic addition in the 2,3′-biquinolyl series (I) we studied the regioselectivity of the reaction of the products of its quaternization (II) with "soft" nucleophiles: enolates, indolesodium, and cyanide ion.

With an excess of alkylating reagents 2,3′-biquinolyl, which is an ambident nucleophile, forms exclusively the products from monoalkylation at position 1′, i.e., the 1-alkyl-3-(2-quinolyl)quinolinium halides (IIa, b) [2, 3]. We established that the procedure for the synthesis of the salts (II) with DMFA as solvent was not very effective for the preparation of the salts (IIc-e) as a result of the reduced yield and the formation of side products. When compound (I) was boiled with alkyl halides in acetonitrile, compounds (IIc-d) were formed with yields close to quantitative.



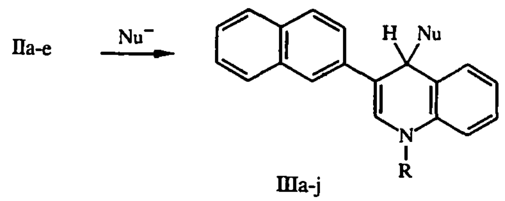
I

IIa-e

II a R = Me, b R = Et, c R = Bu, d R = $CH_2Ph$, e R = $CH_2COPh$;
IIa-d X = I, e X = Br

It is known [4] that the reactions of pyridinium and quinolinium salts with relatively "soft" nucleophiles are subject to orbital control, and this leads to the products from addition at the position with maximum frontier density. In compounds (IIa-e), according to quantum-chemical calculations, position 4 is such a position (Fig. 1).

It could be expected that the "soft" stabilized C-nucleophiles that we employed would add at position 4.



IIIa-j

III a Nu = $CH(CO_2Et)_2$, b Nu = $CH_2COPh$, c–f Nu = 3-indolyl, g-j – Nu = CN;
IIIa-c,g R = Me, d,h R = Et, e R = Bu, f,i R = $CH_2Ph$, j R = $CH_2COPh$

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*For communication 4, see [1].

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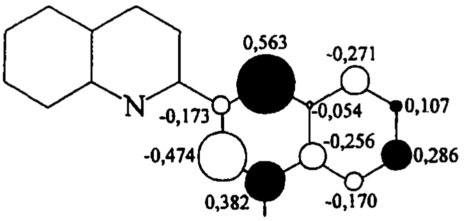

Fig. 1. Coefficients of the LUMO of compound (IIa) according to data from MNDO calculation.

In fact, the adducts at position 4 (III) are formed exclusively in the reaction of compounds (II) with the enolates of malonic ester and acetophenone, indolesodium, and sodium cyanide in THF. The yields of 4'-diethoxycarbonylmethyl- and 4'-phenacyl-1'-methyl-1',4'-dihydro-2,3'-biquinolyl (IIIa) and (IIIb) amount to 78 and 81% respectively. The indole derivatives (IIIc-f) are formed with yields of 65-82%, and the cyano derivatives (IIIg-j) with yields close to quantitative.

Thus, owing to the ambident character of both the electrophile and the nucleophile the "soft"—"soft" reaction mode is realized in these reactions.

## EXPERIMENTAL

The PMR spectra were obtained on Bruker WP-200 and Bruker AM-300 instruments with TMS as internal standard. The reactions and the individuality of the products were monitored on Silufol UV-254 plates in 1:1 mixture of ethyl acetate and hexane. Column chromatography was conducted on silica gel L 40/100. The THF was purified by distillation over lithium aluminum hydride.

**General Method for the Synthesis of 1-Alkyl-3-(2-quinolyl)quinolinium Halides (IIc-e).** A mixture of 2.56 g (10 mmole) of 2,3'-biquinolyl and 12 mmole of the respective halogen derivative[†] in 20 ml of acetonitrile was boiled for 5 h. The precipitate was filtered off, washed with alcohol (3 × 10 ml) and with water (3 × 30 ml), and dried.

**1-Butyl-3-(2-quinolyl)quinolinium Iodide (IIc).** The yield was 4.08 g (93%); mp 233-234°C. PMR spectrum (deuterochloroform, δ, ppm): 1.03 (3H, t, $J$ = 7.20 Hz, 1'-$CH_2CH_2CH_2\underline{CH_3}$); 1.64 (2H, m, 1'-$CH_2CH_2\underline{CH_2}CH_3$); 2.13 (2H, m, 1'-$CH_2\underline{CH_2}CH_2CH_3$); 5.53 (2H, t, $J$ = 7.90 Hz, 1'-$\underline{CH_2}CH_2CH_2CH_3$); 7.59 (1H, dd, $J_{56}$ = 8.06, $J_{67}$ = 7.06 Hz, 6-H); 7.77 (1H, dd, $J_{67}$ = 7.06, $J_{78}$ = 8.33 Hz, 7-H); 7.82 (1H, d, $J_{56}$ = 8.06 Hz, 5-H); 7.91 (1H, dd, $J_{6'7'}$ = 7.21, $J_{7'8'}$ = 8.62 Hz, 7'-H); 8.13 (1H, dd, $J_{5'6'}$ = 8.45, $J_{6'7'}$ = 7.21 Hz, 6'-H); 8.22 (1H, d, $J_{78}$ = 8.33 Hz, 8-H); 8.27 (1H, d, $J_{5'6'}$ = 8.45 Hz, 5'-H); 8.36 (1H, d, $J_{34}$ = 8.54 Hz, 4-H); 8.60 (1H, d, $J_{7'8'}$ = 8.62 Hz, 8-H); 8.95 (1H, d, $J_{34}$ = 8.54, 3-H); 10.17 (1H, d, $J_{2'4'}$ = 1.70 Hz, 4'-H); 10.88 (1H, d, $J_{2'4'}$ = 1.70 Hz, 2'-H). Found %: C 60.05; H 4.69; N 6.41. $C_{22}H_{21}IN_2$. Calculated %: C 59.99; H 4.81; N 6.36.

**1-Benzyl-3-(2-quinolyl)quinolinium iodide (IId).** The yield was 4.16 g (88%); mp 248-249°C. PMR spectrum (deuterochloroform, δ, ppm): 6.82 (2H, s, 1'-$\underline{CH_2}Ph$); 6.82 (5H, s, 1'-$CH_2\underline{Ph}$); 7.63 (1H, dd, $J_{56}$ = 8.08, $J_{67}$ = 7.02 Hz, 6-H); 7.80 (1H, dd, $J_{67}$ = 7.02, $J_{78}$ = 8.31 Hz, 7-H); 7.85 (1H, d, $J_{56}$ = 8.08 Hz, 5-H); 7.91 (1H, dd, $J_{6'7'}$ = 7.23, $J_{7'8'}$ = 8.60 Hz, 7'-H); 8.08 (1H, dd, $J_{5'6'}$ = 8.43, $J_{6'7'}$ = 7.23 Hz, 6'-H); 8.19 (1H, d, $J_{78}$ = 8.31 Hz, 8-H); 8.34 (1H, d, $J_{5'6'}$ = 8.43 Hz, 5'-H); 8.46 (1H, d, $J_{34}$ = 8.53 Hz, 4-H); 8.55 (1H, d, $J_{7'8'}$ = 8.60 Hz, 8'-H); 8.99 (1H, d, $J_{34}$ = 8.53 Hz, 3-H); 10.14 (1H, d, $J_{2'4'}$ = 1.72 Hz, 4'-H); 10.97 (1H, d, $J_{2'4'}$ = 1.72 Hz, 2'-H). Found %: C 63.35; H 3.94; N 5.95. $C_{25}H_{19}IN_2$. Calculated %: C 63.28; H 4.04; N 5.91.

**1-Phenacyl-3-(2-quinolyl)quinolinium Bromide (IIe).** The yield was 4.30 g (95%); mp 260-262°C. PMR spectrum (DMSO-$d_6$, δ, ppm): 7.18 (2H, s, 1'-$\underline{CH_2}COPh$); 7.73 (1H, dd, $J_{56}$ = 8.06, $J_{67}$ = 7.10 Hz, 6-H); 7.75 [3H, m, 3-H, 4-H, 5-H (Ph)]; 7.86 (1H, dd, $J_{67}$ = 7.10, $J_{78}$ = 8.32 Hz, 7-H); 7.95 (1H, d, $J_{56}$ = 8.06 Hz, 5-H); 8.18 (1H, dd, $J_{6'7'}$ = 7.25, $J_{7'8'}$ = 8.67 Hz, 7'-H); 8.19 (1H, d, $J_{78}$ = 8.32 Hz, 8-H); 8.21 [2H, d, $J$ = 7.13 Hz, 2-H, 6-H (Ph)]; 8.28 (1H, dd, $J_{5'6'}$ = 8.49, $J_{6'7'}$ = 7.25 Hz, 6'-H); 8.52 (1H, d, $J_{34}$ = 8.77 Hz, 4-H); 8.55 (1H, d, $J_{5'6'}$ = 8.49 Hz, 5'-H); 8.69 (1H, d, $J_{7'8'}$

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[†] A mixture of 1.52 g (12 mmole) of benzyl chloride and 2 g (12 mmole) of potassium iodide was used for the preparation of compound (IId).

= 8.67 Hz, 8'-H); 8.77 (1H, d, $J_{34}$ = 8.77 Hz, 3-H); 10.28 (1H, d, $J_{2'4'}$ = 1.83 Hz, 4'-H); 10.51 (1H, d, $J_{2'4'}$ = 1.83 Hz, 2'-H). Found %: C 68.78; H 4.11; N 6.21. $C_{26}H_{19}BrN_2O$. Calculated %: C 68.71; H 4.22; N 6.17.

**4'-Diethoxycarbonylmethyl-1'-methyl-1',4'-dihydro-2,3'-biquinolyl (IIIa).** To a solution of 0.48 g (3 mmole) of malonic ester in 10 ml of absolute THF we added 0.17 g (7 mmole) of sodium hydride, and we stirred the mixture for 5 min. We then added 1 g (2.5 mmole) of 1-methyl-3-(2-quinolyl)quinolinium iodide to the reaction mixture and boiled the mixture with stirring for 1.5 h in an atmosphere of nitrogen. After this the reaction mixture was treated with 2 ml of ethanol and poured into 50 ml of water and extracted with benzene (3 × 30 ml). The organic layer was separated, dried over sodium sulfate, and evaporated. The obtained yellow oil crystallized with the addition of ether. The yield was 0.84 g (78%); mp 128-129°C (from ether). PMR spectrum (chloroform, δ, ppm): 1.00 (3H, t, $J$ = 5.65 Hz, A-$CH_2\underline{CH_3}$); 1.08 (3H, t, $J$ = 5.65 Hz, B-$CH_2\underline{CH_3}$); 3.42 (3H, s, 1'-$CH_3$); 3.77 [1H, d, $J$ = 5.80 Hz, 4'-$\underline{CH}(CO_2Et)_2$]; 3.84 (2H, q, $J$ = 5.65 Hz, A-$\underline{CH_2}CH_3$); 3.96 (2H, q, $J$ = 5.65 Hz, B-$\underline{CH_2}CH_3$); 5.54 (1H, d, $J$ = 5.80 Hz, 4'-H); 6.89 (1H, d, $J_{7'8'}$ = 8.04 Hz, 8'-H); 7.01 (1H, dd, $J_{5'6'}$ = 7.62, $J_{6'7'}$ = 7.79 Hz, 6'-H); 7.24 (1H, dd, $J_{6'7'}$ = 7.79, $J_{7'8'}$ = 8.04 Hz, 7'-H); 7.37 (1H, dd, $J_{56}$ = 7.98, $J_{67}$ = 7.46 Hz, 6-H); 7.45 (1H, s, 2'-H); 7.53 (1H, d, $J_{5'6'}$ = 7.62 Hz, 5'-H); 7.59 (1H, d, $J_{34}$ = 8.54 Hz, 3-H); 7.60 (1H, dd, $J_{67}$ = 7.46, $J_{78}$ = 8.55 Hz, 7-H); 7.69 (1H, d, $J_{56}$ = 7.98 Hz, 5-H); 7.92 (1H, d, $J_{34}$ = 8.54 Hz, 4-H); 7.96 (1H, d, $J_{78}$ = 8.55 Hz, 8-H). Found %: C 72.59; H 5.93; N 6.57. $C_{26}H_{26}N_2O_4$. Calculated %: C 72.52; H 6.09; N 6.53.

**1'-Methyl-4'-phenacyl-1',4'-dihydro-2,3'-biquinolyl (IIIb).** A mixture of 1 g (2.5 mmole) of 1-methyl-3-(2-quinolyl)quinolinium iodide, 0.36 g (3 mmole) of acetophenone, and 0.17 g (7 mmole) of sodium hydride in 10 ml of absolute THF was stirred in an atmosphere of nitrogen at room temperature for 2 h. The reaction mixture was then treated with 2 ml of ethanol, poured into 50 ml of water, and extracted with benzene (3 × 30 ml). The organic layer was removed, dried over sodium sulfate, and evaporated. The residue was chromatographed with benzene as eluant, the first colored fraction was collected, and the solvent was distilled. The yield was 0.97 g (81%); mp 138-139°C (from benzene with hexane). $R_f$ 0.56 (Silufol UV-254, 1:1 ethyl acetate—hexane). PMR spectrum (acetone-$d_6$, δ, ppm): 2.96 (1H, dd, $J_{AB}$ = 13.15, $J_{4'A}$ = 9.39 Hz, 4'-$C\underline{H}^AH^BCOPh$); 3.47 (3H, s, 1'-$CH_3$); 3.52 (1H, dd, $J_{AB}$ = 13.15, $J_{4'B}$ = 3.84 Hz, 4'-$CH^A\underline{H}^BOPh$); 5.36 (1H, dd, $J_{4'A}$ = 9.39, $J_{4'B}$ = 3.84 Hz, 4'-H); 6.87 (1H, dd, $J_{5'6'}$ = 7.64, $J_{6'7'}$ = 7.79 Hz, 6'-H); 6.98 (1H, d, $J_{7'8'}$ = 8.03 Hz, 8'-H); 7.02 (1H, d, $J_{5'6'}$ = 7.64 Hz, 5'-H); 7.18 (1H, dd, $J_{6'7'}$ = 7.79, $J_{7'8'}$ = 8.03 Hz, 7'-H); 7.42 (1H, dd, $J_{56}$ = 7.98, $J_{67}$ = 7.37 Hz, 6-H); 7.58 [3H, m, 3-H, 4-H, 5-H (Ph)]; 7.65 (1H, dd, $J_{67}$ = 7.37, $J_{78}$ = 8.57 Hz, 7-H); 7.68 (1H, s, 2'-H); 7.80 (1H, d, $J_{56}$ = 7.98 Hz, 5-H); 7.83 (1H, d, $J_{34}$ = 8.97 Hz, 3-H); 7.94 (1H, d, $J_{78}$ = 8.57 Hz, 8-H); 8.09 (1H, d, $J_{34}$ = 8.97 Hz, 4-H); 8.26 [2H, d, $J$ = 7.26 Hz, 2-H, 6-H (Ph)]. Found %: C 83.13; H 5.54; N 7.21. $C_{27}H_{22}N_2O$. Calculated %: C 83.05; H 5.68; N 7.17.

**General Procedure for the Synthesis of 1'-Alkyl-4'-(3-indolyl)-1',4'-dihydro-2,3'-biquinolyls (IIIc-f).** To a solution of 0.32 g (2.75 mmole) of indole in 10 ml of dry THF we added 0.13 g (5.5 mmole) of sodium hydride, and we stirred the mixture for 5 min. To the reaction mixture we then added 2.5 mmole of the 1-alkyl-3-(2-quinolyl)quinolinium halide. The reaction mixture was then stirred in an atmosphere of nitrogen at room temperature for 3 h. It was then treated with 2 ml of alcohol, poured into 50 ml of water, and extracted with ethyl acetate (3 × 30 ml). The organic layer was separated, dried over sodium sulfate, and evaporated. The residue was recrystallized from benzene or from benzene with hexane.

**4'-(3-Indolyl)-1'-methyl-1',4'-dihydro-2,3'-biquinolyl (IIIc).** The yield was 0.89 g (92%); mp 132-133°C (from benzene). PMR spectrum (deuterochloroform, δ, ppm): 3.52 (3H, s, 1'-$CH_3$); 5.87 (1H, s, 4'-H); 6.88 (1H, dd, $J_{5'6'}$ = 7.65, $J_{6'7'}$ = 7.77 Hz, 6'-H); 6.90 (1H, d, $J_{7'8'}$ = 8.02 Hz, 8'-H); 7.11 (3H, m, 7'-H, 5"-H, 6"-H); 7.13 (1H, d, $J_{NH\text{-}2''H}$ = 2.31 Hz, 2"-H); 7.21 (1H, d, $J_{6''7''}$ = 7.56 Hz, 7"-H); 7.35 (1H, dd, $J_{56}$ = 8.04, $J_{67}$ = 7.42 Hz, 6-H); 7.43 (1H, dd, $J_{5'6'}$ = 7.65 Hz, 5'-H); 7.58 (1H, dd, $J_{67}$ = 7.42, $J_{78}$ = 8.60 Hz, 7-H); 7.67 (1H, d, $J_{56}$ = 8.04 Hz, 5-H); 7.70 (1H, d, $J_{34}$ = 8.77 Hz, 3-H); 7.81 (1H, d, $J_{78}$ = 8.60 Hz, 8-H); 7.90 (1H, d, $J_{4''5''}$ = 7.96 Hz, 4"-H); 7.92 (1H, s, 2'-H); 7.93 (1H, d, $J_{34}$ = 8.77 Hz, 4-H); 9.83 (1H, bs, NH). Found %: C 83.77; H 5.32; N 10.91. $C_{27}H_{21}N_3$. Calculated %: C 83.68; H 5.47; N 10.85.

**4'-(3-Indolyl)-1'-ethyl-1',4'-dihydro-2,3'-biquinolyl (IIId).** The yield was 0.75 g (75%); mp 121-123°C (from benzene). PMR spectrum (acetone-$d_6$, δ, ppm): 1.47 (3H, t, $J$ = 6.95 Hz, 1'-$CH_2\underline{CH_3}$); 4.06 (3H, m, $J_{gem}$ = 14.99, $J_{vic}$ = 6.95 Hz, 1'-$\underline{CH_2}CH_3$); 6.10 (1H, s, 4'-H); 6.84 (1H, dd, $J_{5'6'}$ = 7.63, $J_{6'7'}$ = 7.77 Hz, 6'-H); 6.96 (2H, m, 5"-H, 6"-H); 7.08 (1H, d, $J_{NH\text{-}2''}$ = 2.19 Hz, 2"-H); 7.11 (1H, dd, $J_{6'7'}$ = 7.77, $J_{7'8'}$ = 8.06 Hz, 7'-H); 7.21 (1H, d, $J_{7'8'}$ = 8.06 Hz, 8'-H); 7.26 (1H, d, $J_{6''7''}$ = 7.58 Hz, 7"-H); 7.32 (1H, dd, $J_{56}$ = 8.02, $J_{67}$ = 7.49 Hz, 6-H); 7.41 (1H, d, $J_{5'6'}$ = 7.63 Hz, 5'-H); 7.58 (1H, dd, $J_{67}$ = 7.49, $J_{78}$ = 8.59 Hz, 7-H); 7.68 (1H, d, $J_{56}$ = 8.02 Hz, 5-H); 7.70 (1H, d, $J_{34}$ = 8.77 Hz, 3-H); 7.88 (1H, d, $J_{78}$ = 8.59 Hz, 8-H); 7.90 (1H, d, $J_{4''5''}$ = 7.89 Hz, 4"-H); 7.92 (1H, s, 2'-H); 7.95 (1H, d, $J_{34}$ = 8.77 Hz, 4-H); 9.84 (1H, bs, NH). Found %: C 83.84; H 5.63; N 10.53. $C_{28}H_{23}N_3$. Calculated %: C 83.75; H 5.78; N 10.47.

**1′-Butyl-4′-(3-indolyl)-1′,4′-dihydro-2,3′-biquinolyl (IIIe).** The yield was 0.82 g (76%); mp 107-108°C (from benzene with hexane). PMR spectrum (acetone-$d_6$, δ, ppm): 1.04 (3H, t, $J$ = 7.17 Hz, 1′-$CH_2CH_2CH_2\underline{CH_3}$); 1.55 (2H, m, 1′-$CH_2CH_2\underline{CH_2}CH_3$); 1.58 (2H, m, 1′-$CH_2\underline{CH_2}CH_2CH_3$); 3.89 (1H, m, 1′-$\underline{CH}^AH^BCH_2CH_2CH_3$); 4.03 (1H, m, 1′-$CH^A\underline{H}^BCH_2CH_2CH_3$); 6.10 (1H, s, 4′-H); 6.83 (1H, dd, $J_{5'6'}$ = 7.63, $J_{6'7'}$ = 7.78 Hz, 6′-H); 6.96 (2H, m, 5″-H, 6″-H); 7.04 (1H, d, $J_{NH\text{-}2''}$ = 2.20 Hz, 2″-H); 7.09 (1H, dd, $J_{6'7'}$ = 7.78, $J_{7'8'}$ = 8.06 Hz, 7′-H); 7.23 (1H, d, $J_{7'8'}$ = 8.06 Hz, 8′-H); 7.25 (1H, d, $J_{6''7''}$ = 7.61 Hz, 7″-H); 7.30 (1H, dd, $J_{56}$ = 8.01, $J_{67}$ = 7.41 Hz, 6-H); 7.40 (1H, d, $J_{5'6'}$ = 7.63 Hz, 5′-H); 7.57 (1H, dd, $J_{67}$ = 7.41, $J_{78}$ = 8.56 Hz, 7-H); 7.68 (1H, d, $J_{56}$ = 8.01 Hz, 5-H); 7.69 (1H, d, $J_{34}$ = 8.78 Hz, 3-H); 7.87 (1H, d, $J_{78}$ = 8.56 Hz, 8-H); 7.90 (1H, s, 2′-H); 7.92 (1H, d, $J_{4''5''}$ = 7.90 Hz, 4″-H); 7.94 (1H, d, $J_{34}$ = 8.78 Hz, 4-H); 9.82 (1H, bs, NH). Found %: C 83.97; H 6.18; N 9.85. $C_{30}H_{27}N_3$. Calculated %: C 83.87; H 6.34; N 9.79.

**1′-Benzyl-4′-(3-indolyl)-1′,4′-dihydro-2,3′-biquinolyl (IIIf).** The yield was 0.95 g (82%); mp 134-135°C (from benzene). PMR spectrum (DMSO-$d_6$, δ, ppm): 5.16 (1H, d, $J_{AB}$ = 12.89 Hz, 1′-$C\underline{H}^AH^BPh$); 5.21 (1H, d, $J_{AB}$ = 12.89 Hz, 1′-$CH^A\underline{H}^BPh$); 6.06 (1H, s, 4′-H); 6.77 (1H, d, $J_{7'8'}$ = 8.06 Hz, 8′-H); 6.86 (1H, dd, $J_{5'6'}$ = 7.63, $J_{6'7'}$ = 7.80 Hz, 6′-H); 6.95 (3H, m, 7′-H, 5″-H, 6″-H); 7.11 (1H, s, 2″-H); 7.21 (1H, d, $J_{6''7''}$ = 7.57 Hz, 7″-H); 7.32 (1H, dd, $J_{56}$ = 8.01, $J_{67}$ = 7.51 Hz, 6-H); 7.38 [3H, m, 3-H, 4-H, 5-H (Ph)]; 7.41 (1H, d, $J_{5'6'}$ = 7.63 Hz, 5′-H); 7.44 [2H, m, 2-H, 6-H (Ph)]; 7.59 (1H, dd, $J_{67}$ = 7.51, $J_{78}$ = 8.54 Hz, 7-H); 7.70 (1H, d, $J_{56}$ = 8.01 Hz, 5-H); 7.73 (1H, d, $J_{34}$ = 8.79 Hz, 3-H); 7.80 (1H, d, $J_{78}$ = 8.54 Hz, 8-H); 7.83 (1H, d, $J_{4''5''}$ = 7.88 Hz, 4″-H); 8.01 (1H, d, $J_{34}$ = 8.79 Hz, 4-H); 8.03 (1H, s, 2′-H); 10.52 (1H, bs, NH). Found %: C 85.67; H 5.16; N 9.17. $C_{33}H_{25}N_3$. Calculated %: C 85.58; H 5.30; N 9.12.

**General Method for the Synthesis of 1′-Alkyl-4′-cyano-1′,4′-dihydro-2,3′-biquinolyls (IIIg-j).** A mixture of 2.5 mmole of 1-alkyl-3-(2-quinolyl)quinolinium halide and 0.17 g (3.5 mmole) of sodium cyanide in 10 ml of THF was boiled and stirred for 3 h. The reaction mixture was poured into 200 ml of water, and the precipitate was filtered off, dried, and recrystallized from benzene or from benzene with hexane. The yield before recrystallization was close to quantitative.

**1′-Methyl-4′-cyano-1′,4′-dihydro-2,3′-biquinolyl (IIIg).** The yield was 0.62 g (84%); mp 195-196°C (from benzene). PMR spectrum (deuterochloroform, δ, ppm): 3.42 (3H, s, 1′-$CH_3$); 5.88 (1H, s, 4′-H); 6.93 (1H, d, $J_{7'8'}$ = 8.07 Hz, 8′-H); 7.12 (1H, dd, $J_{5'6'}$ = 7.62, $J_{6'7'}$ = 7.78 Hz, 6′-H); 7.33 (1H, dd, $J_{6'7'}$ = 7.78, $J_{7'8'}$ = 8.07 Hz, 7′-H); 7.35 (1H, s, 2′-H); 7.43 (1H, dd, $J_{56}$ = 8.01, $J_{67}$ = 7.36 Hz, 6-H); 7.48 (1H, d, $J_{5'6'}$ = 7.62 Hz, 5′-H); 7.54 (1H, d, $J_{34}$ = 8.85 Hz, 3-H); 7.66 (1H, dd, $J_{67}$ = 7.36, $J_{78}$ = 8.24 Hz, 7-H); 7.72 (1H, d, $J_{56}$ = 8.01 Hz, 5-H); 8.00 (1H, d, $J_{34}$ = 8.85 Hz, 4-H); 8.05 (1H, d, $J_{78}$ = 8.24 Hz, 8-H). Found %: C 80.85; H 4.93; N 14.22. $C_{20}H_{15}N_3$. Calculated %: C 80.77; H 5.09; N 14.14.

**4′-Cyano-1′-ethyl-1′,4′-dihydro-2,3′-biquinolyl (IIIh).** The yield was 0.64 g (82%); mp 158-159°C (from benzene with hexane). PMR spectrum (deuterochloroform, δ, ppm): 1.45 (3H, t, $J$ = 6.93 Hz, 1′-$CH_2\underline{CH_3}$); 3.40 (2H, m, 1′-$\underline{CH_2}CH_3$); 5.87 (1H, s, 4′-H); 6.92 (1H, d, $J_{7'8'}$ = 8.02 Hz, 8′-H); 7.10 (1H, dd, $J_{5'6'}$ = 7.67, $J_{6'7'}$ = 7.81 Hz, 6′-H); 7.32 (1H, dd, $J_{6'7'}$ = 7.81, $J_{7'8'}$ = 8.02 Hz, 7′-H); 7.33 (1H, s, 2′-H); 7.43 (1H, dd, $J_{56}$ = 8.02, $J_{67}$ = 7.55 Hz, 6-H); 7.47 (1H, d, $J_{5'6'}$ = 7.67 Hz, 5′-H); 7.54 (1H, d, $J_{34}$ = 8.84 Hz, 3-H); 7.66 (1H, dd, $J_{67}$ = 7.55, $J_{78}$ = 8.25 Hz, 7-H); 7.72 (1H, d, $J_{56}$ = 8.02 Hz, 5-H); 8.00 (1H, d, $J_{34}$ = 8.83 Hz, 4-H); 8.05 (1H, d, $J_{78}$ = 8.25 Hz, 8-H). Found %: C 81.07; H 5.35; N 13.58. $C_{21}H_{17}N_3$. Calculated %: C 80.99; H 5.51; N 13.50.

**1′-Benzyl-4′-cyano-1′,4′-dihydro-2,3′-biquinolyl (IIIi).** The yield was 0.76 g (82%); mp 156-157°C (from benzene). PMR spectrum (DMSO-$d_6$, δ, ppm): 5.15 (1H, d, $J_{AB}$ = 12.91 Hz, 1′-$C\underline{H}^AH^BPh$); 5.21 (1H, d, $J_{AB}$ = 12.91 Hz, 1′-$CH^A\underline{H}^BPh$); 5.93 (1H, s, 4′-H); 7.02 (1H, d, $J_{7'8'}$ = 8.08 Hz, 8′-H); 7.08 (1H, dd, $J_{5'6'}$= 7.61, $J_{6'7'}$ = 7.80 Hz, 6′-H); 7.25 (1H, dd, $J_{6'7'}$ = 7.80, $J_{7'8'}$ = 8.08 Hz, 7′-H); 7.38 (5H, m, 1′-$CH_2Ph$); 7.48 (1H, dd, $J_{56}$ = 8.02, $J_{67}$ = 7.35 Hz, 6-H); 7.58 (1H, d, $J_{5'6'}$ = 7.61 Hz, 5′-H); 7.72 (1H, dd, $J_{67}$ = 7.35, $J_{78}$ = 8.26 Hz, 7-H); 7.87 (1H, d, $J_{56}$ = 8.02 Hz, 5-H); 7.94 (1H, d, $J_{34}$ = 8.86 Hz, 3-H); 7.96 (1H, d, $J_{78}$ = 8.26 Hz, 8-H); 8.13 (1H, s, 2′-H); 8.21 (1H, d, $J_{34}$ = 8.86 Hz, 4-H). Found %: C 83.70; H 4.97; N 11.33. $C_{26}H_{19}N_3$. Calculated %: C 83.61; H 5.13; N 11.26.

**1′-Phenacyl-4′-cyano-1′,4′-dihydro-2,3′-biquinolyl (IIIj).** The yield was 0.76 g (76%); mp 194-195°C (from benzene). PMR spectrum (DMSO-$d_6$, δ, ppm): 5.53 (1H, d, $J_{AB}$ = 13.21 Hz, 1′-$C\underline{H}^AH^BCOPh$); 5.69 (1H, d, $J_{AB}$ = 13.21 Hz, 1′-$CH^A\underline{H}^BCOPh$); 5.92 (1H, s, 4′-H); 6.93 (1H, d, $J_{7'8'}$ = 8.09 Hz, 8′-H); 7.13 (1H, dd, $J_{5'6'}$ = 7.64, $J_{6'7'}$ = 7.81 Hz, 6′-H); 7.26 (1H, dd, $J_{6'7'}$ = 7.81, $J_{7'8'}$ = 8.09 Hz, 7′-H); 7.48 (1H, dd, $J_{56}$ = 8.03, $J_{67}$ = 7.55 Hz, 6-H); 7.58 (1H, d, $J_{5'6'}$ = 7.64 Hz, 5′-H); 7.65 [2H, m, 3-H, 5-H (Ph)]; 7.71 (1H, dd, $J_{67}$ = 7.55, $J_{78}$ = 8.24 Hz, 7-H); 7.74 [1H, m, 4-H (Ph)]; 7.84 (1H, d, $J_{56}$ = 8.03 Hz, 5-H); 7.87 (1H, d, $J_{34}$ = 8.85 Hz, 3-H); 7.95 (1H, s, 2′-H); 7.97 (1H, d, $J_{78}$ = 8.24 Hz, 8-H); 8.12 [2H, d, $J$ = 7.15 Hz, 2-H, 6-H (Ph)]; 8.22 (1H, d, $J_{34}$ = 8.85 Hz, 4-H). Found %: C 80.85; H 4.65; N 10.53. $C_{27}H_{19}N_3O$. Calculated %: C 80.77; H 4.77; N 10.47.

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