

## Synthesis of 2-(2-Naphthyl)quinolines from Z-3-(2-Naphthyl)-3-chloro-2-propenal

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**Abstract**—By reaction of Z-3-(2-naphthyl)-3-chloro-2-propenal and aromatic amines 1-(2-naphthyl)-3-iminoaryl-1-propenylarylamines were prepared which at heating in the glacial acetic acid afforded the corresponding 2-(2-naphthyl)quinolines.

Functionally-substituted quinolines and naphthalenes possess a versatile biological activity [1, 2]. The quinoline ring constitutes a structural part of molecules of alkaloids cinchonine and quinine, of a number of antispasmodic and antihistamine medicines [1, 3]. Naphthalene derivatives possess neuroleptic activity [4], are constituents of the drugs for treating psychic, neuro-degenerative diseases [5], stenocardia, ischemia, and atherosclerosis [6]. Therefore the synthesis of compounds combining in one molecule both quinoline and naphthalene fragments is especially interesting. The known methods for synthesis of 2-naphthylquinolines by reaction of di-2-quinoly-methane with quinaldine [7] or by condensation of methyl 2-naphthyl ketone with *o*-aminobenzaldehyde or isatin [8] furnish the target products in low yields and are hardly suitable as preparative procedures.

We developed a preparation method for 2-(2-naphthyl)quinolines from an accessible Z-3-(2-naphthyl)-3-chloro-2-propenal (**I**) which in its turn was obtained from 2-acetylnaphthalene (**II**). By reaction of ketone **II** with Vilsmeier-Haak complex along procedure [9] *N,N*-(dimethyl)-3-(2-naphthyl)-3-chloro-2-propen-1-immonium chloride (**III**) was obtained in 90% yield, and the treatment of compound **III** with sodium acetate afforded in 72% yield the desired naphthylchloropropenal **I**. The composition and structure of compounds **I**, **III** were established from elemental analyses, IR, <sup>1</sup>H NMR, and mass spectra (see EXPERIMENTAL). The values of coupling constants <sup>3</sup>*J* of the proton signals belonging to the side chains in the <sup>1</sup>H NMR spectra of both compounds equal respectively to 7.7 (**I**) and 9 (**III**) Hz indicate that these atoms are located in the *s-cis*-position [10]. It was formerly shown by the study of isomer composition of aldehydes arising from ketones [2-acetonaphthone (**II**) in particular] in the course of

Vilsmeier-Haak reaction that naphthylchloropropenal **I** formed exclusively as *Z*-isomer [11]. Our data show that naphthylimmonium chloride **III** and aldehyde **I** have *s-cis-Z*-configuration of the side chain.

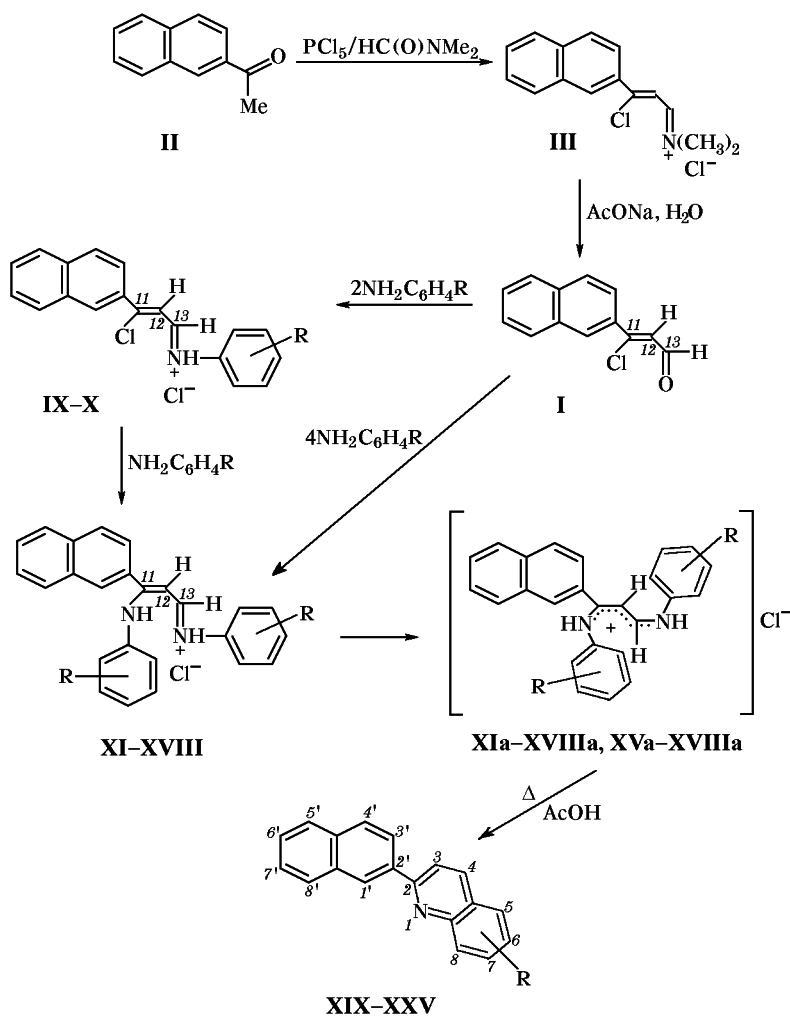
Naphthylchloropropenal **I** readily reacted with various primary aromatic amines, and the process may be performed stepwise by varying the reagents ratio. At the ratio aldehyde to amine equal to 1:2 the reaction occurred at the carbonyl group affording the corresponding *N*-aryl-3-(2-naphthyl)-3-chloro-2-propen-1-immonium chlorides **IV-X** in 64-77% yields. With excess amine the reaction proceeded further at the exocyclic vinyl group involving replacement of the chlorine atom and furnishing *N*-aryl-3-(2-naphthyl)-3-arylamino-2-propen-1-immonium chlorides **XI-XVIII** in 53-84% yield with respect to initial chloropropenal **I**. Compounds **XI-XVIII** were also obtained by treating with amines the preliminary isolated *N*-arylimmonium chlorides **IV-X**. The following amines were brought into the reaction with propenal **I**: aniline, 4-bromoaniline, 4-iodoaniline, 4-methoxyaniline, 4-ethoxyaniline, 4-methylaniline, 3-methylaniline, 4-ethoxycarbonylaniline, and 1-naphthylamine.

The composition and structure of compounds **IV-XVIII** obtained were established from elemental analyses, IR, <sup>1</sup>H NMR, and mass spectra (Tables 1-3). In the IR spectra of immonium chlorides **IV-X** the vibrations of C=N<sup>+</sup> bonds appeared as a strong band in the region 1600-1640 cm<sup>-1</sup>, the vibrations of C=C bonds were observed as bands at 1490-1510 and 1535-1575 cm<sup>-1</sup>. The wide absorption band with a maximum in the range 3250-3350 cm<sup>-1</sup> corresponded to the NH<sup>+</sup> group. In the <sup>1</sup>H NMR spectra of these compounds the multiplets located in the region 6.97-8.30 ppm belonged to the aromatic protons of naphthyl, aryl-

amine groups, and aliphatic  $\text{CCl}=\text{C}^{12}\text{H}_{\text{aliph}}$  group. The broadened singlet from the fragment  $\text{C}^7\text{H}_{\text{arom}}$  appeared at  $\delta$  8.43–8.84 ppm, and that of the  $\text{NH}^+$  group at 10.2–12.4 ppm. The proton from the fragment  $^+\text{N}=\text{C}^{13}\text{H}_{\text{aliph}}$  was observed as a doublet at 8.62–8.84 ppm with a coupling constant  $^3J$  of 8.4 Hz evidencing the *s-cis*-configuration of the side chain in the immonium chlorides **IV–X** [10]. In the IR spectra of compounds **XI–XVIII** vibrations of the bonds  $\text{C}=\text{N}^+$  were observed as a strong band in the region 1600–1645  $\text{cm}^{-1}$ , the vibrations of  $\text{C}=\text{C}$  bonds corresponded to the bands at 1495–1510 and 1530–1585  $\text{cm}^{-1}$ , the wide band with a maximum within 3310–3350  $\text{cm}^{-1}$  originated from  $\text{NH}^+$  groups. The multiplets in the region 6.80–8.25 ppm of the  $^1\text{H}$  NMR spectra of compounds **XI–XVIII** were due

to aromatic protons of naphthyl and arylamine groups and olefin hydrogens from  $=\text{HC}^{12}-\text{C}^{13}\text{H}=\text{N}$  moiety in the side chain. In the spectrum were also present two broadened singlets at 8.35–8.60 ppm (from the fragment  $\text{C}^4\text{H}_{\text{arom}}$ ) and at 12.00–12.45 ppm (from amino groups). In the spectra of compounds **XII–XIV** we successfully identified the doublet signal belonging to the olefin proton of the fragment  $\text{HC}^{13}=\text{N}$ ,  $\delta$  7.7 ppm,  $^3J$  6.4 Hz. The latter fact confirms, that the side chain retains its *s-cis*-configuration in the course of the reaction.

It should be noted that with 1-naphthylamine we obtained only immonium chloride **X** and failed to isolate immonium enamine for this reaction finished in complete tarring. One of the reasons of this behavior may be sterical hindrances arising in the



R = H (**IV**, **XI**, **XIX**), 4-Br (**V**, **XII**, **XX**), 4-I (**VI**, **XIII**, **XXI**), 4-OEt (**VII**, **XIV**), 3-Me (**VIII**, **XV**, **XXII**), 4-OMe (**IX**, **XVI**, **XXIII**), 4-COOEt (**XVII**, **XXIV**), 4-Me (**XVIII**, **XXV**); for compound (**X**)  $\text{RC}_6\text{H}_4$  = 1-naphthyl.

**Table 1.** Yields, melting points, and elemental analyses of immonium chlorides **IV–X**, immonium enamines **XI–XVIII** and quinolines **XIX–XXV**

Compd. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %				$m/z^a$ found	$M$ calcd.
			C	H	Hlg	N		C	H	Hlg	N		
<b>IV</b>	66	116–118	69.90	4.87	21.50	4.20	C <sub>19</sub> H <sub>15</sub> Cl <sub>2</sub> N	69.52	4.61	21.60	4.27	292	328.23
<b>V</b>	77	145–146	56.47	3.88	37.51	3.41	C <sub>19</sub> H <sub>14</sub> BrCl <sub>2</sub> N	56.04	3.47	37.05	3.44	370	407.13
<b>VI</b>	76	148–149	50.44	3.45	43.86	3.16	C <sub>19</sub> H <sub>14</sub> Cl <sub>2</sub> IN	50.23	3.11	43.57	3.09	326	454.12
<b>VII</b>	69	20–122	67.92	5.34	19.28	3.75	C <sub>21</sub> H <sub>19</sub> Cl <sub>2</sub> NO	67.75	5.14	19.05	3.76	326	372.28
<b>VIII</b>	65	108–109	70.51	5.18	21.05	4.22	C <sub>20</sub> H <sub>17</sub> Cl <sub>2</sub> N	70.18	5.01	20.72	4.09	291	342.26
<b>IX</b>	77	133–135	67.29	5.01	19.93	3.88	C <sub>20</sub> H <sub>17</sub> Cl <sub>2</sub> NO	67.05	4.78	19.79	3.91	326	358.26
<b>X</b>	64	141–143	73.34	4.76	18.65	3.62	C <sub>23</sub> H <sub>17</sub> Cl <sub>2</sub> N	73.02	4.53	18.74	3.71	342	378.29
<b>XI</b>	58	210–212	78.22	5.76	9.02	7.33	C <sub>25</sub> H <sub>21</sub> ClN <sub>2</sub>	78.01	5.50	9.21	7.28	349	384.89
<b>XII</b>	57	221–223	55.20	3.41	35.51	5.18	C <sub>25</sub> H <sub>19</sub> Br <sub>2</sub> ClN <sub>2</sub>	55.33	3.53	35.98	5.16	426	542.69
<b>XIII</b>	68	221–223	47.43	3.12	45.23	4.40	C <sub>25</sub> H <sub>19</sub> ClI <sub>2</sub> N <sub>2</sub>	47.16	3.01	45.43	4.40	382	636.67
<b>XIV</b>	55	198–200	73.32	5.96	7.31	5.73	C <sub>29</sub> H <sub>29</sub> ClN <sub>2</sub> O <sub>2</sub>	73.64	6.18	7.50	5.92	392	472.99
<b>XV</b>	73	203–205	78.93	6.49	8.23	6.71	C <sub>27</sub> H <sub>25</sub> ClN <sub>2</sub>	78.53	6.10	8.59	6.78	377	412.94
<b>XVI</b>	53	191–193	72.93	5.79	7.80	6.43	C <sub>27</sub> H <sub>25</sub> ClN <sub>2</sub> O <sub>2</sub>	72.88	5.66	7.97	6.30	378	444.94
<b>XVII</b>	72	195–198	70.10	5.67	6.49	5.35	C <sub>31</sub> H <sub>29</sub> ClN <sub>2</sub> O <sub>4</sub>	70.38	5.53	6.70	5.30	347	529.01
<b>XVIII</b>	84	223–225	78.77	6.51	8.27	6.70	C <sub>27</sub> H <sub>25</sub> ClN <sub>2</sub>	78.53	6.10	8.59	6.78	377	412.94
<b>XIX</b>	83	170–172	89.75	5.26	–	4.99	C <sub>19</sub> H <sub>13</sub> N	89.38	5.13	–	5.49	255	255.30
<b>XX</b>	81	165–167	68.63	3.22	23.67	4.48	C <sub>19</sub> H <sub>12</sub> BrN	68.28	3.62	23.91	4.19	333	334.21
<b>XXI</b>	79	207–209	59.54	3.35	33.64	3.47	C <sub>19</sub> H <sub>12</sub> IN	59.86	3.17	33.29	3.68	381	381.20
<b>XXII</b>	75	140–142	89.30	5.26	–	5.44	C <sub>20</sub> H <sub>15</sub> N	89.18	5.61	–	5.21	269	269.33
<b>XXIII</b>	84	208–210	83.87	5.22	–	4.85	C <sub>20</sub> H <sub>15</sub> NO	84.18	5.30	–	4.91	285	285.33
<b>XXIV</b>	82	156–158	80.32	5.63	–	4.57	C <sub>22</sub> H <sub>17</sub> NO <sub>2</sub>	80.71	5.24	–	4.28	327	327.37
<b>XXV</b>	85	158–160	88.84	5.37	–	5.79	C <sub>20</sub> H <sub>15</sub> N	89.18	5.61	–	5.21	269	269.33

<sup>a</sup> Maximal  $m/z$  values observed in the mass spectrum are presented corresponding to ions formed by the elimination from the initial molecule of substituent in the aromatic ring and chlorine. For compounds containing chlorine and bromine the given values  $m/z$  values correspond to isotopes <sup>35</sup>Cl and <sup>79</sup>Br.

**Table 2.** IR spectra of immonium chlorides **IV–X**, immonium enamines **XI–XVIII**, and quinolines **XIX–XXV**, cm<sup>-1</sup>

Compd. no.	Absorption bands and their assignment
<b>IV</b>	3280 m (νNH), 3060 m (νCH), 1640 v.s (νC=N), 1535 s, 1495 s (νC=C), 765 s (νCCL)
<b>V</b>	3340 m (νNH), 3050 m (νCH), 1610 v.s (νC=N), 1570 s, 1510 m (νC=C), 824 s (νCCL), 600 v.s (νCBr)
<b>VI</b>	3300 w (νNH), 3060 m (νCH), 1600 v.s (νC=N), 1570 s, 1510 m (νC=C), 825 s (νCCL), 500 m (νCI)
<b>VII</b>	3250 m (νNH), 3000 m (νCH), 1615 s (C=N), 1575 s, 1500 s (νC=C), 824 s (νCCL)
<b>VIII</b>	3340 w (νNH), 3100 m (νCH), 1600 s (νC=N), 1565 s, 1510 m (νC=C), 830 s (νCCL)
<b>IX</b>	3350 w (νNH), 3100 m (νCH), 1610 v.s (νC=N), 1575 m, 1500 s (νC=C), 837 s (νCCL)
<b>X</b>	3300 w (νNH), 3050 m (νCH), 1600 v.s (νC=N), 1570 s, 1510 m (νC=C), 775 s (νCCL)
<b>XI</b>	3340 m (νNH), 3050 m (νCH), 1645 v.s (νC=N), 1530 s, 1495 s (νC=C), 760 s (νCCL)
<b>XII</b>	3350 m (νNH), 3050 m (νCH), 1610 v.s (νC=N), 1565 s, 1510 m (νC=C), 820 s (νCCL), 600 m (νCBr)
<b>XIII</b>	3310 w (νNH), 3055 m (νCH), 1605 v.s (νC=N), 1550 s, 1500 m (νC=C), 830 s (νCCL), 500 m (νCI)
<b>XIV</b>	3350 m (νNH), 3060 m (νCH), 1610 s (νC=N), 1560 s, 1510 v.s (νC=C), 830 s (νCCL)
<b>XV</b>	3330 w (νNH), 3050 m (νCH), 1600 s (νC=N), 1570 s, 1510 s (νC=C), 840 s (νCCL)
<b>XVI</b>	3345 w (νNH), 3065 m (νCH), 1640 v.s (νC=N), 1570 m 1500 v.s (νC=C), 830 s (νCCL)
<b>XVII</b>	3340 w (νNH), 3055 m (νCH), 1720 v.s (νC=O), 1640 v.s (νC=N), 1580 s, 1500 m (νC=C), 825 s (νCCL)

**Table 2** (Contd.)

Compd. no.	Absorption bands and their assignment
<b>XVIII</b>	3350 w (νNH), 3025 m (νCH), 1638 v.s (νC=N), 1585 s, 1510 v.s (νC=C), 817 s (νCCI)
<b>XIX</b>	3050 m (νCH), 1625 v.s (νC=N), 1530 s, 1495 s (νC=C), 1220 m (νC-N)
<b>XX</b>	3053 m (νCH), 1624 v.s (νC=N), 1592 s, 1545 m. (νC=C), 1223 s (νC-N), 746 s (νCBr)
<b>XXI</b>	3050 m (νCH), 1625 v.s (νC=N), 1587 s, 1544 m. (νC=C), 1222 s (νC-N), 476 m (νCI)
<b>XXII</b>	3050 m (νCH), 1600 s (νC=N), 1570 s, 1510 s (νC=C), 1230 s (νC-N)
<b>XXIII</b>	3060 m (νCH), 1620 v.s (νC=N), 1590 m 1550 v.s (νC=C), 1232 s (νC-O)
<b>XXIV</b>	3055 m (νCH), 1720 v.s (νC=O), 1620 v.s (νC=N), 1495 v.s (νC=C), 1270 v.s (νC-O), 825 v.s (νC-N)
<b>XXV</b>	3050 m (νCH), 1596 v.s (νC=N), 1494 v.s (νC=C), 1230 w (νC-N)

**Table 3.** <sup>1</sup>H NMR spectra of immonium chlorides **IV-X**, immonium enamines **XI-XVIII**, and quinolines **XIX-XXV**, δ, ppm

Compd. no.	Signals assignment
<b>IV</b>	7.2–8.2 m (11H arom and 1H, CH aliph=CCI), 8.45 br.s (1H, C <sup>1</sup> H arom), 8.75 d (1H, CH aliph=N, <sup>3</sup> J 8.4 Hz), 12.30 br.s (1H, NH)
<b>V</b>	7.1–8.2 m (10H arom and 1H, CH aliph=CCI), 8.43 br.s (1H, C <sup>1</sup> H arom), 8.73 d (1H, CH aliph=N, <sup>3</sup> J 8.4 Hz), 12.40 br.s (1H, NH)
<b>VI</b>	7.10 d (2H arom), 7.4–8.2 m (8H arom and 1H, CH aliph=CCI), 8.48 br.s (1H, C <sup>1</sup> H arom), 8.73 d (1H, CH aliph=N, <sup>3</sup> J 8.4 Hz), 12.10 br.s (1H, NH)
<b>VII</b>	1.34 t (3H, CH <sub>3</sub> ), 4.06 q (2H, CH <sub>2</sub> O), 6.97 d (2H arom), 7.32 d (2H arom), 7.42–8.10 m (6H arom and 1H, CH aliph=CCI), 8.46 br.s (1H, C <sup>1</sup> H arom), 8.76 d (1H, CH aliph=N, <sup>3</sup> J 8.4 Hz), 12.20 br.s (1H, NH)
<b>VIII</b>	2.30 s (3H, CH <sub>3</sub> ), 7.15–8.10 m (10H arom and 1H, CH aliph=CCI), 8.50 br.s (1H, C <sup>1</sup> H arom), 8.62 d (1H, CH aliph=N, <sup>3</sup> J 8.4 Hz), 12.10 br.s (1H, NH)
<b>IX</b>	3.79 s (3H, CH <sub>3</sub> O), 7.01 d (2H arom), 7.35 d (2H arom), 7.50–8.20 m (6H arom and 1H, CH aliph=CCI), 8.46 br.s (1H, C <sup>1</sup> H arom), 8.78 d (1H, CH aliph=N, <sup>3</sup> J 8.4 Hz), 12.0 br.s (1H, NH)
<b>X</b>	7.20–8.30 m (13H arom and 1H, CH aliph=CCI), 8.54 br.s (1H, C <sup>1</sup> H arom), 8.84 d (1H, CH aliph=N, <sup>3</sup> J 8.4 Hz), 10.20 br.s (1H, NH)
<b>XI</b>	7.25–8.25 m (16H arom and 2H, =CH-CH=N), 8.45 br.s (1H, C <sup>1</sup> H arom), 12.30 br.s (2H, NH)
<b>XII</b>	7.25–8.25 m (14H arom and 2H, =CH-CH=N), 8.35 br.s (1H, C <sup>1</sup> H arom), 12.45 br.s (2H, NH)
<b>XIII</b>	7.00–8.15 m (14H arom and 2H, =CH-CH=N), 8.35 br.s (1H, C <sup>1</sup> H arom), 12.35 br.s (2H, NH)
<b>XIV</b>	1.40 t (3H, CH <sub>3</sub> ), 1.48 t (3H, CH <sub>3</sub> ), 4.05 q (2H, CH <sub>2</sub> O), 4.15 q (2H, CH <sub>2</sub> O), 6.90–8.10 m (14H arom and 2H, =CH-CH=N), 8.60 br.s (1H, C <sup>1</sup> H arom), 12.20 br.s (2H, NH)
<b>XV</b>	2.30 s (3H, CH <sub>3</sub> ), 2.50 s (3H, CH <sub>3</sub> ), 7.00–8.25 m (14H arom and 2H, =CH-CH=N), 8.41 br.s (1H, C <sup>1</sup> H arom), 12.20 br.s (2H, NH)
<b>XVI</b>	3.70 s (3H, CH <sub>3</sub> O), 3.79 s (3H, CH <sub>3</sub> O), 6.80–8.20 m (14H arom and 2H, =CH-CH=N), 8.35 br.s (1H, C <sup>1</sup> H arom), 12.00 br.s (2H, NH)
<b>XVII</b>	1.30 t (6H, 2CH <sub>3</sub> ), 4.25 q (4H, 2CH <sub>2</sub> O), 7.30–8.20 m (14H arom and 2H, =CH-CH=N), 8.44 br.s (1H, C <sup>1</sup> H arom), 12.30 br.s (2H, NH)
<b>XVIII</b>	3.36 s (3H, CH <sub>3</sub> ), 3.42 s (3H, CH <sub>3</sub> ), 7.10–8.10 m (14H arom and 2H, =CH-CH=N), 8.40 br.s (1H, C <sup>1</sup> H arom), 12.10 br.s (2H, NH)
<b>XIX</b>	7.40–8.40 m (12H arom), 8.60 br.s (1H, C <sup>1</sup> H arom)
<b>XX</b>	7.40–8.50 m (11H arom), 8.70 br.s (1H, C <sup>1</sup> H arom)
<b>XXI</b>	7.40–8.40 m (11H arom), 8.60 br.s (1H, C <sup>1</sup> H arom)
<b>XXII</b>	2.20 s (3H, CH <sub>3</sub> ), 7.00–8.25 m (11H arom), 8.50 br.s (1H, C <sup>1</sup> H arom)
<b>XXIII</b>	3.95 s (3H, CH <sub>3</sub> O), 7.10–8.40 m (11H arom), 8.55 br.s (1H, C <sup>1</sup> H arom)
<b>XXIV</b>	1.50 t (3H, CH <sub>3</sub> ), 4.45 q (2H, CH <sub>2</sub> O), 7.40–8.30 m (11H arom and 2H), 8.60 br.s (1H, C <sup>1</sup> H arom)
<b>XXV</b>	2.58 s (3H, CH <sub>3</sub> ), 7.50–8.40 m (11H arom), 8.70 br.s (1H, C <sup>1</sup> H arom)

*s-cis*-configuration of the immonium enamine due to bulky naphthyl substituents.

The heterocyclization of compounds **XI–XIII**, **XV–XVIII** by boiling in the glacial acetic acid by procedure [12, 13] afforded individual 2-(2-naphthyl-6-quinolines and 7-R-quinolines **XIX–XXV**. We presume that heterocyclization of salts **XI–XIII**, **XV–XVIII** proceeds through formation of intermediate cations **XIa–XIIIa**, **XVa–XVIIIa** [13]; therewith the side chains of immonium enamines **XI–XIII**, **XV–XVIII** are likely to isomerize from *s-cis*-configuration into *s-trans* one for instead of 4-naphthylquinolines which should have formed providing the *s-cis*-structure were retained 2-naphthyl-substituted quinolines are obtained.

The composition and structure of compounds **XIX–XXV** were confirmed by elemental analyses, IR, <sup>1</sup>H NMR, and mass spectra (Tables 1–3). In the IR spectra the strong bands at 1596–1660 cm<sup>-1</sup> characterize the vibrations of C=N<sup>+</sup> bonds, the bands in the frequency region 1494–1590 cm<sup>-1</sup> belong to the vibrations of C=C bonds. The absorption bands of N–H groups observed in the spectra of immonium enamines **XI–XVIII** in the range 3200–3350 cm<sup>-1</sup> are lacking in the spectra of quinolines **XIX–XXV**. In the mass spectra of quinolines **XIX–XXV** appear the peaks of molecular ions.

The <sup>1</sup>H NMR spectra of compounds **XIX–XXV** contain multiplets of aromatic rings at δ 7.0–8.7 ppm and the signals of substituents from the quinoline part of the molecule.

In order to determine the position where the naphthyl moiety is attached to the quinoline bicyclic structure we registered <sup>1</sup>H NMR spectrum of compound **XXV** at higher resolution (see EXPERIMENTAL). The protons of compound **XXV** constitute a 15-spin system that can be divided into three weakly interacting spin systems: a methyl group, 3 spins, a singlet at δ 2.58 pp; a quinoline bicycle, 5 spins, and naphthalene, 7 spins, appearing as multiplets in the region 7.5–8.7 ppm. In keeping with the published data [14] the most downfield proton signals belong to hydrogens attached to positions 2 and 4 of the quinoline skeleton or to the hydrogen atoms in the naphthalene moiety the closest to the quinoline part of the molecule. In the spectrum of compound **XXV** the most downfield signal is a multiplet with the largest coupling constant of 1.5 Hz. Thus a structure with a naphthyl substituent in position 4 is excluded for in this case the largest coupling constant in the most downfield signal should have been ~5 Hz [14]. The observed multiplicity of

resonances and the chemical shift values in the spectrum are in agreement with an isomeric structure with a naphthyl substituent in position 2, i.e. with 6-methyl-2-(2-naphthyl)quinoline structure. The four most downfield signals we assigned as follows (δ, ppm): 8.66 (C<sup>1</sup>H), 8.43 (C<sup>4</sup>H), 8.22 (C<sup>4</sup>H), 8.11 (C<sup>3</sup>H). The comparison of the experimental <sup>1</sup>H NMR spectrum with those obtained by computer simulation for isomeric 2-, 3-, and 4-(2-naphthyl)-6-methylquinolines also shows the best agreement were for the structure of 6-methyl-2-(2-naphthyl)quinoline.

## EXPERIMENTAL

IR spectra were recorded on Fourier spectrophotometer Protege-460 from samples pelletized with KBr. <sup>1</sup>H NMR spectra were registered on spectrometer Tesla 567A (100 MHz) from solutions in DMSO-*d*<sub>6</sub> (compounds **IV–XVIII**) and CDCl<sub>3</sub> (compounds **XIX–XXIV**); spectrum of compound **XXV** was taken on Bruker DRX-500 instrument (500 MHz) from solution in DMSO-*d*<sub>6</sub>. Chemical shifts were measured with respect to TMS. Mass spectra were obtained on a mass-spectrometer MKh-1320 at ionizing electrons energy 50 eV.

***s-cis-Z-3-(2-Naphthyl)-3-chloro-2-propenal (I)***. *N,N*-(dimethyl)-3-(2-naphthyl)-3-chloro-2-propen-1-immonium chloride (**III**) (30 g, 0.11 mol) was treated at heating and stirring with water solution of sodium acetate (10 g). On cooling the reaction mixture the separated precipitate was filtered off, washed with water, ethyl ether, dried in a vacuum, and recrystallized from chloroform. Yield of compound **I** 16.7 g (72%), mp 62–63°C. IR spectrum, ν, cm<sup>-1</sup>: 3054, 3033 (C–H), 1668 (C=O), 1588, 1572, 1505 (C=C), 808 (C–Cl). <sup>1</sup>H NMR spectrum, δ, ppm: 6.80 d (1H, CCl=CH), 7.50–8.0 m (6H arom), 8.31 s (1H arom), 10.27 d (1H, CHO, <sup>3</sup>J 7.7 Hz). Found, %: C 72.37; H 4.05; Cl 16.18. C<sub>13</sub>H<sub>9</sub>ClO. [M]<sup>+</sup> 216. Calculated, %: C 72.06; H 4.19; Cl 16.36. M 216.66.

***N,N*-(Dimethyl)-3-(2-naphthyl)-3-chloro-2-propen-1-immonium chloride (III)**. To 134 ml (1.83 mol) of dimethylformamide at 25–30°C was added by portions within 30 min 50.2 g (0.24 mol) of phosphorus pentachloride. The mixture was stirred for 2.5–3 h at 20–25°C and left standing for 8 h. To the formed suspension of the Vilsmeier–Haak complex was added at 25–30°C within 30 min a solution of 33 g (0.185 mol) of 2-acetonaphthone (**II**) in 82.5 ml (1.13 mol) of dimethylformamide. The mixture was stirred at heating to 35–40°C, the separated bright-yellow precipitate was filtered off, washed with water, with ethyl ether, and dried in a vacuum. Yield of compound **III** 48.9 g (90%), mp 168–170°C. IR spectrum, ν, cm<sup>-1</sup>: 3068, 3032 (C–H), 1645

(C=N<sup>+</sup>), 1624, 1595, 1560 (C=C), 845 (C-Cl). <sup>1</sup>H NMR spectrum, δ, ppm: 3.73 s (3H, CH<sub>3</sub>), 3.80 s (3H, CH<sub>3</sub>), 7.65–8.20 m (6H arom and <sup>1</sup>H, CCl=CH), 8.75 s (1H arom), 9.10 d (1H, CH=N<sup>+</sup>, <sup>3</sup>J 9 Hz). Found, %: C 64.50; H 4.93; Cl 25.68; N 4.89. C<sub>15</sub>H<sub>15</sub>Cl<sub>2</sub>N. [M]<sup>+</sup> 279. Calculated, %: C 64.30; H 5.40; Cl 25.30; N 5.00. *M* 280.19.

**N-Arylimmonium chlorides IV–X.** To a solution of 1 g (4.6 mmol) of naphthylchloropropenal **I** in 5 ml of ether was added by portions while stirring a solution of an appropriate amine (9.2 mmol) in 3 ml of ether. In 10–15 min after completion of addition a brightly colored precipitate separated. It was filtered off and washed in succession with water and ether, dried in a vacuum, and recrystallized from methanol. Yields and melting points of the reaction products are listed in Table 1.

**N-Aryl-3-(2-naphthyl)-3-arylamino-2-propenyl-1-immonium chlorides XI–XVIII.** To 1 g (4.6 mmol) of naphthylchloropropenal **I** in 5 ml of ether was added by portions at stirring a solution of an appropriate amine (18.4 mmol) in 3 ml of ether. In 10–15 min after completion of addition a brightly colored precipitate separated. It was filtered off and washed in succession with water and ether, dried in a vacuum, and recrystallized from methanol. Yields and melting points of the reaction products are listed in Table 1.

**2-(2-Naphthyl)-6- and -7-R-quinolines XIX–XXV.** A solution of 2.5 mmol of hydrochloride **XI–XIII**, **XV–XVIII** in 10 ml of glacial acetic acid was heated at reflux for 3 h, then the reaction mixture was treated with concn. aqueous KOH till pH 6–7, the separated precipitate was washed with water and dried in a vacuum. Yields and physicochemical characteristics of compounds **XIX–XXV** are given in Table 1.

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