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Reactions of N- and C-Alkenylanilines: I. Synthesis of Anilides and Amidines from *ortho*-Alkenyl(cycloalkenyl)anilines and Their Transformations

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Abstract—*N*-Acetyl- and *N*-formyl-*ortho*-alkenyl(cycloalkenyl)anilines were synthesized. Their reaction with P_2O_5 or PCl_5 afforded quinolines. By reaction of the *ortho*-alkenyl(cycloalkenyl)anilines with 1-methylimino- or 1-phenylimino-1-chloroethanes amidines were obtained that were cyclized in the polyphosphoric acid. The reaction with the polyphosphoric acid of amidines prepared from alkenylanilines and 1-methylimino-1-chloroethane gave rise to 3-methyl-3,4-dihydroquinazolines; on replacing in the substrate methylimine group for phenylimine one the yield of quinazoline decreased.

Quinazoline series compounds possess a wide range of biological activity and thus attract the interest of researchers [1–12]. The principal methods of preparation thereof is the synthesis from anthranilic acid derivatives [1–5], from 3,1-benzoxazines [6–8] and 2-aminomethylanilines [9, 10], and also by addition of alkyl isocyanates to *N*-triphenylphosphite of methyl aminocinnamate [13]. The anthranilic acids or benzoxazines furnish quinazolin-4-ones, and cyclization of *N*-phenyl-*N*'-acylsubstituted ureas in the polyphosphoric acid gives rise to quinazolin-2-ones [14]. In the synthesis of 4*H*-derivatives are commonly used 2-aminomethylanilines [9, 10] or esters of 2-aminocinnamic acid [13]. The available ortho-alkenylanilines whose preparative synthesis has been known already since 40 years [15] unfortunately are poorly studied in the synthesis of quinazolines. In this investigation we synthesized from the ortho-alkenyl(cycloalkenyl)anilines their N-acetyl, N-formyl or amidine derivatives aiming to perform their cyclization into quinazolines. To convert the *N*-acetyl- and *N*-formyl-*ortho*-alkenylanilines into amidines we planned to apply the known procedures [16, 17]. The amidines prepared along the procedure [17] from the *ortho*-alkenylanilines and 1-methylimino- or 1-phenylimino-1-chloroethanes were subjected to cyclization in the polyphosphoric acid.

It is known [16] that at heating *N*-acetylanthranilic acid with P_2O_5 in the presence of alkylammonium chlorides in a trialkylamine the oxygen atom in the acetyl group is replaced by the alkylamine moiety to furnish amidines that further relatively readily undergo cyclization into quinazolines.

However when we applied this procedure to preparation of amidines (A) or (B) from *N*-acetyl-*ortho*-(1-cycloalken-1-yl)anilines **I** [18] or **II** [19] we obtained only quinolines **III** and **IV** respectively (Scheme 1). Acetyl derivatives **V** [18] or **VI** containing an allyl double bond also easily cyclize into quinolines **III** or **IV** (Table 1). 3,1-Benzoxazine (**VII**) prepared previously by method [18] under these conditions affords quinoline **III** in 36% yield. Apparently under conditions developed in [16] the amidine formation from amides **I, II, V**, and **VI** is impossible, and the reaction is directed to their cyclization into quinolines [20].

Table 1. Yields of quinolines depending on the initial compounds and reagents

Initial compd. no.	Reagent	Quinoline no.	Yield, %
I	P_2O_5/Bu_3N	**III**	43
II	P_2O_5/Bu_3N	**IV**	36
V	P_2O_5/Bu_3N	**II**	37
VI	P_2O_5/Bu_3N	**IV**	31
VII	P_2O_5/Bu_3N	**III**	36
IX	PCl_5	**X**	28
XXVI	Polyphosphoric acid	**III**	6

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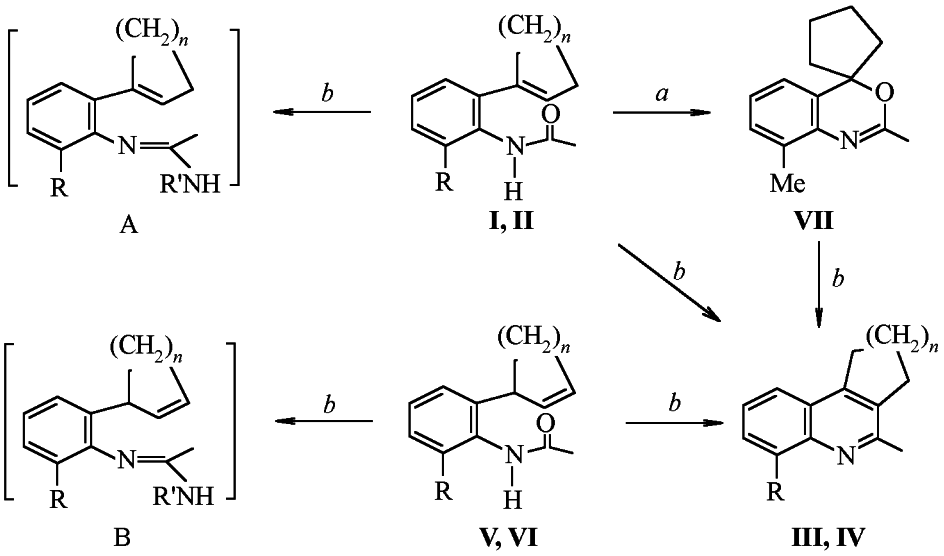
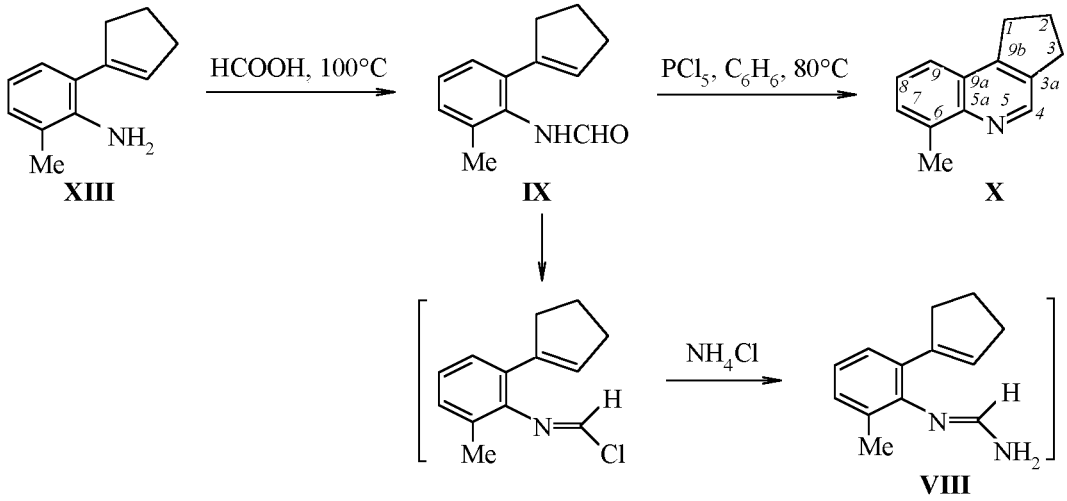
Scheme 1.



n = 1, R = Me (**I, III, V**); *n* = 2, R = H (**II, IV, VI**). Reagents and conditions: *a*, HCl, CH_2Cl_2, 20°C, 9 h; *b*, P_2O_5, Bu_3N, $[MeNH_3]^+Cl^-$ or $[NH_4]^+Cl^-$, 160–170°C, 2 h.

Scheme 2.



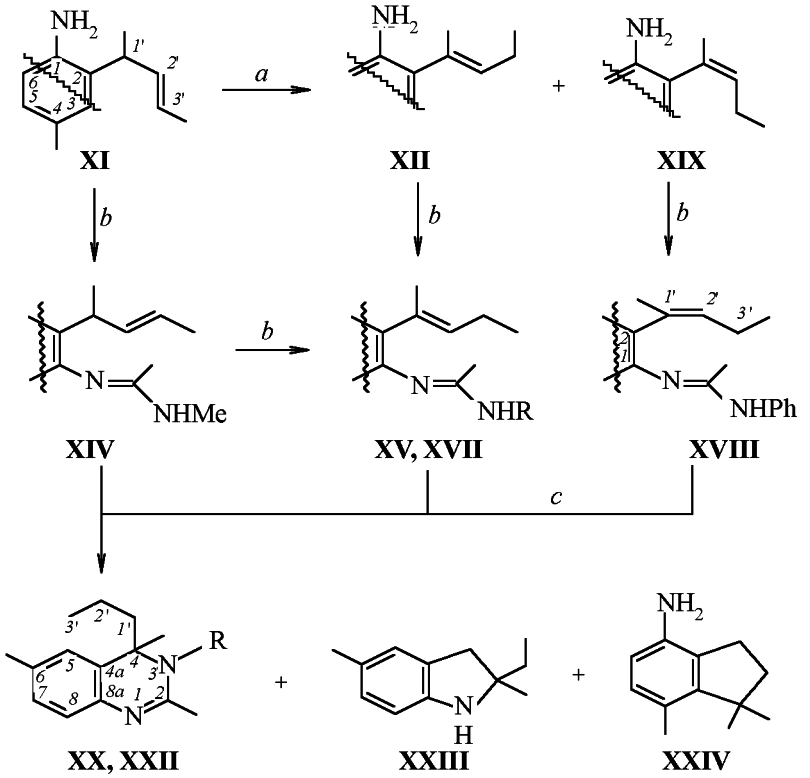
The attempt to obtain amidine **VIII** (Scheme 2) at treating *N*-formyl derivative **IX** with PCl_5 at molar ratio 1 : 1 results in cyclization of compound **IX** into quinoline **X** in 28% yield at 34% conversion of the initial amide **IX**.

The best results in preparation of the target quinazolines were obtained at using amidines synthesized by condensation of 2-[(*E*)-1-methyl-2-buten1-yl]-4-methylaniline (**XI**) [21], 2-[(*E*)-1-methyl-1-buten-1-yl]-4-methylaniline (**XII**) [22] or 2-(1-cyclo-penten-1-yl)-6-methylaniline (**XIII**) [18] with 1-methylimino-1-chloroethane [17] in benzene at 80°C.

Here form in high yield *N*-(alkenylphenyl)-*N*'-methylacetamidines **XIV–XVI** (Schemes 3 and 4).

Amidines **XVII** and **XVIII** were obtained in a similar way by reaction of amine **XII** and 2-[(*Z*)-1-methyl-1-buten-1-yl]-4-methylaniline (**XIX**) [22] with 1-phenylimino-1-chloroethane in 94–95% yield. The keeping of amidines **XIV, XV** in polyphosphoric acid for 4 h at 150–160°C gives rise to cyclized product 2,3,4,6-tetramethyl-4-propyl-3,4-dihydro-1,3-quinazoline (**XX**) (Scheme 3). Under similar conditions amidine **XVI** is converted into 2,3,8-trimethylspiro-(cyclopentane-3,4-dihydroquinazoline) (**XXI**)

Scheme 3.



R = Me (**XV, XX**), Ph (**XVII, XVIII, XXII**). Reagents and conditions: (*a*) KOH, 300°C; (*b*) MeNC(Cl)Me or PhNC(Cl)Me, 80°C, benzene; (*c*) polyphosphoric acid, 150–160°C.

(Scheme 4). In a similar cyclization of amidines **XVII** and **XVIII** into a 3-phenyl-substituted quinazoline **XXII** (Scheme 3) the yield of the product is smaller (Table 2). Amidine **XIV** is converted into quinazoline **XX** through preliminary shift of a double bond toward the aromatic ring resulting in vinyl derivative **XV** (according to GLC data). It is known that in reaction between the polyphosphoric acid and amine **XI** at 100–140°C originally arises *trans*-alkenylaniline **XII** [22] and then the successive isomerizations in the alkenyl fragment result in formation of a mixture of indoline **XXIII** and aminoindane **XXIV** [23].

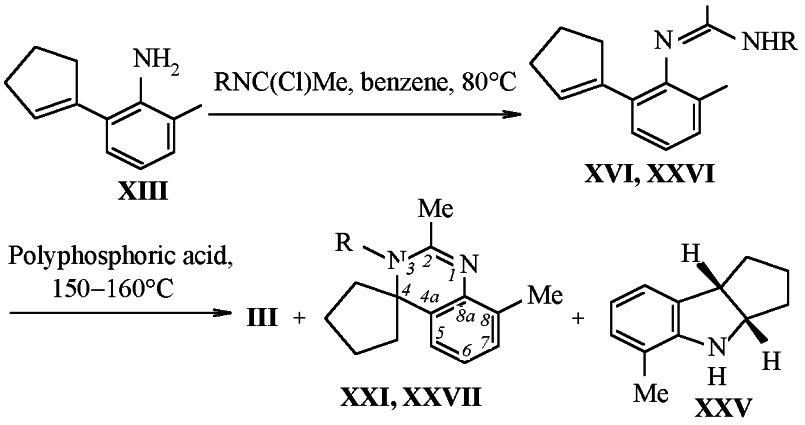
Unlike the reaction described in [23] with amidines **XV** and **XVI** due to the high basicity of the nitrogen atom on the MeNH group occurred intramolecular cyclization into six-membered heterocycles **XX** or **XXI**, and the expected under these relatively stringent conditions indoline **XXIII** and aminoindane **XXIV** from amidines **XIV**, **XV** or perhydrocyclopent[*b*]-indoline (**XXV**) [24] from amidine **XVI** formed in small amount (3–5%).

The replacement of the methyl group by phenyl (Schemes 3 and 4) the basicity of the amine nitrogen in amidines **XVII**, **XVIII, XXVI** is reduced, and the probability of the side processes grows. Therefore in reaction with polyphosphoric acid of amidines **XVII, XVIII** (Scheme 3) decreases the quinazoline yield, and amidine **XXVI** affords alongside quinazoline **XXVII** also indoline **XXV** (up to 24%) and quinoline **III** (6%) (Scheme 4).

We reported formerly on formation of 3,1-benzoxazines from *N*-acetylated derivatives of arylamines **I, II, XII** when treated with HCl gas at room temperature [18, 20]. Apparently due to high thermal stability of salts amidines **XV**, **XVI** do not afford quinazolines even at heating their hydrochlorides to 180°C.

The composition and structure of the compounds synthesized were established from elemental analyses and spectral data. Thus in the ^{1}H NMR spectrum of quinolines **III, IV** are present characteristic triplet signals of methylene protons H^1 and H^3 in the region 3.1 and 3.0 ppm respectively (Table 3). The signals of aromatic protons are observed at 7.3–7.6 ppm, and the signal from H^4 proton of quinoline **X** appears as a downfield singlet (8.8 ppm) [25]. In the ^{13}C NMR

Scheme 4.



R = Me (**XVI, XXI**), Ph (**XXVI, XXVII**).

Table 2. Yields, R_f values, melting points, IR spectra, and elemental analyses of compounds **III, IV, VI, IX, X, XIV–XVIII, XX–XXII, XXVI, XXVII**

Compd. no.	Yield, %	R_f ($CHCl_3$) or mp, °C	IR spectrum, ν, cm^{-1}	Found, %			Formula	Calculated, %		
				C	H	N		C	H	N
III	36–43	0.16	1354, 1450, 1509 [ν(C–C)]	85.02	7.43	6.83	$C_{14}H_{15}N$	85.22	7.67	7.11
IV	31–36	82 (85 [20])	1378, 1441, 1523 [ν(C–C)]	84.85	7.23	6.89	$C_{14}H_{15}N$	85.22	7.67	7.11
VI	95	0.4	3280 (NH)	77.80	7.48	6.16	$C_{14}H_{17}NO$	78.10	7.96	6.50
IX	95	102–104 (from hexane)	3280 (NH)	77.33	7.22	6.54	$C_{13}H_{15}NO$	77.58	7.51	6.96
X	28	82–85[a]	1376, 1460, 1508 [ν(C–C)]	84.97	6.89	7.36	$C_{13}H_{13}N$	85.20	7.16	7.64
XIV	93	0.2	3216 (NH)	77.89	9.33	11.80	$C_{15}H_{22}N_2$	78.21	9.63	12.16
XV	97	95–96 (from pentane)	3210 (NH)	78.02	9.21	11.83	$C_{15}H_{22}N_2$	78.21	9.63	12.16
XVI	94	0.2	3220 (NH)	78.60	8.53	11.94	$C_{15}H_{20}N_2$	78.89	8.83	12.27
XVII	95	0.2	3230 (NH)	82.00	8.07	9.34	$C_{20}H_{24}N_2$	82.15	8.27	9.58
XVIII	94	0.2	3254 (NH)	81.65	8.16	9.40	$C_{20}H_{24}N_2$	82.15	8.27	9.58
XX	70	0.4	1247 (C–N)	77.93	9.29	11.85	$C_{15}H_{22}N_2$	78.21	9.63	12.16
XXI	70	0.4	1245 (C–N)	78.53	8.69	11.97	$C_{15}H_{20}N_2$	78.89	8.83	12.27
XXII	51	0.4	1252 (C–N)	81.70	8.14	9.30	$C_{20}H_{24}N_2$	82.15	8.27	9.58
XXVI	93	0.2	3270 (NH)	82.40	7.31	9.29	$C_{20}H_{22}N_2$	82.72	7.63	9.65
XXVII	40	0.4	1257 (C–N)	82.33	7.55	9.46	$C_{20}H_{22}N_2$	82.72	7.63	9.65

[a] After sublimation in a vacuum.

spectra the signal of C^4 carbon linked directly to nitrogen in quinolines **III, X** (150–154 ppm), and C^6 in 6-methyl-7,8,9,10-tetrahydrophenanthridine (**IV**) (158.3 ppm) are shifted downfield [25] (Table 4).

In the IR spectra of amidines **XIV–XVIII, XXVI** the absorption band of NH group stretching vibrations is present at ν 3200–3270 cm^{-1} (Table 2). In the ^1H NMR spectra of amidines **XV, XVII, XVIII** the protons $H^{2'}$ of alkenyl fragments appear as triplet in the 5.3–5.6 ppm region (J ~6.6–7.1 Hz), and in the spectrum of amidine XVI this signal is a singlet at 5.9 ppm (Table 3). The proton signals from $H^{2'}$ and

Table 3. ^{1}H NMR spectra ($CDCl_3$) of compounds **III, IV, VI, IX, X, XIV–XVIII, XX–XXII, XXVI, XXVII**

Compd. no.	δ, ppm (*J*, Hz)
III	2.2 m (C^2H_2), 2.7 s, 2.8 s (2 CH_3), 3.0 t (C^1H_2, 6.8), 3.2 t (C^3H_2, 7.2), 7.3 m (H^8), 7.5 d (H^9, 6.4), 7.6 d (H^7, 7.8)
IV	1.5–2.6 m (C^8H_2, C^9H_2), 2.5 s (CH_3), 2.6 m ($C^{10}H_2$), 2.9 m (C^7H_2), 7.4 t (H^2, 7.0), 7.5 t (H^3), 7.7 d (H^4, 8.3), 7.9 d (H^1, 8.3)
VI	1.1–2.2 m (3 CH_2), 2.0 s (CH_3), 3.4 m ($C^{1'}H$), 5.6–6.0 m (HC=CH), 6.9–7.7 m (Ar–H), 7.4 s (NH)
IX	2.0 s ($\underline{C}H_3$), 2.0–2.6 m (3 CH_2), 5.9 t, 6.0 t (HC=C, 2.1), 7.1 m (Ar–H), 7.6 s, 8.1 s (NH, CHO)
X	2.2 m (C^2H_2), 2.5 s (CH_3), 3.0 t (C^1H_2, 7.5), 3.2 t (C^3H_2, 7.4), 7.3 m (H^8), 7.4 d (H^7, 8.3), 7.6 d (H^9, 6.3), 8.8 s (H^4)
XIV	1.2 d (7.0), 1.6 d (6.1), 1.7 s, 2.3 s, 2.9 s (5 CH_3), 3.8 m ($C^{1'}H$), 4.4 s (NH), 5.4 d.q ($H^{2'}$, 6.1, 15.4), 5.5 d.d ($H^{3'}$, 7.4), 6.5 d (H^6, 7.1), 6.9 d (H^5, 7.1), 7.9 s(H^3)
XV	1.0 t (7.6), 1.6 s, 1.9 s, 2.2 s, 2.8 s (5 CH_3), 2.1 q ($C^{3'}H_2$, 7.1), 4.4 s (NH), 5.4 t ($H^{2'}$, 7.1), 6.6 d (H^6, 7.8), 6.8 s (H^3), 6.9 d (H^5, 7.8)
XVI	1.4 s, 2.1 s, 2.8 s (3 CH_3), 1.9 m ($C^{4'}H_2$), 2.3 m ($C^{3'}H_2$), 2.7 m ($C^{5'}H_2$), 4.9 s (NH), 5.9 s ($H^{2'}$), 6.8 t (H^4, 7.5), 7.0 d (H^3, 7.5), 7.1 d (H^5)
XVII	1.0 t (7.5), 1.9 m ($C^{3'}H_2$), 2.0 s, 2.1 s, 2.4 s (4 CH_3), 5.6 t ($H^{3'}$, 6.9), 7.0 s (H^3), 7.1–7.4 m (7H, Ar–H), 7.6 s (NH)
XVIII	1.1 t (7.5), 1.9 s, 2.1 s, 2.4 s (4 CH_3), 2.3 q ($C^{3'}H_2$, 7.4), 5.5 t ($H^{2'}$, 6.6), 7.0–7.4 m (8H, Ar–H), 7.3 s (NH)
XX	0.8 t (7.3), 1.3 m ($C^{2'}H_2$), 1.5 s, 1.9 s, 2.2 s, 2.8 s (5 CH_3), 2.1 m ($C^{1'}H_2$), 6.7–6.9 m (3H, Ar–H)
XXI	1.5–2.7 m (4 CH_2), 2.1 s, 2.3 s, 2.9 s (3 CH_3), 6.8–7.9 m (3H, Ar–H)
XXII	0.8 t (7.3), 1.3 m ($C^{2'}H_2$), 1.5 s, 1.9 s, 2.2 s, 2.8 s (5 CH_3), 2.1 m ($C^{1'}H_2$), 6.9–7.4 m (8H, Ar–H)
XXVI	1.6 s, 2.1 s (2 CH_3), 1.7–2.7 m (3 CH_2), 5.9 s ($H^{2'}$), 6.7–7.4 m (8H, Ar–H), 9.4 s (NH)
XXVII	1.5–2.3 m (4 CH_2), 1.5 s, 2.5 s (2 CH_3), 6.6–7.4 m (8H, Ar–H)

$H^{3'}$ at the double bond in amidine **XIV** are observed in the region of 5.4 (d.q, J_1 6.0 and J_2 15.4 Hz) and 5.5 ppm (d.d, *J* 7.4 Hz). The quintet of the methylene protons $C^{3'}H_2$ of amidine **XV** is located in the region of 2.1 ppm (*J* 7.1 Hz), and in the spectrum of quinazoline **XX** the proton signals of the two methylene groups in the propyl moiety are shifted upfield (1.3–1.9 ppm). The carbon resonance from the N=C–N moiety in the ^{12}C NMR spectra of amidines **XIV–XVIII**, **XVI** appears at 156–160 ppm and it does not significantly alter in the quinazoline spectra. In the ^{13}C NMR spectra of compounds **XX, XXI, XXII, XXVII** the signals of nodal carbon atoms C^4 are observed in 61–68 ppm region respectively (Table 4). In the aromatic part of the ^{13}C NMR spectra of quinazolines **XX, XXI** appear 6 signals assigned to respective carbon atoms basing on calculations according to additive parameters [25].

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-300 at operating frequencies 300 and 75 MHz respectively (solvent $CDCl_3$, internal reference TMS). IR spectra were recorded on UR-20 instrument. The purity of products was controlled by GLC on a chromatograph Chrom-5 (stationary phase SE-30 on Chromaton N-AW-DMCS, *l* 1.2 m, flame-ionization detector, temperature programmed at a rate 12 deg min^{-1}, carrier gas helium) and by TLC on Silufol UV-254 plates (eluent $CHCl_3$).

The initial anilides **I, II, V** were prepared by procedure described in [18, 19].

***N*-Acetyl-2-(2-cyclohexen-1-yl)aniline (VI).** To a solution of 1.73 g of 2-(2-cyclohexen-1-yl)aniline in 10 ml of dichloromethane was added 2.04 g of acetic anhydride, and the mixture was left standing for 18 h. Then the reaction mixture was diluted with water, extracted with 100 ml of CH_2Cl_2, the extract was washed with 5% water solution of $NaHCO_3$ till the end of CO_2 liberation, then again with water (20 ml), dried on $MgSO_4$, and evaporated. We obtained 2.04 g (95%) of oily amide **VI**.

***N*-Formyl-2-(1-cyclopenten-1-yl)-6-methylaniline (IX).** A solution of 1 g of amine **XIII** in 10 ml of

Table 4. ^{13}C NMR spectra ($CDCl_3$) of synthesized compounds **III, IV, VI, IX, X, XIV–XVIII, XX–XXII, XXVI, XXVII**

Compd. no.	Chemical shifts, δ_C, ppm
III	18.2 (CH_3), 23.2 (CH_3) 23.3 (C^2), 30.9 (C^3), 32.1 (C^1), 121.5 (C^{9a}), 121.7 (C^8), 124.6 (C^9), 127.8 (C^7), 136.4 (C^6), 137.2 (C^{3a}), 145.9 (C^{9b}), 148.9 (C^{5a}), 154.1 (C^4)
IV	21.7 (C^8), 22.2 (C^9), 23.2 (CH_3), 25.2 (C^7), 26.5 (C^{10}), 122.1 (C^1), 125.1 (C^4), 126.4 (C^{10b}), 127.6 (C^3), 128.7 (C^2), 140.6 (C^{10a}), 145.2 (C^{4a}), 158.3 (C^6),
VI	21.4 ($C^{5'}$), 24.8 ($C^{6'}$), 24.9 (CH_3), 29.8 ($C^{4'}$), 39.1 ($C^{1'}$), 121.4 (C^6), 125.7 ($C^{3'}$), 127.9 (C^3), 128.2 (C^5), 129.5 (C^4), 129.8 ($C^{2'}$), 136.4 (C^2), 138.5 (C^1), 168.5 (C=O)
IX	18.9 (CH_3), 23.8 ($C^{4'}$), 33.4 and 33.6 ($C^{3'}$), 36.0 and 36.3 ($C^{5'}$), 126.3, 127.0, 127.2, 127.4, 129.4, 129.6, 130.7, 130.8, 132.0, 134.3, 135.7, 136.0, 141.1 (C arom, $C^{1'}$, $C^{2'}$), 159.7 and 165.1 (C=O)
X	18.8 (CH_3), 24.6 (C^2), 31.2 (C^3), 31.4 (C^1), 122.3 (C^{9a}), 122.5 (C^8), 126.6 (C^9), 128.6 (C^7), 136.5 (C^{3a}), 137.5 (C^6), 146.2 (C^{9b}), 146.5 (C^{5a}), 150.2 (C^4)
XIV	17.4, 18.0, 20.0, 21.0, 28.5 (CH_3), 122.2, 122.7, 126.8, 127.7, 131.8, 136.6, 138.0, 142.3 (C arom, $C^{1'}$,$C^{2'}$), 156.0 (N=CN)
XV	14.2, 16.3, 17.7, 20.8, 21.8 (CH_3), 28.5 (NCH_3), 122.5 (C^3), 127.7 (C^5), 129.7 ($C^{2'}$), 131.1 ($C^{1'}$), 131.2 (C^6), 136.1 (C^4), 138.3 (C^2), 141.0 (C^1), 156.1 (N=CN)
XVI	16.9, 18.1, 23.7 (3 CH_3), 27.7 (NCH_3), 33.2 ($C^{3'}$), 35.5 ($C^{5'}$), 121.1 (C^4), 126.1 ($C^{2'}$), 127.9 (C^5), 128.2 (C^3), 129.16 (C^6), 142.1 ($C^{1'}$), 147.8 (C^1), 155.2 (N=CN)
XVII	13.9, 17.0, 20.4, 24.3 (CH_3), 22.3 ($C^{3'}$), 121.1 (C^6), 127.9 (C^5), 128.5 ($C^{2'}$), 130.7 (C^3), 132.1 (C^2), 133.2 (C^4), 133.4 ($C^{1'}$), 145.2 (C^1), 151.1 (N=CN), 122.4, 127.7, 128.5, 130.7 (Ph–H)
XVIII	13.7, 17.3, 18.0, 20.2 (CH_3), 21.4 ($C^{3'}$), 121.2 (C^6), 128.8 (C^5), 129.3 ($C^{2'}$), 132.1 (C^2), 132.9 ($C^{1'}$), 134.0 (C^3), 139.2 (C^4), 143.0 (C^1), 154.0 (N=CN), 122.7, 127.8, 128.8, 134.1 (Ph–H)
XX	13.9, 21.0, 23.2, 28.7 (CH_3), 17.5 ($C^{2'}$), 31.3 (NCH_3), 43.2 ($C^{1'}$), 61.2 (C^4), 122.5 (C^8), 124.5 (C^7), 127.3 (C^{4a}), 132.8 (C^6), 138.9 (C^{8a}), 156.3 (C^2)
XXI	17.8, 24.3 (CH_3), 26.2 ($C^{3'}$,$C^{4'}$), 32.7 (NCH_3), 40.8 ($C^{2'}$,$C^{5'}$), 66.3 (C^4), 121.6 (C^7), 123.2 (C^5), 128.9 (C^6), 130.8 (C^8), 131.6 (C^{4a}), 139.8 (C^{8a}), 156.4 (C^2)
XXII	13.4, 20.8, 22.7, 28.6 (CH_3), 17.0 ($C^{2'}$), 45.0 ($C^{1'}$), 62.4 (C^4), 121.4 (C^8), 124.3 (C^5), 126.9 (C^{4a}), 128.3 (C^7), 133.6 (C^6), 138.7 (C^{8a}), 156.0 (C^2), 128.8, 129.3, 130.7, 136.3 (Ph–H)
XXVI	16.4, 18.2 (CH_3), 23.4 ($C^{4'}$), 33.1 ($C^{3'}$), 35.4 ($C^{5'}$), 123.0, 125.4, 125.8, 126.3, 128.6, 128.8, 129.0, 130.3, 132.9, 133.3, 137.8, 140.6 (Ar–H, $C^{1'}$, $C^{2'}$), 160.2 (N=CN)
XXVII	17.7, 24.4 (CH_3), 23.3 ($C^{3'}$, $C^{4'}$), 38.3 ($C^{2'}$, $C^{5'}$), 63.3 (C^4), 123.7, 123.9, 125.4, 129.1, 129.2, 130.2, 130.8, 132.2, 134.9, 139.3 (Ar–H), 159.7 (C^2)

anhydrous formic acid was heated at reflux for 40 min, and excess acid was evaporated in a vacuum. The residue was dissolved in toluene, and the solvent was evaporated in a vacuum; this procedure was repeated twice. Then the residue was recrystallized from hexane. Yield 1.1 g (95%).

Cyclization of anilides I, II, V, VI in the presence of P_2O_5. To a mixture of 1.1 mmol of methylamine hydrochloride or NH_4Cl and 10 mmol of P_2O_5 was added 100 mmol of tributylamine and then 1 mmol of the appropriate acetanilide **I, II, V**, or **VI**. The reaction mixture was heated to 160–170°C for 2 h and on cooling to room temperature it was diluted with 100 ml of water. In small portions was added 20% water solution of NaOH till alkaline reaction. Reaction product **III** or **IV** was extracted into benzene and dried on KOH. The solvent was evaporated in a vacuum, and the residue was subjected to chromatography on a column (0.5 × 30 cm) packed with silica gel (3 g), elution first with benzene, then with a mixture benzene–methanol, 9 : 1.

4,6-Dimethyl-2,3-dihydro-1*H*-cyclopent[c]-quinoline (III). In a mixture of NH_4Cl, P_2O_5, and tributylamine prepared as above was dissolved 0.22 g of benzoxazine **VII**. The reaction and workup of products was carried out as above.

6-Methyl-2,3-dihydro-1*H*-cyclopent[c]quinoline (X). To a solution of 0.48 g of PCl_5 in 10 ml of benzene was added slowly by small portions 0.4 g of formanilide **IX**. Then to the mixture was added 2 mmol of NH_4Cl. The reaction mixture was heated

for 2.5 h at 80°C, cooled, treated with 10% water solution of NaOH, and extracted with $CHCl_3$ (2×20 ml). The extract was dried on Na_2SO_4, the solvent was evaporated in a vacuum, the residue was washed with hot pentane or hexane (3×10 ml), the hydrocarbon solutions were combined, evaporated, and the residue was subjected to chromatography on silica gel (eluent $CHCl_3$). We separated 0.27 g (66%) of the original amide **IX** and 0.1 g (28%) of quinoline **X**.

Amidines XIV–XVIII, XXVI. To a cooled solution of 0.023 mol of PCl_5 in 20 ml of $CHCl_3$ or benzene was added slowly by small portions 0.02 mol of an appropriate *N*-methyl- or *N*-phenylacetamide. On completion of the reaction to the mixture was added 0.02 mol of an appropriate alkenylaniline dissolved in 10 ml of $CHCl_3$ or benzene. Then the reaction mixture was heated for 2.5 h at 80°C, cooled, treated with 10% water solution of NaOH, the product was extracted into $CHCl_3$ (2×20 ml), and dried on Na_2SO_4. The solvent was evaporated in a vacuum, the residue was washed with hot pentane or hexane (3×10 ml), the hydrocarbon solutions were combined, cooled, the precipitate was separated and dried in a vacuum.

Cyclization of amidines XIV–XVIII, XXVI. Amidine **XIV–XVIII, XXVI** (1 mmol) was mixed with 1.5 g of polyphosphoric acid and heated to 150–160°C for 4 h. Then the reaction mixture was cooled to room temperature, washed with small portions of a concn. water solution of Na_2CO_3 till alkaline reaction by universal indicator strips. The reaction product was extracted into ethyl acetate (3...10 ml), dried on Na_2SO_4, the solvent was evaporated at reduced pressure.

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