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NEW APPROACH TO THE SYNTHESIS OF 1,2,3,4-TETRAHYDROQUINOLIN-4-ONES

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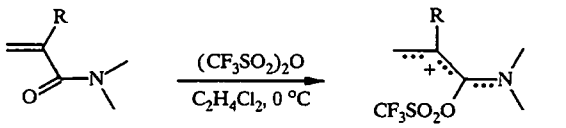
The reaction of aromatic amines with complexes of N,N-dimethylacrylamide and N,N-dimethylmethacrylamide with trifluoromethanesulfonic anhydride leads to the formation of tetrahydro-4-quinolones and 3-methyltetrahydro-4-quinolones respectively.

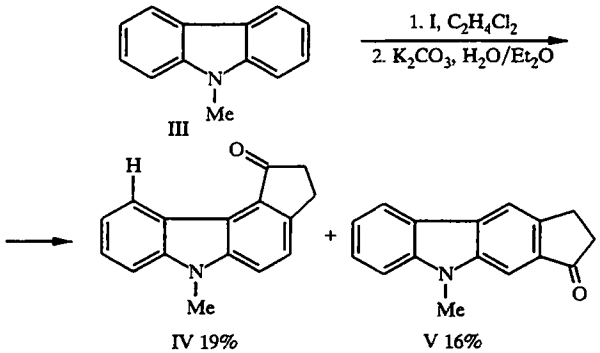
In previous studies [1-3] we proposed a new electrophilic reagent, viz. the complex of N,N-dimethylacrylamide with trifluoromethanesulfonic anhydride (I), and investigated its behavior with several aromatic and heteroaromatic substrates containing electron-donating substituents. The complex is an imminium salt with the positive charge delocalized between the nitrogen atom, the carbonyl carbon, and the terminal olefinic carbon atoms [2].



R = H I
R = Me II

This reagent has two electrophilic centers of different natures, the imminium carbon atom and the terminal carbon atom of the double bond, and is able to react with reactive aromatic compounds with the formation of indanones and 1,3-diarylpropanones. The course of the reaction depends on the ratio of the reactivities of the adjacent positions in the aromatic ring. Thus if the nucleophilicities of these positions are close to one another cyclization occurs with the formation of indanones.

While continuing the investigation of the behavior of heteroaromatic substrates in the reaction with complex (I) we found that the reaction of this complex with N-methylcarbazole (III) leads to the formation of two compounds namely the isomeric cyclopentacarbazoles (IV) and (V) in a 1:1 ratio. The initial attack occurs at the most reactive position 3 of the carbazole molecule [4]. The cyclization step is less selective [2] and takes place at both positions 2 and 4. Compounds (IV) and (V) may be separated chromatographically. A characteristic feature of the PMR spectrum of compound (IV) is the significant displacement towards low field of the 10-H signal (9.20 ppm) caused by the effect of the spatial proximity of the 10-H proton and the carbonyl carbon atom.



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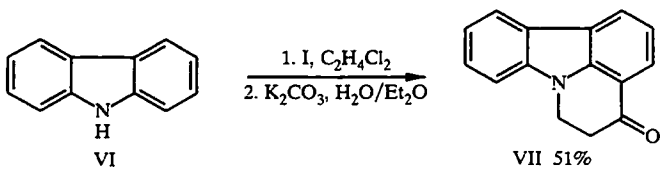
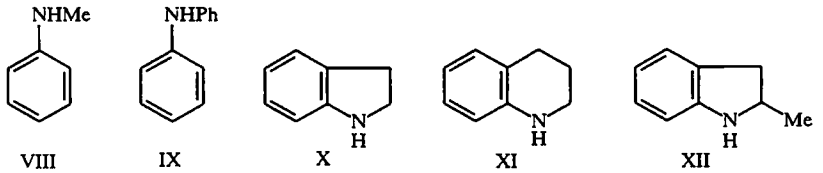
In the case of unsubstituted carbazole (VI) the initial attack of the electrophile occurs not at the aromatic ring but at the nitrogen atom. Subsequent cyclization at the ortho position leads to the formation of a single reaction product — the tetrahydropyridocarbazole (VII), i.e. unlike N-methylcarbazole reacting as a C-nucleophile, carbazole reacts with complex (I) as an N-nucleophile. Reaction occurs with the initial attack at the nitrogen atom by the terminal carbon atom of the double bond of the complex with subsequent heterocyclization to a quinolone derivative.



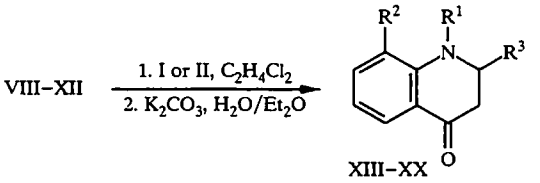
VI VII 51%

We investigated the behavior of secondary aromatic amines of various structure (VIII)-(XII) in the reaction with complex (I) and found that the sole reaction product in every case was the corresponding tetrahydroquinolone (XIII)-(XVII).



VIII IX X XI XII

Complex (II) possesses a significantly lower electrophilicity and does not react with the majority of aromatic substrates. However it reacts with alkylarylamines (VIII)-(X) with the formation of 3-methyltetrahydro-4-quinolones (XVIII)-(XX). Primary aromatic and tertiary amines do not react with complexes (I) and (II).



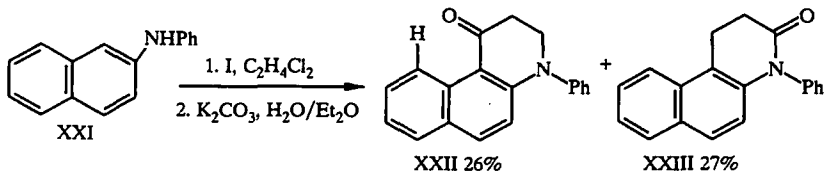
XIII–XX

XIII R^1 = Me, R^2 = H, R^3 = H; XIV R^1 = Ph, R^2 = H, R^3 = H; XV $R^1 + R^2 = (CH_2)_2$, R^3 = H; XVI $R^1 + R^2 = (CH_2)_3$, R^3 = H; XVII $R^1 + R^2 = CH(CH_3)CH_2$, R^3 = H; XVIII R^1 = Me, R^2 = H, R^3 = Me; XIX $R^1 + R^2 = (CH_2)_2$, R^3 = Me; XX $R^1 + R^2 = (CH_2)_3$, R^3 = Me

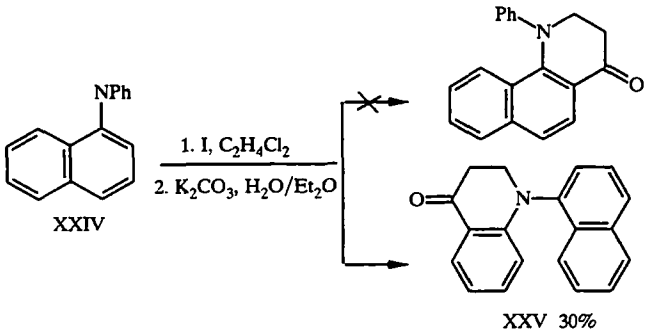
There are systems of signals in the PMR spectra of compounds (XIII), (XIV), and (XVIII) at 6.6-7.8 ppm characteristic of an ortho disubstituted benzene nucleus. In the spectra of compounds (XV)-(XVII), (XIX), and (XX) the system of signals at 6.6-7.4 ppm is characteristic of a 1,2,3 trisubstituted benzene nucleus.

The usual method of obtaining compounds of this class has been known for a fairly long time and is the cyclization of N,N-disubstituted β-alanines catalyzed by polyphosphoric acid or liquid HF [5, 6] or cyclization of β-aminopropionitriles with the aid of strong Lewis acids, primarily $AlCl_3$ [7]. It was shown recently [8-11] that acrylic acid reacts with aromatic amines in polyphosphoric acid giving the corresponding tetrahydroquinolones. However the reaction is accompanied by marked resinification and yields of reaction products varied in the range 5-10%. The merit of our one-step method of synthesizing tetrahydro-4-quinolones must be the use of readily available starting materials. In addition, reaction yields are significantly higher than on using acrylic acid.

An unexpected result was obtained on reacting complex (I) with N-phenyl-2-naphthylamine (XXI). Two substances were isolated, a tetrahydro-4-quinolone (XXII) and a tetrahydro-2-quinolone (XXIII) in a 1 : 1 ratio. The formation of compound (XXIII) occurs as a result of the initial attack of complex (I) at the α position of the naphthalene ring and not at the nitrogen atom. This indicates that the nitrogen atom and carbon atom $C_{(1)}$ in the amine (XXII) possess comparable nucleophilicities. A characteristic feature of the PMR spectrum of compound (XXII) was the presence of a significant displacement of the 10-H signal (9.43 ppm) towards low field caused, as for compound (IV), by the effect of the carbonyl carbon atom.



Reaction with N-phenyl-1-naphthylamine (XXIV) proceeds unambiguously and is accompanied by considerable resinification. The sole isolated compound was a yellow crystalline substance. Signals characteristic of a monosubstituted benzene nucleus were absent from the ^1H and ^{13}C NMR and IR spectra of this compound. Using the two dimensional COSY procedure we succeeded in completely assigning the proton signals in the PMR spectrum and determined that the substance isolated was the N-naphthyltetrahydroquinolone (XXV) formed by cyclization onto the phenyl and not the naphthyl ring. The significant displacement to high field of the 8-H signal in the PMR spectrum of compound (XXV) [$\Delta\delta$ = 0.5 ppm compared to N-phenyltetrahydroquinolone (XIV)] may probably be explained by the effect of the closely positioned naphthalene ring.



We have studied the behavior of complexes of N,N-dimethylacrylamide and N,N-dimethylmethacrylamide with trifluoromethylsulfonic anhydride in reactions with secondary aromatic amines. A new convenient method of obtaining tetrahydro-4-quinolones and 3-methyltetrahydro-4-quinolones has been developed based on this reaction.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on Varian VXR 400 and Bruker AMX 400 spectrometers (operating frequencies 400 MHz and 100 MHz respectively) in $CDCl_3$, TMS was used as internal standard. The IR spectra were obtained on a UR 20 spectrometer in Nujol. Analysis by TLC was carried out on Silufol UV 254 plates, visualizing with acidified $KMnO_4$ solution and with iodine vapor. Trifluoromethylsulfonic anhydride was obtained according to the procedure described in [12].

General Method for the Synthesis of 1,2,3,4-Tetrahydroquinolin-4-ones. A solution of $(CF_3SO_2)_2O$ (1.25 g, 4.4 mmole) in absolute dichloroethane (15 ml) was added dropwise with vigorous stirring to a cooled (0°C) solution of N,N-dimethylacrylamide (0.44 g, 4.4 mmole) in absolute dichloroethane (30 ml). The appropriate aromatic amine (3.5 mmole) in absolute dichloroethane (15 ml) was then added. The reaction mixture was boiled for 2-4 h, then poured into a mixture of ether and aqueous K_2CO_3 solution. The organic phase was separated, the aqueous layer extracted with ether, and dried over $CaCl_2$. The solvent was evaporated in vacuum and the residue chromatographed on a column of silica gel. Eluents were hexane–ethyl acetate 10 : 1 or benzene.

6-Methyl-1,2,3,4-tetrahydrocyclopenta[c]carbazol-1-one (IV). Yield was 0.18 g (19%), mp 205-208°C. IR spectrum: 1700 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 9.20 (1H, d, ^3J = 8.0 Hz, 10-H); 7.65 (1H, d, ^3J = 8.0 Hz, 4-H or 5-H); 7.54 (1H, d.d, ^3J = 8.0, ^3J = 7.6 Hz, 8-H); 7.49 (1H, d, ^3J = 8.0 Hz, 4-H or 5-H); 7.42 (1H, d, ^3J = 8.0 Hz, 7-H); 7.31 (1H, d.d, ^3J = 8.0, ^3J = 7.6 Hz, 9-H); 3.90 (3H, s, NCH_3); 3.30 (2H, m, 3-CH_2); 2.83 ppm (2H, m, 2-CH_2). ^{13}C NMR spectrum ($CDCl_3$): 207.56 ($C_{(1)}$); 148.75 ($C_{(3a)}$); 141.50 ($C_{(5a)}$ or $C_{(6a)}$); 140.13 ($C_{(5a)}$ or $C_{(6a)}$); 131.79 ($C_{(10c)}$); 126.88, 126.32, 122.71, 119.38, and 115.26 (5-CH_{arom}); 121.91 ($C_{(10a)}$ or $C_{(10b)}$); 118.68 ($C_{(10a)}$ or $C_{(10b)}$); 108.18 ($C_{(9)}$); 37.04 ($C_{(2)}$); 29.41 (NCH_3); 26.50 ppm ($C_{(3)}$). Found, %: c 81.14; H 5.63. $C_{16}H_{13}NO$. Calculated, %: C 81.70; H 5.53.

5-Methyl-5,7,8,9-tetrahydrocyclopenta[b]carbazol-7-one (V). Yield was 0.16 g (16%), mp 178-180°C. IR spectrum: 1700 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 8.10 (1H, d, ^3J = 8.0 Hz, 1-H); 8.06 (1H, s, 10-H); 7.72 (1H, s, 6-H); 7.54 (1H, d.d, ^3J = 8.2, ^3J = 7.6 Hz, 3-H); 7.37 (1H, d, ^3J = 8.2 Hz, 4-H); 7.25 (1H, d.d, ^3J = 8.0, ^3J = 7.6, 2-H); 3.82 (3H, s, NCH_3); 3.29-3.20 (2H, m, 9-CH_2); 2.83-2.74 ppm (2H, m, 8-CH_2). ^{13}C NMR spectrum ($CDCl_3$): 207.43 ($C_{(7)}$); 145.13 ($C_{(10a)}$); 143.15 ($C_{(5a)}$ or $C_{(6a)}$); 140.70 ($C_{(5a)}$ or $C_{(6a)}$); 134.51 ($C_{(7a)}$); 129.69 ($C_{(10a)}$ or $C_{(10b)}$); 121.56 ($C_{(10a)}$ or $C_{(10b)}$); 127.72, 121.30, 119.22, 116.99, 108.74, and 102.68 (6-CH_{arom}); 37.24 ($C_{(8)}$); 29.17 (NCH_3); 25.36 ppm ($C_{(9)}$). Found, %: C 81.23; H 5.45. $C_{16}H_{13}NO$. Calculated, %: C 81.70; H 5.53.

5,6-Dihydro-4H-pyrido[3,2,1-jk]carbazol-4-one (VII). Yield was 0.40 g (51%), mp 97-99°C, (according to [6] mp 98-100°C). IR spectrum: 1690 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 8.00 (1H, d, ^3J = 7.6 Hz, 1-H); 7.91 (1H, d, ^3J = 8.0 Hz, 11-H); 7.76 (1H, d, ^3J = 7.6 Hz, 3-H); 7.37 (1H, d.d, ^3J = 8.2, ^3J = 7.4 Hz, 9-H); 7.21 (1H, d, ^3J = 8.2 Hz, 8-H); 7.15 (1H, d.d, ^3J = 8.0, ^3J = 7.4 Hz, 10-H); 7.09 (1H, t, ^3J = 7.6 Hz, 2-H); 4.22 (2H, t, ^3J = 7.2 Hz, CH_2N); 2.95 ppm (2H, t, ^3J = 7.2 Hz, CH_2CO). ^{13}C NMR spectrum ($CDCl_3$): 192.19 ($C_{(4)}$); 143.47 ($C_{(3b)}$); 140.31 ($C_{(7a)}$); 126.40 ($C_{(1)}$ or $C_{(3)}$); 126.27 ($C_{(1)}$ or $C_{(3)}$); 123.06 ($C_{(11a)}$ or $C_{(11b)}$); 122.92 ($C_{(11a)}$ or $C_{(11b)}$); 121.96, 121.04, 119.90, and 119.25 (4CH_{arom}); 116.95 ($C_{(3a)}$); 108.91 ($C_{(8)}$); 40.54 ($C_{(6)}$); 37.29 ppm ($C_{(5)}$).

4-Methyl-1,2,3,4-tetrahydroquinolin-1-one (XIII). Yield was 0.22 g (39%), oil, n_D^{20} 1.6170, (according to [10] n_D^{20} 1.6191). IR spectrum: 1685 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.80 (1H, d.d, ^4J = 1.5, ^3J = 8.1 Hz, 8-H); 7.29 (1H, d.d.d, ^4J = 1.5, ^3J = 8.1, ^3J = 7.9 Hz, 6-H); 6.64 (1H, d.d.d, ^4J = 1.5, ^3J = 8.1, ^3J = 7.9 Hz, 7-H); 6.60 (1H, d.d, ^4J = 1.5, ^3J = 8.1 Hz, 5-H); 3.34 (2H, t, ^3J = 7.2 Hz, CH_2N); 2.85 (3H, s, CH_3N); 2.60 ppm (2H, t, ^3J = 7.2 Hz, CH_2CO). ^{13}C NMR spectrum ($CDCl_3$): 193.29 ($C_{(1)}$); 152.36 ($C_{(4a)}$); 135.08 ($C_{(6)}$ or $C_{(8)}$); 127.51 ($C_{(6)}$ or $C_{(8)}$); 119.43 ($C_{(8a)}$); 116.61 ($C_{(5)}$ or $C_{(7)}$); 112.96 ($C_{(5)}$ or $C_{(7)}$); 50.95 ($C_{(3)}$); 38.89 (CH_3); 37.84 ppm ($C_{(2)}$).

4-Phenyl-1,2,3,4-tetrahydroquinolin-1-one (XIV). Yield was 0.30 g (32%), mp 81-82°C (according to [13] mp 82-83°C). IR spectrum: 1690 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.88 (1H, d.d, ^4J = 1.4, ^3J = 8.0 Hz, 8-H); 7.47 (2H, d.d, ^3J = 8.1, ^3J = 7.9 Hz, 3-H, 5-H_{Ph}); 7.20 (3H, m, 6-H_Q, 2-H, 6-H_{Ph}); 7.13 (1H, d.d.d, ^4J = 1.4, ^3J = 8.1, ^3J = 7.9 Hz, 4-H_{Ph}); 6.70 (1H, d.d.d, ^4J = 1.5, ^3J = 8.1, ^3J = 7.9 Hz, 7-H); 6.57 (1H, d.d, ^4J = 1.5, ^3J = 8.1 Hz, 5-H); 3.83 (2H, t, ^3J = 7.0 Hz, CH_2N); 2.76 ppm (2H, t, ^3J = 7.0 Hz, CH_2CO). ^{13}C NMR spectrum ($CDCl_3$): 193.35 ($C_{(1)}$); 151.16 ($C_{(4a)}$); 145.77 ($C_{(1Ph)}$); 134.74 ($C_{(6)}$ or $C_{(8)}$); 129.84 (2C, $C_{(3)}$, $C_{(5Ph)}$); 127.94 ($C_{(6)}$ or $C_{(8)}$); 125.96 (2C, $C_{(2)}$, $C_{(6Ph)}$); 125.68 ($C_{(4Ph)}$); 120.18 ($C_{(8a)}$); 118.24 ($C_{(5)}$ or $C_{(7)}$); 115.43 ($C_{(5)}$ or $C_{(7)}$); 50.61 ($C_{(3)}$); 38.27 ppm ($C_{(2)}$).

1,2,5,6-Tetrahydro-4H-pyrrolo[3,2,1-ij]quinolin-6-one (XV). Yield was 0.26 g (46%), mp 56-58°C (according to [9] mp 57-58°C). IR spectrum: 1680 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.44 (1H, d.d, ^4J = 1.3, ^3J = 8.0 Hz, 7-H); 7.13 (1H, d.d, ^4J = 1.3, ^3J = 7.8 Hz, 9-H); 6.64 (1H, d.d, ^3J = 7.8, ^3J = 8.0 Hz, 8-H); 3.32 (2H, t, ^3J = 8.0 Hz, 2-CH_2); 3.23 (2H, t, ^3J = 7.2 Hz, 4-CH_2); 2.98 (2H, t, ^3J = 8.0 Hz, 1-CH_2); 2.67 ppm (2H, t, ^3J = 7.2 Hz, 5-CH_2). ^{13}C NMR spectrum ($CDCl_3$): 192.93 ($C_{(6)}$); 158.17 ($C_{(3a)}$); 130.98 ($C_{(9a)}$); 129.49 ($C_{(7)}$ or $C_{(9)}$); 123.37 ($C_{(7)}$ or $C_{(9)}$); 118.71 ($C_{(8)}$); 116.49 ($C_{(6a)}$); 54.85 ($C_{(2)}$); 48.45 ($C_{(4)}$); 38.21 ($C_{(5)}$); 29.01 ppm ($C_{(1)}$).

2,3,6,7-Tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-1-one (XVI). Yield was 0.21 g (34%), mp 63-64°C (according to [8] mp 62-63°C). IR spectrum: 1680 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.66 (1H, d, ^3J = 7.9 Hz, 10-H); 7.04 (1H, d, ^3J = 7.4 Hz, 8-H); 6.58 (1H, d.d, ^3J = 7.4, ^3J = 7.9 Hz, 9-H); 3.32 (2H, m, 3-CH_2 or 5-CH_2); 3.17 (2H, m, 3-CH_2 or 5-CH_2); 2.71 (2H, m, 1-CH_2 or 6-CH_2); 2.64 (2H, m, 1-CH_2 or 6-CH_2); 2.00 ppm (2H, m, 2-CH_2). ^{13}C NMR spectrum ($CDCl_3$): 193.70 ($C_{(1)}$); 149.50 ($C_{(4a)}$); 134.61 ($C_{(8)}$ or $C_{(10)}$); 125.79 ($C_{(8)}$ or $C_{(10)}$); 123.70 ($C_{(7a)}$ or $C_{(10a)}$); 119.07 ($C_{(7a)}$ or $C_{(10a)}$); 116.56 ($C_{(9)}$); 50.04 ($C_{(3)}$ or $C_{(5)}$); 50.00 ($C_{(3)}$ or $C_{(5)}$); 37.84 ($C_{(2)}$); 26.53 ($C_{(7)}$); 21.47 ppm ($C_{(6)}$).

2-Methyl-2,4,5,6-tetrahydro-1H-pyrrolo[3,2,1-ij]quinolin-6-one (XVII). Yield was 0.29 g (44%), mp 62-63°C (according to [9] mp 64°C). IR spectrum: 1680 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.42 (1H, d, ^3J = 8.0 Hz, 7-H); 7.08 (1H, d, ^3J = 7.8 Hz, 9-H); 6.59 (1H, d.d, ^3J = 7.8, ^3J = 8.0 Hz, 8-H); 3.50-3.40 (2H, m, 2-CH, 4-C<u>H</u>H); 3.07 (1H, d.d, ^2J = 15.6, ^3J = 7.9 Hz, 1-C<u>H</u>H); 2.95 (1H, d.d.d, ^2J = 4.4, ^3J = 14.1, ^3J = 10.4 Hz, 4-C<u>H</u>H); 2.77-2.57 (3H, m, 1-C<u>H</u>H, 5-CH_2); 1.32 ppm (3H, d, ^3J = 6.2 Hz, CH_3). ^{13}C NMR spectrum ($CDCl_3$); 193.03 ($C_{(6)}$); 158.08 ($C_{(3a)}$); 130.02 ($C_{(9a)}$); 129.26 ($C_{(7)}$ or $C_{(9)}$); 123.33 ($C_{(7)}$ or $C_{(9)}$); 118.50 ($C_{(8)}$); 116.00 ($C_{(6a)}$); 62.74 ($C_{(2)}$); 45.93 ($C_{(4)}$); 38.18 ($C_{(1)}$ or $C_{(5)}$); 37.37 ($C_{(1)}$ or $C_{(5)}$); 18.30 ppm (CH_3).

2,4-Dimethyl-1,2,3,4-tetrahydroquinolin-1-one (XVIII). Yield was 0.20 g (32%), mp 73-74°C (according to [10] mp 72-73°C). IR spectrum: 1685 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.80 (1H, d.d, ^4J = 1.5, ^3J = 8.0 Hz, 8-H); 7.29 (1H, d.d.d, ^4J = 1.5, ^3J = 8.0, ^3J = 7.8 Hz, 6-H); 6.64 (1H, d.d.d, ^4J = 1.5, ^3J = 8.0, ^3J = 7.8 Hz, 7-H); 6.60 (1H, d.d, ^4J = 1.5, ^3J = 8.0 Hz, 5-H); 3.35 (1H, d.d, ^2J = 12.0, ^3J = 7.2 Hz, CH<u>H</u>$_{eq}$N); 3.13 (1H, d.d, ^2J = 12.0, ^3J =

11.6 Hz, CH$\underline{H}_{ax}$N); 2.90 (3H, s, CH_3N); 2.67 (1H, d.q, ^3J = 6.8, ^3J = 11.6 Hz, 2-CH); 1.15 ppm (3H, d, ^3J = 6.8 Hz, CH($\underline{CH}_3$)CO). ^{13}C NMR spectrum ($CDCl_3$): 196.40 ($C_{(1)}$); 152.38 ($C_{(4a)}$); 135.10 ($C_{(6)}$ or $C_{(8)}$); 128.28 ($C_{(6)}$ or $C_{(8)}$); 119.43 ($C_{(8a)}$); 117.02 ($C_{(5)}$ or $C_{(7)}$); 113.00 ($C_{(5)}$ or $C_{(7)}$); 58.05 ($C_{(3)}$); 41.19 ($C_{(2)}$); 39.22 (NCH_3); 12.50 ppm (CH$\underline{CH}_3$).

5-Methyl-1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolin-6-one (XIX). Yield was 0.18 g (30%), mp 87-89°C. IR spectrum: 1675 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.42 (1H, d, ^3J = 8.0 Hz, 7-H); 7.10 (1H, d, ^3J = 7.8 Hz, 9-H); 6.58 (1H, d.d, ^3J = 7.8, ^3J = 8.0 Hz, 8-H); 3.46 (1H, d.d, ^2J = 13.4, ^3J = 8.6 Hz, 2-$\underline{CH}$H); 3.29 (1H, d.d, ^2J = 10.8, ^3J = 5.2 Hz, 4-CH$\underline{H}_{eq}$); 3.12 (1H, d.d, ^2J = 17.5, ^3J = 8.6 Hz, 2-$\underline{CH}$H); 2.95 (2H, m, 1-CH_2); 2.85 (1H, d.d, ^2J = 10.8, ^3J = 11.2 Hz, 4-CH$\underline{H}_{ax}$); 2.64 (1H, m, 5-CH); 1.15 ppm (3H, d, ^3J = 6.8 Hz, CH_3). ^{13}C NMR spectrum ($CDCl_3$): 195.67 ($C_{(6)}$); 157.82 ($C_{(3a)}$); 130.96 ($C_{(9a)}$); 129.23 ($C_{(7)}$ or $C_{(9)}$); 123.71 ($C_{(7)}$ or $C_{(9)}$); 118.71 ($C_{(8)}$); 115.84 ($C_{(6a)}$); 55.26 ($C_{(2)}$ or $C_{(4)}$); 54.87 ($C_{(2)}$ or $C_{(4)}$); ($C_{(2)}$); 41.69 ($C_{(5)}$); 28.91 ($C_{(1)}$); 13.25 ppm (CH_3). Found, %: C 76.78; H 6.99. $C_{12}H_{13}NO$. Calculated, %: C 77.00; H 6.95.

2-Methyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-1-one (XX). Yield was 0.22 g (33%), mp 96-98°C. IR spectrum: 1680 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.68 (1H, d, ^3J = 8.0 Hz, 10-H); 7.05 (1H, d, ^3J = 7.8 Hz, 8-H); 6.57 (1H, d.d, ^3J = 7.8, ^3J = 8.0 Hz, 8-H); 3.29 (1H, d.d, ^2J = 11.9, ^3J = 5.5 Hz, 3-CH$\underline{H}_{eq}$); 3.24 (1H, m, 5-$\underline{CH}$H); 3.12 (1H, m, 5-$\underline{CH}$H); 3.07 (1H, d.d, ^2J = 11.9, ^3J = 11.8 Hz, 3-CH$\underline{H}_{ax}$); 2.65 (1H, m, 2-CH); 2.01 (2H, m, 6-CH_2); 1.17 ppm (3H, d, ^3J = 6.9 Hz, CH_3). ^{13}C NMR spectrum ($CDCl_3$): 196.43 ($C_{(1)}$); 149.17 ($C_{(4a)}$); 134.28 ($C_{(8)}$ or $C_{(10)}$); 126.04 ($C_{(8)}$ or $C_{(10)}$); 123.48 ($C_{(7a)}$ or $C_{(10a)}$); 118.37 ($C_{(7a)}$ or $C_{(10a)}$); 116.50 ($C_{(9)}$); 56.65 ($C_{(3)}$); 49.92 ($C_{(5)}$); 40.81 ($C_{(2)}$); 26.51 ($C_{(7)}$); 21.47 ($C_{(6)}$); 12.53 ppm (CH_3). Found, %: C 76.76; H 7.47. $C_{13}H_{15}NO$. Calculated, %: C 77.58; H 7.51.

4-Phenyl-1,2,3,4-tetrahydrobenzo[f]quinolin-1-one (XXII). Yield was 0.22 g (26%), mp 137-139°C. IR spectrum: 1655 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 9.43 (1H, d, ^3J = 8.3 Hz, 10-H); 7.55-7.15 (9H, m); 6.70 (1H, d, ^3J = 8.8 Hz, 5-H); 3.88 (2H, t, ^3J = 7.2 Hz, 3-CH_2); 2.83 ppm (2H, t, ^3J = 7.2 Hz, 2-CH_2). ^{13}C NMR spectrum ($CDCl_3$): 193.90 ($C_{(1)}$); 152.67 ($C_{(4a)}$); 145.92 ($C_{(1a)ph}$); 135.82, 129.51, 128.15, 126.53, 125.71, and 123.64 (6C, 6-CH_{arom}); 132.61 ($C_{(10b)}$); 130.06 (2C, $C_{(3)}$, $C_{(5)ph}$); 127.77 ($C_{(6a)}$ or $C_{(10a)}$); 126.26 (2C, $C_{(2)}$, $C_{(6)ph}$); 125.68 ($C_{(6a)}$ or $C_{(10a)}$); 117.46 ($C_{(5)}$); 51.08 ($C_{(3)}$); 39.38 ppm ($C_{(2)}$). Found, %: C 82.90; H 5.64. $C_{19}H_{15}NO$. Calculated, %: C 83.49; H 5.53.

4-Phenyl-1,2,3,4-tetrahydrobenzo[f]quinolin-3-one (XXIII). Yield was 0.23 g (27%), mp 166-167°C. IR spectrum: 1690 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.90 (1H, d, ^3J = 8.4 Hz, 7-H or 10-H); 7.67 1H, d, ^3J = 8.0 Hz, 7-H or 10-H); 7.50-7.30 (6H, m); 7.19 (2H, d, ^3J = 8.5 Hz, 2-H, 6-H_{ph}); 6.57 (1H, d, ^3J = 8.8 Hz, 5-H); 3.36 (2H, t, ^3J = 7.8 Hz, ^{1}-CH_2); 2.85 ppm (2H, t, ^3J = 7.8 Hz, 2-CH_2). ^{13}C NMR spectrum ($CDCl_3$): 170.00 ($C_{(3)}$); 138.72 ($C_{(4a)}$ or $C_{(1)ph}$); 138.69 ($C_{(4a)}$ or $C_{(1)ph}$); 131.01 ($C_{(6a)}$ or $C_{(10a)}$); 130.06 ($C_{(6a)}$ or $C_{(10a)}$); 129.77 (2C, $C_{(3)}$, $C_{(5)ph}$); 128.50, 128.08, 127.38, 126.97, 124.61, and 122.83 (6C, 6-CH_{arom}); 119.22 ($C_{(10b)}$); 117.76 ($C_{(5)}$); 31.77 ($C_{(2)}$); 20.95 ppm ($C_{(1)}$). Found, %: C 84.05; H 5.85. $C_{16}H_{13}NO$. Calculated, %: 83.49; H 5.53.

1-(1-Naphthyl)-1,2,3,4-tetrahydroquinolin-4-one (XXV). Yield was 0.30 g (30%), mp 85-87°C. IR spectrum: 1685 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$): 7.97 (2H, m, 5-H, 5'-H); 7.92 (1H, d, ^3J = 8.0 Hz, 8'-H); 7.85 (1H, d, ^3J = 8.3 Hz, 4'H); 7.55-7.49 (2H, m, 3'-H, 7'-H); 7.08 (1H, t, ^3J = 8.2 Hz, 6'-H); 7.38 (1H, d, ^3J = 8.0 Hz, 2'-H); 7.08 (1H, t, ^3J = 8.4 Hz, 7-H); 6.72 (1H, t, ^3J = 8.2 Hz, 6-H); 6.08 (1H, d, ^3J = 8.4 Hz, 8-H); 4.00 (1H, m, N$\underline{CH}$H); 3.83 (1H, m, N$\underline{CH}$H); 3.00 (1H, m, $\underline{CH}$HCO); 2.84 ppm (1H, m, $\underline{CH}$HCO). ^{13}C NMR spectrum ($CDCl_3$): 193.33 ($C_{(4)}$); 152.10 ($C_{(8a)}$); 142.37 ($C_{(1')}$); 134.92, 128.62, 127.76, 127.70, 126.85, 126.62, 126.36, 124.24, and 123.04 (9C, CH_{arom}); 134.87 ($C_{(4a)}$); 129.39 ($C_{(4'a)}$ or $C_{(8'a)}$); 122.63 ($C_{(6a)}$ or $C_{(10a)}$); 117.71 ($C_{(5)}$ or $C_{(7)}$); 115.78 ($C_{(5)}$ or $C_{(7)}$); 50.99 ($C_{(2)}$); 38.48 ppm ($C_{(3)}$). Found, %: C 82.85; H 5.77. $C_{16}H_{13}NO$. Calculated, %: C 83.49; H 5.53.

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