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Superacid catalyzed reactions of 5-amino-1-naphthol with benzene and cyclohexane☆

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Abstract—5-Amino-1-naphthol undergoes ionic hydrogenation with cyclohexane and condenses with benzene when reacted in the presence of excess of aluminum halides to give 5-amino-1-tetralone (**10**) and 5-amino-3-phenyl-1-tetralone, respectively. In CF_3SO_3H as well as CF_3SO_3H–SbF_5 superacidic media 5-amino-1-naphthol gave N,C-diprotonated dication that can be considered as the superelectrophilic intermediate in the reactions with cyclohexane and benzene. The mechanism of these reactions is discussed.

1. Introduction

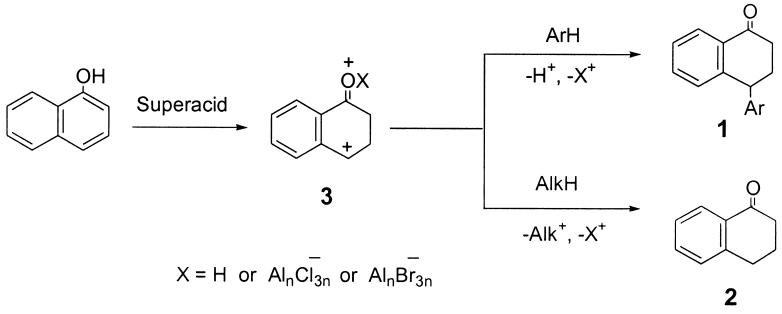
1-Naphthol undergoes condensation with arenes (ArH) and selective ionic hydrogenation with alkanes (AlkH) in Bronsted superacids or in the presence of excess of aluminum halides to give 4-aryl-1-tetralones[2] (**1**) and 1-tetralone[3] (**2**), respectively (Scheme 1). The key superelectrophilic[4] intermediates of these reactions was found to be dicationic species **3**, corresponding to C,C-diprotonation of the naphthalene ring system.[5]

Recently, we have found that the isomeric hydroxyquinolines react similarly with benzene and cyclohexane in the presence of aluminum halides.[1,6] The key intermediates of these reactions were shown to be superelectrophilic dicationic species derived from N,C-diprotonation of quinoline rings. For example, 5-hydroxyquinoline (**4**) condensed with benzene and underwent ionic hydrogenation with cyclohexane through dication **5** according to Scheme 2.

In continuation of our studies on superelectrophilic activation in strong acids, we now report investigation of the reactivity of 5-amino-1-naphthol (**6**) towards cyclohexane and benzene. Naphthol **6**, in principle, could be activated either similar to 1-naphthol (by C,C-diprotonation) or quinoline **4** (by N,C-diprotonation) to give respective products of the reactions.

2. Results and discussion

Protonation of 5-amino-1-naphthol **6** at room temperature in trifluoroacetic acid (H_o=−2.7) gave N-protonated



Scheme 1.

☆ Chemistry in superacids. Part 58. For part 57, see Ref. 1.

Keywords: aminonaphthol; superacid; superelectrophile; condensation; ionic hydrogenation.
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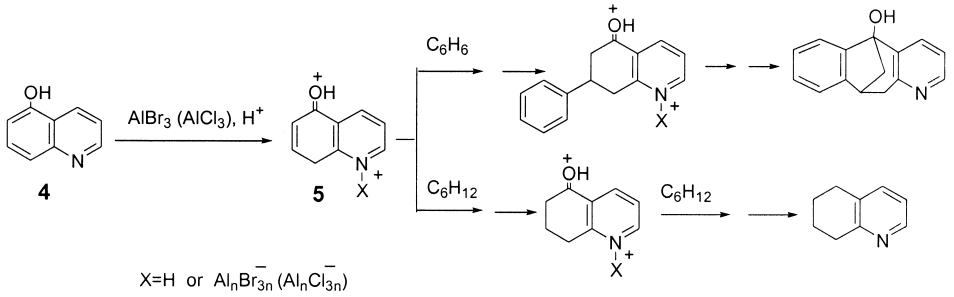
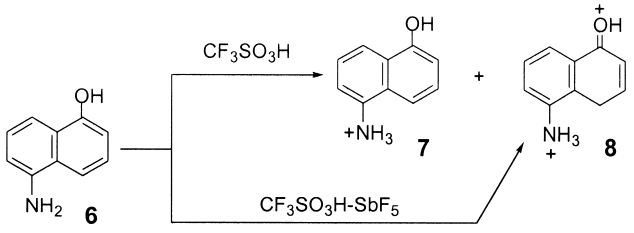


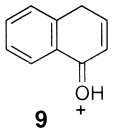
Scheme 2.



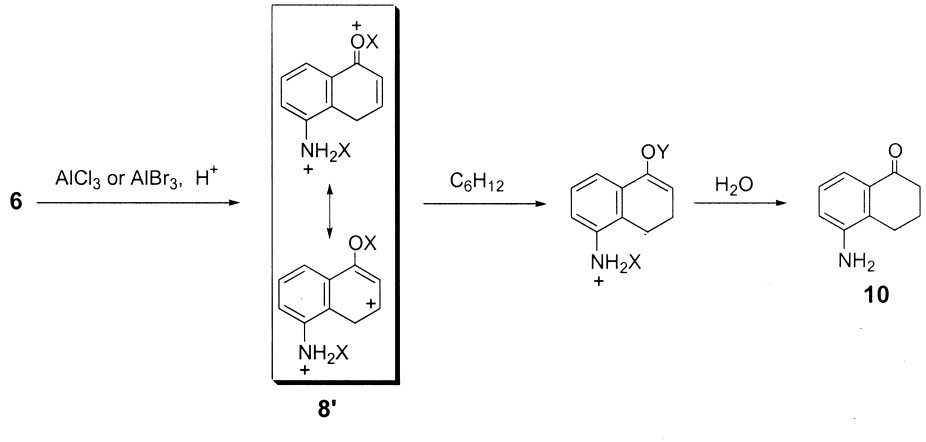
Scheme 3.

monocation **7**. In more acidic triflic acid (CF_3SO_3H, $H_o=-14.1$) **6** gave a mixture of ion **7** and N,C-diprotonated dication **8** in a molar ratio 1:1. After addition of SbF_5 to the reaction mixture, ion **7** was completely converted into the dication **8** (Scheme 3).

Dication **8** can be considered as a derivative of 4-hydroxy-1-naphthalenonium ion (**9**) which is known to be a weak electrophile and does not react with benzene and cyclohexane.[5b] On the other hand, **8** is an isoelectronic analog of reactive dication **5** containing charged nitrogen site attached to the π-system.

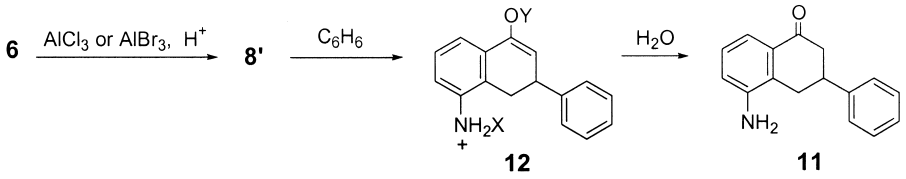


Previously, we have shown that a good correlation exists between experimentally found reactivity of electrophiles and their computed values of the energy level of lowest unoccupied molecular orbital (ε_{LUMO}) and atomic charge of reaction center (q_i).[1] For example, for dication **5** and monocation **9** the values of ε_{LUMO} are −11.988 and −7.277 eV and the values of q_i are 0.34 and 0.25, respectively.[1] To estimate the relative electrophilicity of dication **8**, we have calculated it's values of ε_{LUMO} and q_i. Calculations were carried out with the Gaussian 98 program system.[7] The geometry optimization was performed using the DFT[8] method at the B3LYP[9]/6-31G* level.[10] Vibrational frequency at the B3LYP/6-31G*//B3LYP/6-31G* level was used to characterize stationary point as minimum (number of imaginary frequency (NIMAG)=0). The atomic charge localized at the C^3 carbon atom and pendent hydrogen atom (q_3)[†] was obtained using natural bond orbital analysis (NBO) method.[11] Computed values of $\varepsilon_{LUMO}=-10.979$ eV and $q_3=0.3$ of the dication **8** show it to be a stronger electrophile than the monocation **9**, but somewhat weaker than dication **5**. The latter did not react with cyclohexane in Bronsted superacids at 25°C, but the corresponding quinoline **4** was shown to react slowly under the influence of $AlCl_3$ at 90°C (Scheme 2).[1] In agreement with theoretical calculations, **6** also does not react with cyclohexane in CF_3SO_3H or CF_3SO_3H–SbF_5 superacid media. However, reaction with cyclohexane, occurred with the use of four



Scheme 4.

[†] The numbering of the carbon atoms is given in accordance with the numbering in **6**.



Scheme 5.

molar excess of $AlCl_3$ or $AlBr_3$ at 80–110°C to give 5-amino-1-tetralone (**10**) in 70–80% yield (Scheme 4).[12] According to the Scheme 4, the preferred mechanism of the reaction includes generation of dicationic intermediate **8′**,[‡] followed by selective ionic hydrogenation with cyclohexane. As opposed to the reaction of **4**, in this case the reaction stops at the ketone stage.

The study of reactivity of **6** towards benzene showed that reaction also takes place in the presence of **4** molar excess of $AlCl_3$ (at 90°C) or $AlBr_3$ (at 20–60°C) to give 5-amino-3-phenyl-1-tetralone (**11**) in 15–40% yield (Scheme 5). It seems likely that the yield of the reaction corresponds to respective equilibrium concentrations of intermediate **12** (Scheme 5).

Increasing the reaction time did not change the ratio of **6** and **11**. Analogous behavior was found previously for **4**, which gave respective product of condensation with benzene in 15–30% yield.[1] This reflects similar electrophilicity of dications **5** and **8** and is in agreement with the results of theoretical calculations.

3. Conclusions

In summary, we have found that the 5-amino-1-naphthol **6** gives N,C-diprotonated dication **8** in CF_3SO_3H and CF_3SO_3H–SbF_5 superacidic media. Computed values of the ε_{LUMO} and charge of reaction center q_3 of the dication **8** indicate that the presence of protonated amino group significantly enhances its electrophilicity. Dication **8** can be regarded as a superelectrophilic intermediate in the reactions with benzene and cyclohexane. Ionic hydrogenation with cyclohexane can be conveniently employed in the synthesis of aminotetralone **10**. Reaction with benzene can be utilized for the synthesis of phenylated aminotetralones previously unknown in the literature.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were recorded on a 300 MHz superconducting NMR spectrometer. High-resolution mass spectrum was measured at the Southern California Mass Spectrometry Facility at the University of California at Riverside. Triflic acid was purchased from 3 M Co, trifluoroacetic acid, aluminum bromide, aluminum chloride were from Aldrich. Antimony pentafluoride was distilled under argon. Naphthol **6** (Aldrich) was recrystallized from aqueous ethanol. Elevated temperature reactions were carried out in 15 mL Ace Pressure Tubes (Aldrich).

4.2. Procedures for the protonation of 6

Samples of **6** (30 mg) were dissolved in trifluoroacetic and triflic acid in 5 mm NMR tubes at room temperature. Antimony pentafluoride was added to the triflic acid solution (molar ratio CF_3SO_3H/SbF_5=5:1) also at room temperature.

4.2.1. Ion 7. ^1H NMR (CF_3CO_2H) δ 6.47 (dd, J=7.7, 1.7 Hz, 1H), 6.78–6.85 (m, 3H), 6.98 (d, J=7.3 Hz, 1H), 7.68 (d, J=9.7 Hz, 1H), 8.39 (br s, 3H).[§] ^{13}C NMR (CF_3CO_2H) δ 111.2, 111.6, 121, 123.2, 123.5, 123.9, 125, 126.5, 128.1, 150.5.[¶]

4.2.2. Dication 8. ^1H NMR (CF_3SO_3H–SbF_5) δ 3.45 (s, 2H), 6.54 (d, J=10.8 Hz, 1H), 6.99 (t, J=9 Hz, 1H), 7 (br s, 3H), 7.17 (d, J=9 Hz, 1H), 7.73 (dt, J=10.8, 2.5 Hz, 1H), 7.81 (d, J=9 Hz, 1H), 11.18 (s, 1H). ^{13}C NMR (CF_3SO_3H–SbF_5) δ 31.8, 122.8, 125.8, 126.2, 130.5, 131.7, 133.6, 140.6, 171.5, 189.8.[¶]

4.2.3. 5-Amino-1-tetralone (10). To a suspension of $AlCl_3$ (0.34 g, 2.5 mmol) in cyclohexane (3 mL) was added **6** (0.1 g, 0.63 mmol). The resulting mixture was stirred at 110°C for 72 h,[13] followed by cooling and pouring the mixture over several grams of ice. The reaction mixture was made basic with concentrated NaOH and extracted with ether. The organic phase was dried over anhydrous $MgSO_4$. Concentration in vacuo provided a residue that was purified by column chromatography with CH_2Cl_2 to obtain **10** (0.071 g, 70%) as a crystalline product: mp 118–119°C (hexanes–$CHCl_3$), lit.[14] mp 119–120°C. ^1H NMR ($CDCl_3$) δ 2.17 (p, J=7 Hz, 2H), 2.63 (t, J=7 Hz, 2H), 2.69 (t, J=7 Hz, 2H), 3.72 (br s, 2H), 6.88 (d, J=8.07 Hz, 1H), 7.13 (t, J=8.07 Hz, 1H), 7.52 (d, J=8.07 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 22.2, 23.8, 38.5, 117.6, 119.7, 126.8, 128.6, 133.3, 144, 198.8.

To a suspension of $AlBr_3$ (0.67 g, 2.5 mmol) in cyclohexane

[‡] For structures **8′** (X=$AlCl_3^-$) and **8′** (X=$Al_2Cl_6^-$) the calculated values of q_3 are 0.28 and 0.3, respectively.

[§] Protons bonded to oxygen are not observed due to rapid proton exchange with the acid.

[¶] The chemical shifts were measured with reference to the signals of $(CD_3)_2CO$ as external standard (2.04 and 206 ppm in the ^1H and ^{13}C NMR spectra, respectively).

(3 mL) was added **6** (0.1 g, 0.63 mmol). The resulting mixture was stirred at 110°C for 40 h and after workup described above gave **10** (0.082 g, 81%).

4.2.4. 5-Amino-3-phenyl-1-tetralone (11). To a suspension of $AlCl_3$ (0.34 g, 2.5 mmol) in benzene (3 mL) was added **6** (0.1 g, 0.63 mmol). The resulting mixture was stirred at 90°C for 48 h, followed by cooling mixture was poured over several grams of ice. Reaction mixture was made basic with concentrated NaOH and extracted with ether. The organic phase was dried over anhydrous $MgSO_4$. Concentration in vacuo then provided the crude product, which was purified by column chromatography with $CHCl_3$ to give **11** (0.021 g, 14%) as a crystalline product: mp 107–108°C (cyclohexane–benzene). ^{1}H NMR ($CDCl_3$) δ 2.7–3.06 (m, 4H), 3.45 (tt, J=13, 5.3 Hz, 1H), 3.85 (br s, 2H), 6.93 (dd, J=8.07, 1.3 Hz, 1H), 7.19 (t, J=8.07 Hz, 1H), 7.26–7.42 (m, 5H), 7.58 (dd, J=8.07, 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 32.5, 40.3, 45, 117.8, 120.1, 126.8, 127.1, 127.1, 127.7, 128.9, 132.9, 143.6, 143.8, 198.1. HRMS $C_{16}H_{15}NO$ calcd 237.1154, found 237.1151.

To a solution of $AlBr_3$ (0.67 g, 2.5 mmol) in benzene (3 mL) was added **6** (0.1 g, 0.63 mmol). The resulting mixture was stirred at 60°C for 20 h, followed by workup described above to give **11** (0.055 g, 37%).[15]

Acknowledgements

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