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Superelectrophilic Activation of 8-Hydroxyquinoline in Acid Media and Its Reactions with Weak Nucleophiles*, **

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Abstract—According to the ^{1}H and ^{13}C NMR data, 5-azonia-4-hydroxynaphthalen-1-onium cation, generated by protonation of 8-hydroxyquinoline in the system CF_3SO_3H–SbF_5, reacts with cyclohexane to give diprotonated 5,6,7,8-tetrahydroquinolin-8-one. Further reaction of the latter with cyclohexane yields 5,6,7,8-tetrahydroquinolinium ion. The reaction of 8-hydroxyquinoline with benzene in the presence of aluminum bromide or chloride gives 6-phenyl-5,6,7,8-tetrahydroquinolin-8-one and product of its intramolecular cyclization, 11-hydroxy-6,11-dihydro-6,11-methano-5*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridine. The effect of the protonated nitrogen atom on the electrophilicity of dications is discussed.

We previously showed that compounds of the 1- and 2-naphthol series in the presence of strong protic or Lewis acids undergo superelectrophilic activation through formation of C,C-diprotonated species or structurally similar protonated complexes [2, 3]. Likewise, α,β-unsaturated ketones undergo protonation at the oxygen and carbon atoms or give rise to the corresponding complexes, depending on the acid system [4]. As a result, the above substrates can be involved in reactions with such weak nucleophiles as alkanes and arenes. The reactions with alkanes gave products of selective ionic hydrogenation, and with arenes arylation products were obtained [2, 3, 5–7].

Electrophilic activation of quinoline derivatives in acid media have not been studied previously. The present work was aimed at establishing pathways of electrophilic activation of 8-hydroxyquinoline (**I**) in protic acids and in the presence of Lewis acids with the goal of involving compound **I** in reactions with cyclohexane and benzene. The choice of quinoline **I** as substrate was dictated by the presence of several basic centers in its molecule, which provides the possibility for polyprotonation and formation of intermediates with enhanced electrophilicity.

Electrophilic activation pathways of quinoline **I** in protic acids at 25°C were studied by ^{1}H and ^{13}C NMR spectroscopy. Dissolution of 8-hydroxyquinoline (**I**) in CF_3COOH (H_0 = –2.7 [8]) or CF_3SO_3H (H_0 = –14.1 [9]) leads to formation of 8-hydroxyquinolinium ion **II**. A different pattern was observed on dissolution of hydroxyquinoline **I** in the system CF_3SO_3H–SbF_5 (molar ratio 3.4 : 1). In this case, 5-azonia-4-hydroxynaphthalen-1-onium ion **III** is generated via protonation of both nitrogen and carbon atoms. Signals in the ^{1}H and ^{13}C NMR spectra of ion **III** were assigned using the ^{1}H–^{13}C correlation technique. The ^{1}H NMR spectrum of **III** contains a singlet at δ 5.25 ppm from the methylene protons and two broadened singlets at δ 13.7 and 13.8 ppm, which belong to the OH and NH^+ groups. The ^{13}C chemical shifts of dication **III** appreciably differ from the corresponding values found for its closest structural analog, 4-hydroxynaphthalen-1-onium ion. This concerns mainly the C^2 and C^6 atoms (cf. [10, 11]).

Our study of the reactivity of cation **II** has shown its inertness toward cyclohexane and benzene. Both nucleophiles failed to react with **II** in CF_3SO_3H at 25°C over a period of 5 and 24 h, respectively. By contrast, dication **III** smoothly reacted with cyclohexane (the reaction of **III** with benzene resulted in formation of a number of unidentified products). Addition of cyclohexane to an acid solution of dication **III** (molar ratio 8-hydroxyquinoline–cyclohexane 1 : 1.4) in 10 min quantitatively yielded the

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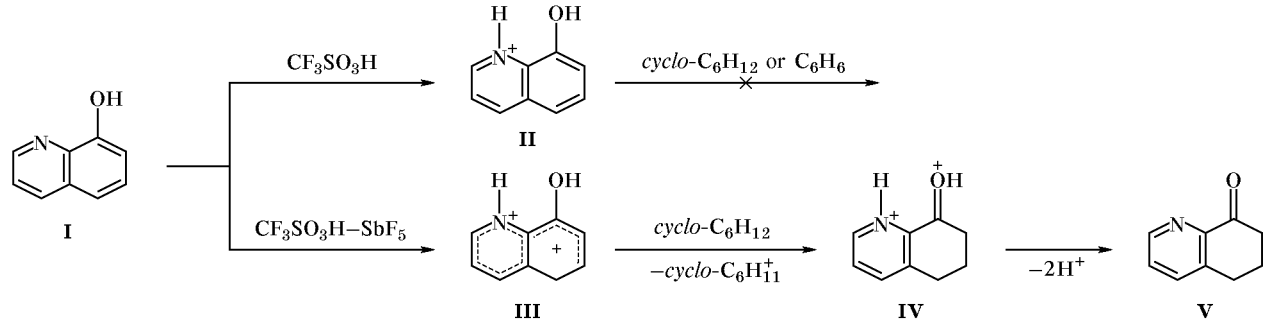
Scheme 1.



corresponding ionic hydrogenation product, O,N-diprotonated 5,6,7,8-tetrahydroquinolin-8-one (**IV**) (Scheme 1).

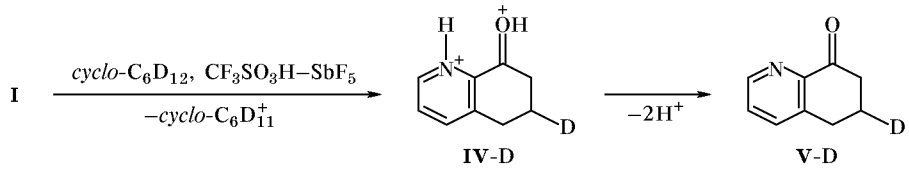
Dication **IV** shows in the ^{1}H NMR spectrum signals in the region δ 2.7–3.9 ppm, belonging to three methylene groups, and a singlet at δ 13.8 ppm from the NH^+ proton. No HO^+ signal was observed due to fast exchange with the medium; however, the presence of an oxonium moiety in **IV** can be assumed taking into account the known [8] ability of ketones to undergo complete protonation in strongly acidic media. After appropriate treatment of the reaction mixture, we isolated 5,6,7,8-tetrahydroquinolin-8-one (**V**) (Scheme 1).

The possibility for hydride ion transfer from cyclohexane to dication **III** was confirmed by studying the regioselectivity of the process. For this purpose, quinoline **I** was brought into reaction with cyclohexane-d_{12}. On the basis of the known data [10] on charge distribution in naphthalenonium ions, we expected that dication **III** will attack cyclohexane molecule by the C^6 atom; as a result, the reduction product should contain deuterium just at C^6. In fact, addition of cyclohexane-d_{12} to an acid solution of **III**, followed by keeping of the mixture for 50 min at 25°C, resulted in appearance in the ^{1}H NMR spectrum of signals from O,N-diprotonated 6-deutero derivative **IV**-D. After appropriate treatment, we isolated a mixture of compound **I** and 6-[^{2}H]-5,6,7,8-tetrahydroquinolin-8-one (**V**-D) at a ratio of 1.6:1 (Scheme 2). In the ^{1}H NMR spectrum of **IV**-D we observed a multiplet signal from 6-H at δ 2.73 ppm and doublet signals from 7-H and 5-H at δ 3.68 and 3.93 ppm, respectively. The spectrum of the mixture (after treatment) contained signals belonging to hydroxyquinoline **I** and also a multiplet at δ 2.2 ppm (6-H) and two doublets at δ 2.81 and 3.04 ppm (7-H and 5-H, respectively), belonging to tetrahydroquinoline **V**-D. Compound **V**-D showed in the ^{2}H NMR spectrum a multiplet at 2.1 ppm (3-D). The C^6 signal of **V**-D in the ^{13}C NMR spectrum was split due to coupling with deuterium.

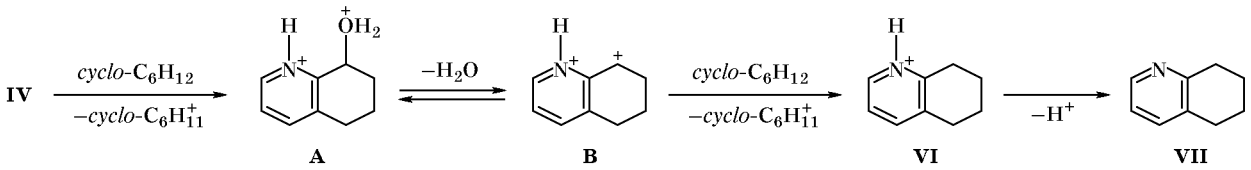
The above reaction of dication **III** with cyclohexane is an example of reactions of naphthalenonium ion with weak nucleophiles. It should be noted that, according to our earlier data [2, 3], 4-hydroxynaphthalen-1-onium ions exhibit no superelectrophilic properties and do not react with weak nucleophiles (as was shown using reactions of 1-naphthol derivatives with arenes and alkanes). Our results lead us to presume that the high electrophilicity of dication **III** is determined by participation of the protonated nitrogen atom in the π-electron system.

Dication **IV** formed by ionic hydrogenation and subsequent protonation also shows superelectrophilic properties and is capable of abstracting hydride ion from alkane. After addition of excess cyclohexane to an acid solution of dication **IV** and keeping of the reaction mixture for 80 min at 25°C, the ^{1}H NMR data indicated quantitative formation of 5,6,7,8-tetrahydroquinolinium ion (**VI**). By appropriate treatment of the mixture we isolated 5,6,7,8-tetrahydroquinoline (**VII**) (Scheme 3).

Scheme 2.



Scheme 3.



Obviously, the formation of cation **VI** is preceded by reduction in acid medium of the carbonyl group to hydroxy to give dication **A**. The latter or product of its dehydration (dication **B**) abstracts hydride ion from cyclohexane, affording the final reduction product, cation **VI**. However, we failed to detect dications **A** and **B** by NMR spectroscopy. Some notes should be given on participation of dications **A** and **B** in the hydride transfer process. According to published data [12], neither ketones nor alcohols react with alkanes under conditions ensuring their complete protonation with formation of oxonium ions [12]. In particular, tetrahydronaphthalenones do not react with arenes and alkanes in fairly acidic media [2, 3, 5]. Ionic hydrogenation of ketones with alkanes occurs only in media with increased acidity, where additional protonation (protosolvation) is assumed to be possible. The reaction stops at the stage of formation of alcohol [13]. The subsequent ionic hydrogenation of alcohol was reported only for methanol by the action of sodium tetrahydridoborate in trifluoromethanesulfonic acid [14]. These findings prompted the researchers to postulate additional protonation (protosolvation) of oxonium cations formed initially from alcohols [12].

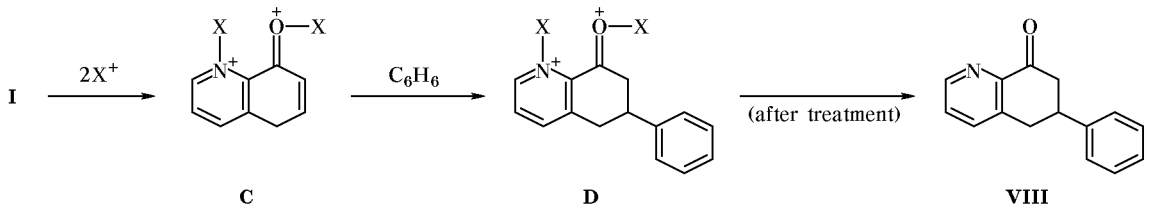
Presumably, superelectrophilic activation of dications **IV** and **A**, which is required for the reaction with alkane to occur, is achieved due to the presence of nearby protonated nitrogen atom rather than due to additional protonation of oxonium ion. Activating effect of protonated nitrogen was recently reported for the reactions of 3-formylpyridinium ion and oxopiperidine derivatives with arenes in trifluoromethanesulfonic acid [15]. An analogous activation of cationic center with respect to arenes was achieved through assistance by other charged or neutral electron-acceptor groups, e.g., CCl_3 or CF_3 [16].

With the goal of estimating electrophilic properties of dications **III** and **IV** and also of the assumed short-lived intermediates **A** and **B** on a quantitative level, we performed MNDO quantum-chemical calculations of some their parameters (the complete results of MNDO and 3-21G calculations of dications **III**, **IV**, **A**, and **B** will be reported elsewhere). The calculated energies of the lowest unoccupied molecular orbitals (ε_{LUMO}) of dications **III**, **IV**, **A**, and **B** turned out to be fairly low: –10.83, –11.04, –9.57, and –11.79 eV, respectively. These values approach those found for C,C-diprotonated 1- and 2-naphthol derivatives which showed superelectrophilic properties toward alkanes and arenes [2, 3, 5]. Taking into account the above data and also the inertness of the corresponding carbon analogs with respect to benzene and alkanes, we can conclude that just the presence of protonated nitrogen atom is reponsible for superelectrophilic properties of dications **III**, **IV**, **A**, and **B**.

Superelectrophilic activation of quinoline **I** toward another weak nucleophile, benzene, was achieved by the action of Lewis acids. The reaction of quinoline **I** with benzene occurred in the presence of excess aluminum chloride or bromide. By stirring a mixture of 8-hydroxyquinoline (**I**), benzene, and aluminum bromide at a molar ratio of 1:10:5 for 24 h at 20°C (the mixture was preliminarily saturated with hydrogen bromide) we obtained 6-phenyl-5,6,7,8-tetrahydroquinolin-8-one (**VIII**) in 68% yield (Scheme 4).

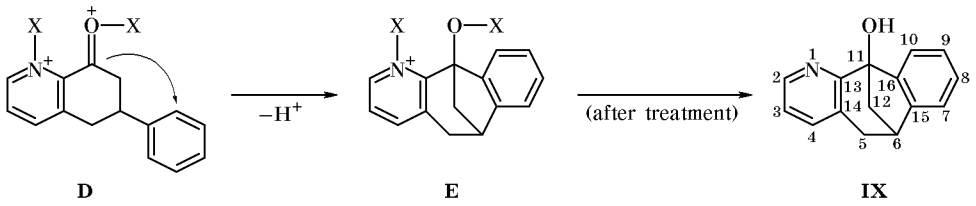
The regioselectivity of this reaction may be explained on the assumption that quinoline **I** is activated through formation of intermediate **C**, a structural

Scheme 4.



X = $Al_mBr_{3m}^-$, $Al_mCl_{3m}^-$, H.

Scheme 5.



D **E** **IX**

X = $Al_mBr_{3m}^-$, $Al_mCl_{3m}^-$, H.

analog of dication **III**. The reaction of **C** with benzene leads to formation of another intermediate **D**, and subsequent treatment of the reaction mixture yields final product **VIII**.

We previously studied reactions of 1-naphthol derivatives with benzene and found that aluminum halide complexes with the corresponding keto forms are not active intermediates therein [2, 3, 17]. Therefore, superelectrophilic properties of intermediate **C** may be attributed to its dicationic nature.

When the reaction of hydroxyquinoline **I** with benzene in the presence of aluminum bromide was performed for 75 h with subsequent heating for 5 h under reflux, we isolated 85% of 11-hydroxy-6,11-dihydro-6,11-methano-5*H*-benzo[5,6]cyclohepta[1,2-*b*]-pyridine (**IX**) (Scheme 5). The same product was obtained when the reaction mixture was perliminarily saturated with hydrogen bromide. In this case the reaction was complete in 300 h at 20°C or in 20 h under reflux (yield 63 and 54%, respectively). The reaction of **I** with benzene in the presence of excess aluminum chloride instead of bromide required 40 h under reflux, and the yield of **IX** was 43%.

As shown in Scheme 5, primary intermediate **D** undergoes intramolecular cyclization to give complex **E**. The possibility of such cyclization in acid medium (X = H) was proved by special experiment. Tetrahydroquinoline **VIII** was dissolved in CF_3SO_3H, and the solution was kept for 45 min at 25°C to obtain cation **E** (X = H); after appropriate treatment, we isolated compound **IX** in quantitative yield.

The ability of oxonium ions to react with benzene (either inter- or intramolecularly) was reported in [12, 15]. These reactions usually require strongly acidic media which ensure additional protonation (protosolvation). The intramolecular reaction in intermediate **D** is likely to be facilitated by complex formation (protonation) at the nitrogen atom.

Thus, the results of our study allowed us to extend the number of stable carbocations exhibiting superelectrophilic properties due to additional activation by the second cationic center [2–5, 12, 15]. From the preparative viewpoint, the reaction of 8-hydroxyquinoline (**I**) with benzene provides a convenient procedure for synthesizing aryl-substituted tetrahydroquinolinones and compounds like **IX**. Its advantage is accessibility of initial compounds. Known tetrahydroquinolinones are few in number because of the lack of general procedures for their synthesis. We have found no analogs of compound **IX** in the literature.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 spectrometer operating at 250.13 and 62.9 MHz, respectively. The ^2H NMR spectrum was obtained on a Bruker AM-400 instrument (61.42 MHz). The chemical shifts of cationic species were measured relative to $(CH_3)_4N^+ BF_4^-$ (δ 3.2 ppm and δ_C 54 ppm), and those of neutral compounds, relative to $CDCl_3$ (δ 7.28 ppm and δ_C 76.9 ppm). The IR spectra were recorded on a Vector-22 spectrophotometer in KBr. The molecular weights were determined by high-resolution mass spectrometry using a Finnigan MAT MS 8200 mass spectrometer. The progress of reactions was monitored by TLC on DC-Alufolien Kieselgel 60 F254 plates (Merck) with benzene–acetone as eluent.

We used trifluoromethanesulfonic acid, $AlCl_3$, and 8-hydroxyquinoline from Merck, chemically pure trifluoroacetic acid, and $AlBr_3$ and benzene of analytical grade. Cyclohexane-d_{12} (from *Izotop*) contained 99.5% of deuterium. Technical-grade SbF_5 was purified by distillation. The reactions in CF_3SO_3H and in the system CF_3SO_3H–SbF_5 were carried out in NMR ampules. MNDO quantum-chemical calculations with full geometry optimization were performed using MOPAC-7 software [18].

8-Hydroxyquinolinium ion (II). Compound **I**, 40 mg (0.26 mmol), was dissolved at 25°C in 0.7 g (4.7 mmol) of trifluoroacetic acid. A solution containing cation **II** was thus obtained. ^1H NMR spectrum, δ, ppm: 7.57 d.d (1H, 7-H, J = 7.11, 1.9 Hz), 7.77 m (2H, 5-H, 6-H), 7.99 d.d (1H, 3-H, J = 8.53, 5.69 Hz), 8.94 d.d (1H, 2-H, J = 7.58, 5.69 Hz),

9.00 d (1H, 4-H, J = 8.53 Hz), 13.6 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 115.76 (C^7), 118.6 (C^5), 120.01 (C^3), 127.42 (C^9), 128.97 (C^{10}), 130.1 (C^6), 140.62 (C^2), 144.72 (C^8), 146.46 (C^4).

5-Azonia-4-hydroxy-1*H*$^+$-naphthalenium ion (III). A 0.27-g (1.25-mmol) portion of SbF_5 was added at 25°C to a solution of 19 mg (0.13 mmol) of hydroxyquinoline **I** in 0.63 g (4.2 mmol) of trifluoromethanesulfonic acid. Quantitative formation of ion **III** was observed. ^{1}H NMR spectrum, δ, ppm: 5.25 s (2H, 1-H), 8.05 d (1H, 3-H, J = 8.53 Hz), 8.78 br.s (1H, 7-H), 9.28 d (1H, 2-H, J = 8.53 Hz), 9.35 br.s (1H, 6-H), 9.48 br.s (1H, 8-H), 13.66 br.s and 13.8 br.s (1H each, OH and NH). ^{13}C NMR spectrum, δ_C, ppm: 37.95 (C^1), 123.69 (C^3), 130.79 (C^9), 132.54 (C^7), 146.29 (C^8), 147.88 (C^2), 148.61 (C^{10}), 181.54 (C^4), 183.71 (C^6).

O,N-Diprotonated 5,6,7,8-tetrahydroquinolin-8-one (IV). Cyclohexane, 15 mg (0.18 mmol), was added at 25°C to a solution of ion **III**, prepared by the above procedure. After 10 min, dication **III** was completely converted into dication **IV**. ^{1}H NMR spectrum, δ, ppm: 2.73 m (2H, 6-H), 3.68 t (2H, 7-H, J = 6.5 Hz), 3.93 t (2H, 5-H, J = 5.8 Hz), 8.72 d.d (1H, 3-H, J = 9, 7 Hz), 9.01 d (1H, 4-H, J = 9 Hz), 9.18 d (1H, 2-H, J = 7 Hz), 13.4 s (1H, NH). The mixture was poured onto ice and washed with diethyl ether, and the aqueous phase was neutralized with $NaHCO_3$. The product was extracted into diethyl ether, the extract was dried over $MgSO_4$, and the solvent was removed to obtain 13 mg (65%) of tetrahydroquinolinone **V**. IR spectrum: ν(C=O) 1702 cm^{-1} (cf. [19]). ^{1}H NMR spectrum, δ, ppm: 2.21 m (2H, 6-H), 2.82 t (2H, 7-H, J = 6.54 Hz), 3.05 t (2H, 5-H, J = 5.81 Hz), 7.39 d.d (1H, 3-H, J = 7.27, 3.28 Hz), 7.67 d (1H, 4-H, J = 7.27 Hz), 8.72 d (1H, 2-H, J = 3.28 Hz) (cf. [19]). ^{13}C NMR spectrum, δ_C, ppm: 22.49 (C^6), 28.97 (C^5), 39.49 (C^7), 126.86 (C^3), 137.5 (C^4), 140.62 (C^{4a}), 147.99 (C^{8a}), 148.96 (C^2), 196.7 (C^8).

Reaction of dication III with cyclohexane-d_{12}. Cyclohexane-d_{12}, 16 mg (0.17 mmol), was added to a solution of 19 mg (0.13 mmol) of compound **I** and 0.27 g (1.25 mmol) of SbF_5 in 0.63 g (4.2 mmol) of CF_3SO_3H. After 50 min, the ^{1}H NMR spectrum of the resulting solution contained signals of dications **III** and **IV**-D. ^{1}H NMR spectrum of **IV**-D, δ, ppm: 2.73 m (1H, 6-H), 3.68 d (2H, 7-H, J = 5.21 Hz), 3.93 d (2H, 5-H, J = 7.81 Hz). The mixture was poured onto ice and treated as described above to obtain 15 mg of a mixture of quinoline **I** and tetrahydroquinolinone **V**-D at a ratio of 1.6 : 1. ^{1}H NMR spectrum of **V**-D, δ, ppm: 2.2 m (1H, 6-H), 2.81 d (2H, 7-H, J = 6.54 Hz), 3.04 d (2H, 5-H, J = 5.81 Hz). ^{2}D NMR spectrum, δ, ppm: 2.1 m (6-D). ^{13}C NMR spectrum, δ_C, ppm: 22.14 (C^6, $J_{C,D}$ = 20.23 Hz), 28.87 (C^5), 39.37 (C^7).

5,6,7,8-Tetrahydroquinoline (VII). To the solution of dication **IV**, prepared by the above procedure, we added an additional 50-mg (0.6-mmol) portion of cyclohexane. The mixture was kept for 80 min at 25°C with occasional shaking. The transformation of dication **IV** into tetrahydroquinolinium ion **VI** was observed. ^{1}H NMR spectrum, δ, ppm: 2.05 m (4H, 6-H, 7-H), 3.05 t (1H, 5-H, J = 5 Hz), 3.17 t (1H, 8-H, J = 6 Hz), 7.79 t (1H, 3-H, J = 8 Hz), 8.34 m (2H, 2-H, 4-H), 11.71 br.s (1H, NH). The mixture was treated as described above to isolate 16 mg (90%) of tetrahydroquinoline (**VII**). ^{1}H NMR spectrum, δ, ppm: 1.85 m (4H, 6-H, 7-H), 2.78 t (2H, 5-H, J = 5.81 Hz), 2.94 t (2H, 8-H, J = 5.45 Hz), 7.04 d.d (1H, 3-H, J = 8.7, 5 Hz), 7.36 d (1H, 4-H, J = 8.7 Hz), 8.36 d (1H, 2-H, J = 5 Hz) (cf. [20]). ^{13}C NMR spectrum, δ, ppm: 22.52 (C^6), 22.9 (C^7), 28.6 (C^5), 32.29 (C^8), 120.72 (C^3), 132.17 (C^{10}), 136.66 (C^4), 146.53 (C^2), 157.20 (C^9) (cf. [20]).

6-Phenyl-5,6,7,8-tetrahydroquinolin-8-one (VIII). 8-Hydroxyquinoline (**I**), 2 g (14 mmol), was added to a solution of 20 g (75 mmol) of aluminum bromide in 18 g (230 mmol) of benzene, and the solution was saturated with hydrogen bromide [the weight of the mixture increased by 2.5 g (31 mmol of HBr)]. The mixture was kept for 24 h at 20°C and poured onto ice, 40 ml of concentrated hydrochloric acid was added, the aqueous phase was separated and washed with diethyl ether, and a 10% solution of NaOH was added to make it strongly alkaline. The precipitate was filtered off and dissolved in benzene, and the solution was filtered through a layer of Al_2O_3 and evaporated. The residue was recrystallized from a 1 : 2 mixture of benzene with petroleum ether (bp 70–100°C) to obtain 2.1 g (68%) of compound **VIII** with mp 138–139°C. IR spectrum: ν(C=O) 1697 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.8–3.3 m (4H, 5-H, 7-H), 3.4–3.6 m (1H, 6-H), 7.22–7.35 m (6H, 3-H, H_{arom}), 7.65 d (1H, 4-H, J = 7.8 Hz), 8.69 d (1H, 2-H, J = 4.5 Hz). ^{13}C NMR spectrum, δ, ppm: 36.64 (C^5); 40.11 (C^6); 46.07 (C^7); 126.27, 126.88, 126.91, 128.55 (C^6, C^o, C^m, C^p); 137.37 (C^4); 139.23, 142.27, 147.55 (C^i, C^{4a}, C^{8a}); 149.03 (C^2); 195.57 (C^8). Found: $[M]^+$ 223.09948. $C_{15}H_{13}NO$. Calculated: M 223.09971.

11-Hydroxy-6,11-dihydro-6,11-methano-5*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridine (IX). *a*. Hydroxyquinoline **I**, 2.3 g (16 mmol), was added to a solution

of 20 g (75 mmol) of aluminum bromide in 18 g (23 mmol) of benzene, and the resulting solution was saturated with hydrogen bromide until a gain in weight of 2.5 g (31 mmol of HBr) was attained. The mixture was kept for 75 h at 20°C, heated for 5 h under reflux, poured onto ice, and treated as described above in the synthesis of compound **VIII**. Recrystallization from ethanol gave 3 g (85%) of compound **IX** with mp 135–137°C. IR spectrum: ν(O–H) 3416 cm^{-1}. ^1H NMR spectrum, δ, ppm: 2.28 d (1H, 12-H, J = 10.2 Hz), 2.7–2.9 m (2H, 5-H, 12-H), 3.34 d.d (1H, 5-H, J = 17.1, 5.1 Hz), 3.58–3.65 m (1H, 6-H), 5.73 s (1H, OH), 7.0–7.4 m (6H, 3-H, 4-H, 7-H, 8-H, 9-H, 10-H), 8.28 d (1H, 2-H, J = 4.5 Hz) (the signals were assigned using ^1H COSY technique). ^{13}C NMR spectrum, δ_C, ppm: 33.99 (C^5); 37.63 (C^6); 46.76 (C^{10}); 79.42 (C^{11}); 119.71 (C^3); 122.76, 123.02 (C^8, C^9); 126.86, 127.37 (C^7, C^{10}); 128.29 (C^{14}); 136 (C^4); 143.07 (C^{15}); 144.64 (C^2); 149.9 (C^{16}); 160.42 (C^{13}). Found: $[M]^+$ 223.10014. $C_{15}H_{13}NO$. Calculated: M 223.09971.

b. Hydroxyquinoline **I**, 2 g (14 mmol), was added to a solution of 20 g (75 mmol) of aluminum bromide in 15.6 g (200 mmol) of benzene, and the mixture was kept for 300 h at 20°C. It was then treated by the procedure described above for compound **VIII** to obtain 1.95 g (63%) of product **IX**.

c. Compound **I**, 3 g (20 mmol), was added to a solution of 26 g (100 mmol) of aluminum bromide in 26 g (330 mmol) of benzene, and the resulting dispersion was stirred for 20 h on heating under reflux. After appropriate treatment, 2.5 g (54%) of compound **IX** was isolated.

d. A mixture of 0.5 g (3.5 mmol) of compound **I**, 5 g (38 mmol) of aluminum chloride, and 9 g (120 mmol) of benzene was stirred for 40 h on heating under reflux. After appropriate treatment, 0.33 g (43%) of compound **IX** was isolated.

e. Tetrahydroquinoline **VIII**, 15 mg (0.07 mmol), was added to 0.7 g (4.7 mmol) of trifluoromethanesulfonic acid. The solution was kept for 45 min at 25°C and poured onto ice. The aqueous phase was neutralized with a 10% aqueous solution of NaOH, and the precipitate was filtered off. Yield of compound **IX** 14 mg (93%).

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