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REACTIONS OF 2-, 3-, AND 4-QUINOLINOLS WITH CYCLOHEXANE AND BENZENE IN SUPERACIDS[1]

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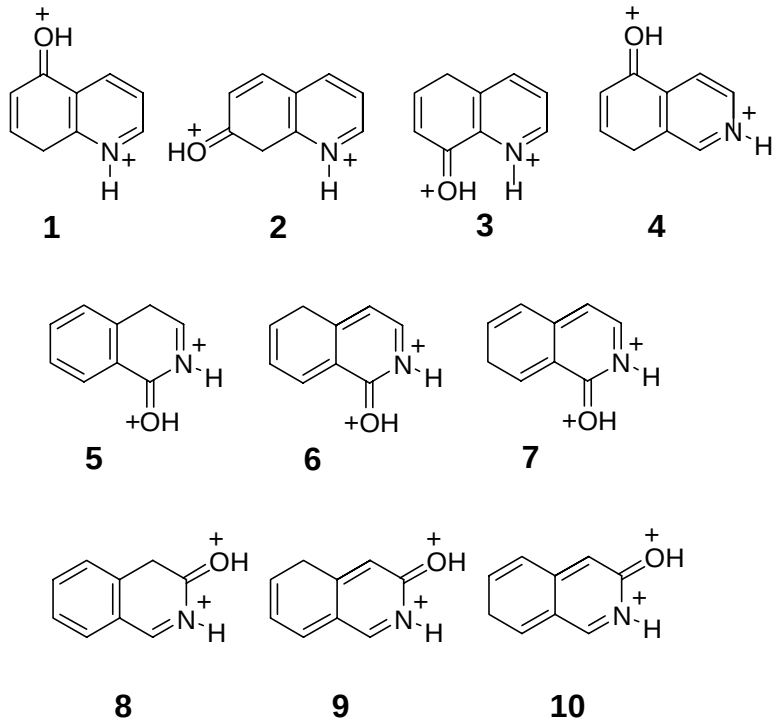
Dedicated to Professor Leo A. Paquette on the occasion of his seventieth birthday

Abstract – Isomeric 2-, 3- and 4-quinolinols (**11**-**13**) underwent selective ionic hydrogenation with cyclohexane in CF_3SO_3H-SbF_5 system to give 5,6,7,8-tetrahydro-2(1*H*)-quinolinone, 5,6,7,8-tetrahydro-3-quinolinol and 5,6,7,8-tetrahydro-4(1*H*)-quinolinone (**28**-**30**), respectively. When reaction was carried out in the presence of excess of aluminum chloride, **11** gave 3,4-dihydro-2(1*H*)-quinolinone (**31**), whereas **13** gave the product (**30**). Compounds (**11**) and (**13**) condense with benzene in the presence of aluminum halides producing phenyl substituted derivatives of **28**, **31** and **30** (products **32**-**34**), respectively. The mechanism of these and related reactions involving superelectrophilic dicationic intermediates is discussed.

INTRODUCTION

Recently, we have reported that the isomeric 5-, 7-, 8-quinolinols and 1-, 3-, 5-isoquinolinols react with cyclohexane and benzene in superacids or in the presence of an excess of aluminum halides offering a new and useful synthetic approach for the preparation of heterocyclic compounds.[2] The key intermediates of

these reactions were recognized to be *N*-protonated arenium ions of the heterocycles – *i.e.* superelectrophilic[3] dications (**1-10**) or the analogous complexes with aluminum halides.



The most stable dications such as **1-4** have been generated in CF_3SO_3H-SbF_5 acid system as long-living species, whereas more electrophilic less stable ions, such as **5-10** have not been detected by NMR spectrum but proposed as plausible reactive intermediates. Furthermore, the theoretical estimations of the reactivity either of the generated as well as the postulated dications were in a good agreement with the obtained experimental results strongly supporting the suggested reaction mechanism.

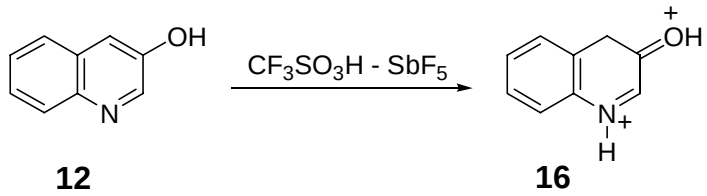
Similar reactivity of the quinolines, containing hydroxy group in pyridine ring of quinoline system has not been investigated thus far. In continuation of our interest on superelectrophilic activation of heteroarenes in superacids we have now extended our investigation to isomeric 2-, 3- and 4-quinolinols (**11-13**) with their reactions with cyclohexane and benzene, in superacids.

RESULTS AND DISCUSSION

NMR Spectroscopic study of protonation of 2-, 3-, and 4-quinolinols and related compounds. Initially, we examined the process of protonation of **11-13** and related 4-methyl-2-quinolinol (**14**) and 4-hydroxy-1-methyl-2(1*H*)-quinolinone (**15**) in protonic superacid CF_3SO_3H (triflic acid, Ho = -14.1) and

CF_3SO_3H-SbF_5 acid system at room temperature by means of ^1H and ^{13}C NMR spectroscopy. The spectral characteristics of generated ions are given in Table 1. Protonation of quinolinols (**11-14**) and quinolinone (**15**) in triflic acid gave only the respective *N*-protonated monocations (**11a-14a**) and the analogous carbonyl-protonated ion (**15a)**. However, in the more acidic CF_3SO_3H-SbF_5 system, precursors (**11**, **13** and **14**) have shown the similar behavior, whereas **12** gave *N*,*C*-diprotonated dication (**16**) (Scheme 1). The NMR spectra of the dication (**16**) contain the signal of the CH_2 group at δ 4.47 in the ^1H NMR and at δ 51.6 in the ^{13}C NMR spectrum. At the same time, the proton spectrum contains the signal of the hydrogen bound to nitrogen. The coupling of H^2 by the N-H proton is also observed. Dication (**16**) is structurally similar to isomeric dications (**2**) and (**8**). On the other hand, it can be regarded as a derivative of the ethylene dication stabilized by adjacent electron-donating arylamino and hydroxy groups.[4]

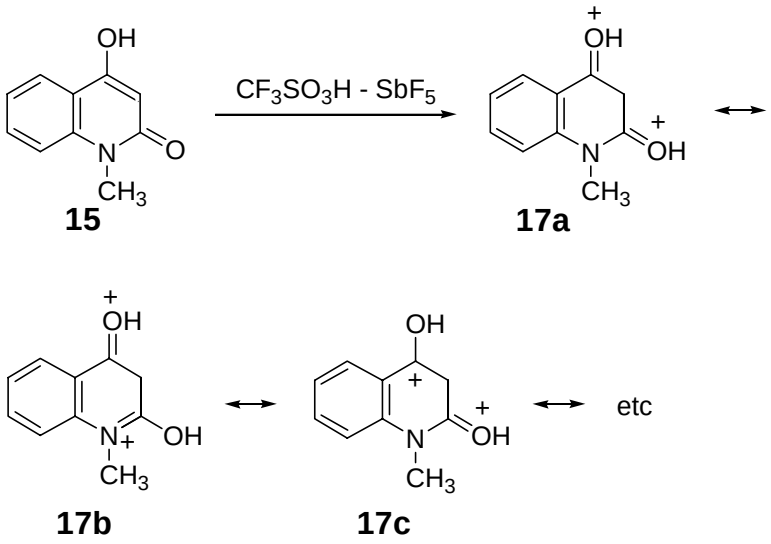
Scheme 1



12 **16**

Protonation of the compound (**15**) in CF_3SO_3H-SbF_5 acid system gave *O*,*C*-diprotonated dication (**17**) significantly stabilized by the electron-donating effect of hydroxy group adjacent to C[4] (Scheme 2). This dication can be considered as an analogous *O*,*O*-diprotonated forms of 1,3-diketones.[4a-c]

Scheme 2



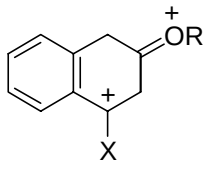
15 **17a** **17b** **17c**

Table 1. ^{1}H and ^{13}C NMR Spectroscopic data of mono- and diprotonated ions of compounds (11-15) at 25 ^{o}C[a]

Ion	^{1}H NMR signals (J, Hz)[b]	^{13}C NMR signals
11a[c]	**6.49 dt (9.2, 2.5), 6.93 t (7.8), 7.00 d (7.8), 7.17 t (7.8), 7.23 d (7.8), 7.93 dd (9.2, 2.5), 10.70 br s**	**111.2, 118.3, 124, 128.6, 129.5, 135.3, 135.7, 150.7, 160.5**
12a[c]	**7.02 d (6.2), 7.10 t (7.8), 7.27 t (7.8), 7.41 d (7.8), 7.59 d (7.8), 8.06 d (7.5), 11.10 br s**	**114.5, 121.7, 127.8, 129.5, 130.9, 131.8, 136.4, 138.6, 152.1**
16[d]	**4.47 s 2H, 7.30 t (7.8), 7.40 d (7.8), 7.54 t (7.8), 7.81 d (7.8), 8.25 d (8.5), 9.70 br d (~8)**	**51.6, 122.8, 129.9, 135, 139.1, 141.6, 148.9, 167, 204.5**
13a[c]	**6.34 dd (6.9, 1.1), 6.96 t (8.2), 7.07 d (8.2), 7.19 t (8.2), 7.58 d (8.2), 7.68t (6.9), 10.60 br s**	**105.2, 118.9, 119.7, 123.3, 128.9, 135.8, 138.8, 143.9, 169.3**
14a[c]	**2.00 s 3H, 6.31 s, 6.90 t (7.8), 6.93 d (7.8), 7.10 t (7.8), 7.32 d (7.8), 10.40 br s**	**18.6, 110.5, 123.2, 125.3, 127.8, 134.1, 134.6, 158.9, 162.8**
15a[c]	**3.17 s 3H, 5.74 s, 6.82 t (7.8), 7.04 d (7.8), 7.14 t (7.8), 7.49 d (7.8)**	**32.2, 93, 116.7, 117.7, 124.6, 127.1, 135.7, 138.7, 161.3, 168.2**
17[d]	**2.92 s 3H, 3.91 s 2H, 6.86 t (7.8), 6.92 d (7.8), 7.50 t (7.8), 7.61 d (7.8), 10.90 s, 12.59 s**	**33.9, 38.1, 116.3, 120.8, 131.4, 133.9, 144.7, 152, 170.5, 199.6**

[a]Chemical shifts are given with respect to $(CD_3)_2CO$ as external standard (2.04 and 206 ppm respectively in ^{1}H and ^{13}C NMR spectra). [b]Protons bonded to oxygen are not observed due to rapid proton exchange with the acid, except in the case of ion **17**. [c]Data for CF_3SO_3H solution. [d]Data for CF_3SO_3H-SbF_5 solution.

Dication (**17**) can also be regarded as an isoelectronic analog of *C*,*C*-diprotonated dications (**18**), which were previously obtained by the protonation of 2-naphthol and its derivatives in the extremely strong acid systems such as HF-SbF_5(1:1)-SO_2ClF and HSO_3F-SbF_5(1:1)-SO_2ClF at low temperatures.[5] The successful generation of dications such as **17** and **18** supports the possibility of formation of the analogous N,C-diprotonated dication (**19**) from quinolinol (**11**) in superacid media.



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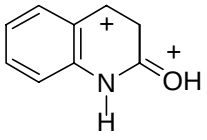


19

R= H, CH_3;
X= H, Cl, CH_3, C_6H_5, OR

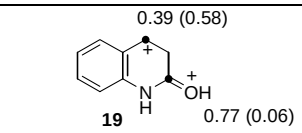
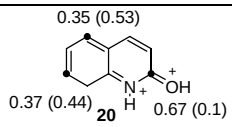
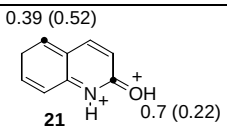
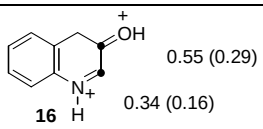
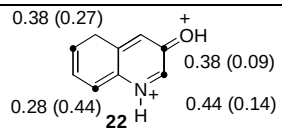
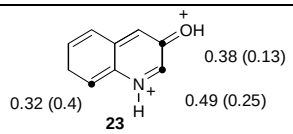
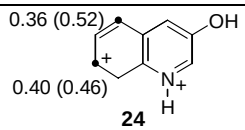
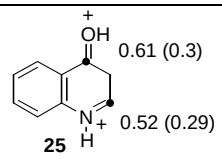
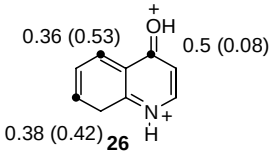
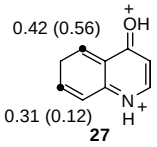
Theoretical study of the stabilities and electrophilicities of *N*,*C*-diprotonated dications of 11-13. To establish the relative stabilities and the electrophilicities of the generated and postulated *N*,*C*-diprotonated

dications (**16**) and (**19-27**)[6] (Table 2) derived from compounds (**11-13**), we have calculated their relative energies, the energies of lowest unoccupied molecular orbital (ε_{LUMO}), the squares of the coefficients of carbon atoms at LUMO of electrophilic centers ($c_{\bullet}^2$) and the atomic charges of electrophilic centers ($q_{\bullet}$) localized at carbon atoms and pendent hydrogen atoms. 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 values of $q_{\bullet}$ were obtained using natural bond orbital analysis[11] (NBO) method. Results of calculations are summarized in Table 2.

The computed relative energies show dications (**19-21**) and (**25-27**) to be energetically similar. The relative energies of dications (**16**)**,** and (**22-24**) are higher. The computed highest relative energy of **16** is in sharp contrast to its experimental observation under superacidic conditions. This can be rationalized by solvation effects as well as favorable kinetic factors. Thermodynamically all dications (**16**) and (**19-27**) according to their calculated ε_{LUMO} values, could be as electrophilic as dications (**1-4**) (ε_{LUMO}s= -12.263 to -11.988 eV)[2a] and some of them more reactive than dications (**5-10**) (ε_{LUMO}s= -12.653 to -12.312 eV).[1] The calculated value of the ε_{LUMO} = -13.402 eV of dication (**16**) seems to be an extremely low for this group of dications. The energy difference between this orbital and the second unoccupied MO (ε_{LUMO+1} = -9.965 eV) is also unusually significant.[12] Consideration of the distribution of the calculated c_i^2 at LUMO and q_i values allows the prediction of the reaction centers to be C^4, C^7 or C^5 and C^5 for dications **19-21**; C^6 or C^8, C^8 and C^5 or C^7 for **22-24**; and C^2 or C^4, C^5 or C^7 and C^5 for **25-27**, respectively.[13] Electrophilic center C^2 of dication **16** can hardly be expected as a probable reaction center due to negligible value of c_2^2 at LUMO (0.16). More promising from this point of view seems to be position C^3. Nevertheless, localization of positive charge on this site (q_3 = 0.55) is not so significant as was estimated earlier for strongly activated carbonyl groups (q = 0.68 to 0.73), which were electrophilic enough to react with benzene or cyclohexane.[2a] For these reasons it is possible that dication (**16**), which thermodynamically (according to the lowest ε_{LUMO} value) is a strong electrophile, but kinetically could be the weakest electrophile among the computed structures.

Reactions with cyclohexane and benzene. Quinolinols (**11-13**) do not react with cyclohexane in triflic acid. However, in the more acidic CF_3SO_3H-SbF_5 system over 2-30 h at room temperature reacted to give 5,6,7,8-tetrahydro-2(1*H*)-quinolinone, 5,6,7,8-tetrahydro-3-quinolinol and 5,6,7,8-tetrahydro-4(1*H*)-

Table 2. Energies of the LUMO (ε_{LUMO}), the Square of the Coefficiets on carbon atoms at the LUMO (c_i^2),[a] NBO Charges on CH groups (q_i)[a] and Total Energies (-au), ZPE, and Relative Energies of dications 16 and 19-27 calculated by the DFT method

dication, $q_\bullet$ and ($c_\bullet^2$)	ε_{LUMO}, eV	B3LYP/6-31G*// B3LYP/6-31G*	ZPE	rel energy, kcal/mol
 **19**	-12.511	477.69562	101.1	6.2
 **20**	-12.364	477.70537	101.0	0.0
 **21**	-12.243	477.70357	100.7	0.8
 **16**	-13.402	477.66992	101.0	22.3
 **22**	-12.582	477.69283	101.0	7.9
 **23**	-12.644	477.68418	100.6	12.9
 **24**	-12.672	477.68743	100.8	11.1
 **25**	-12.109	477.69870	101.6	4.8
 **26**	-12.448	477.70586	101.3	0.0
 **27**	-12.378	477.70251	100.9	1.7

[a] These parameters are given for positions with the most significant values of c_i^2 at LUMO or q_i.

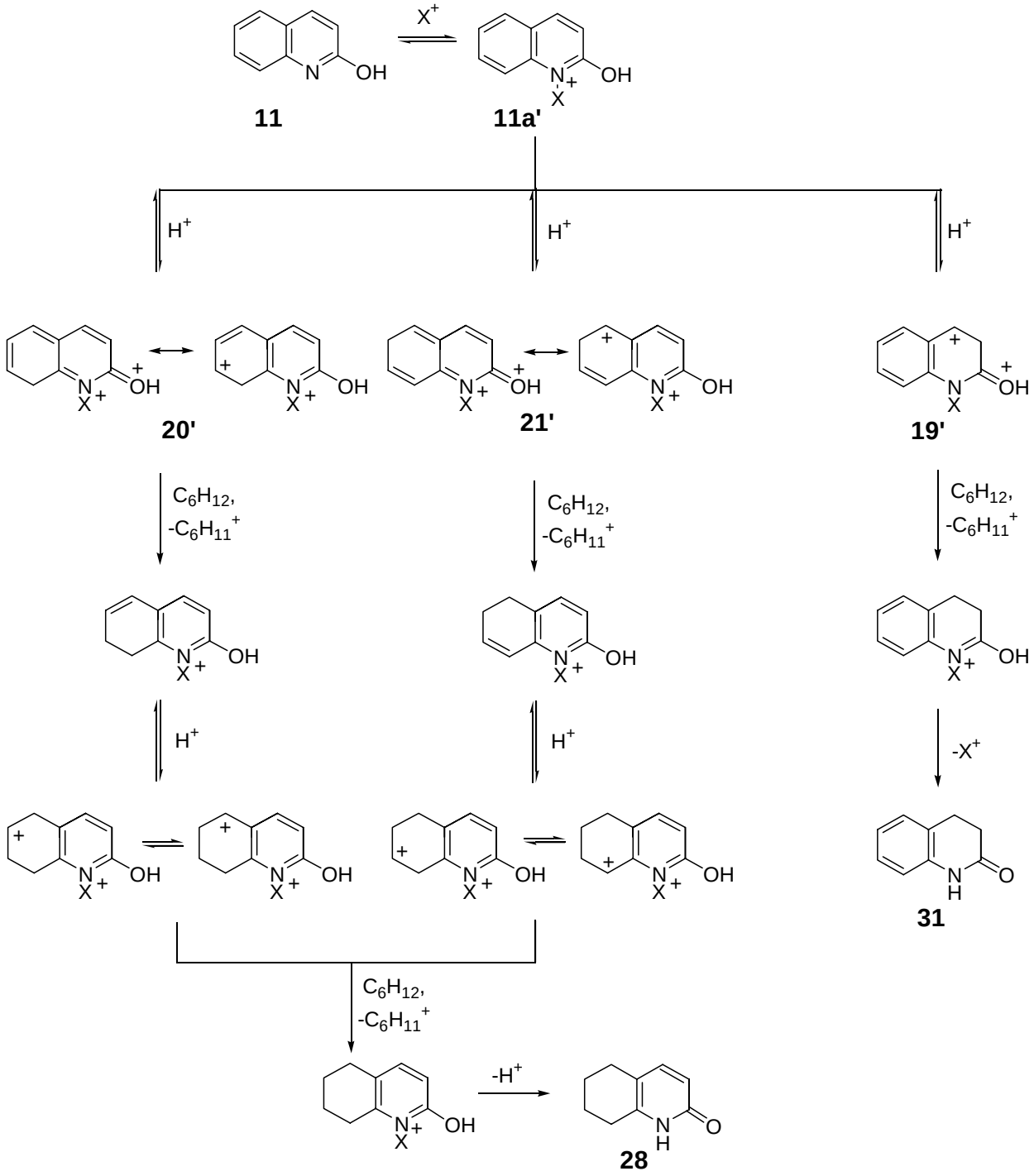
quinolinone (**28**-**30**), respectively, in 70 to 90% yield (Schemes 3 and 4). The likely mechanism of the reaction of compound (**11**), according to Scheme 3, includes generation of dications (**20**) or **(21**) followed by their selective ionic hydrogenation with cyclohexane. The plausible mechanism of reaction of compounds (**12**) and (**13**) including generation of dications (**22**-**24** and **26)** or (**27**), respectively, is considered similar to that described in Scheme 3. It is remarkable that **12** did not give any expected product corresponding to the reaction of the generated dication (**16**), which appears to be a weaker electrophile than postulated dications (**22**-**24**).

Reaction of **11** and **13** with cyclohexane also occurred by using 5-7 molar excess of $AlCl_3$ at 90 ^oC.[14] Quinolinol (**11**) gave 3,4-dihydro-2(1*H*)-quinolinone (**31**) in 80% yield over period 24 h. This reaction pathway corresponds to the participation of dicationic species (**19′**) as a key intermediate (Scheme 3). Compound (**13**) gave hydroquinolinone (**30**) over period 50 - 100 h in ~70 % yield, similar to the reaction in CF_3SO_3H-SbF_5 system. Quinolinol (**12**) was found to be inert towards cyclohexane under similar conditions.

Compounds (**11**) and (**13**) react with benzene in the presence of excess of aluminum halides. Similar to the reaction with cyclohexane, the reaction of (**11**) can take place by two pathways corresponding to the participation of dications (**19′**) and (**21′**) (or **20′**) to give 4-phenyl-3,4-dihydro-2(1*H*)-quinolinone (**32**) and 5,7-diphenyl-5,6,7,8-tetrahydro-2(1*H*)-quinolinone (**33**), respectively (Scheme 5). Product (**32**) was obtained only in 5% yield when the reaction was carried out in the presence of $AlBr_3$ at room temperature for several hours. The yield corresponds to the equilibrium concentration of the product. This was confirmed by the reaction of **32** with $AlBr_3$ in benzene to give a mixture of **11**, **32** and **33** (the ratio ~90:5:5, respectively) over a 40 h period at 25 ^oC. Product (**33**) was obtained in 30-40% yield when **11** was reacted with benzene in the presence of $AlBr_3$ at room temperature over ~250 h.[15]

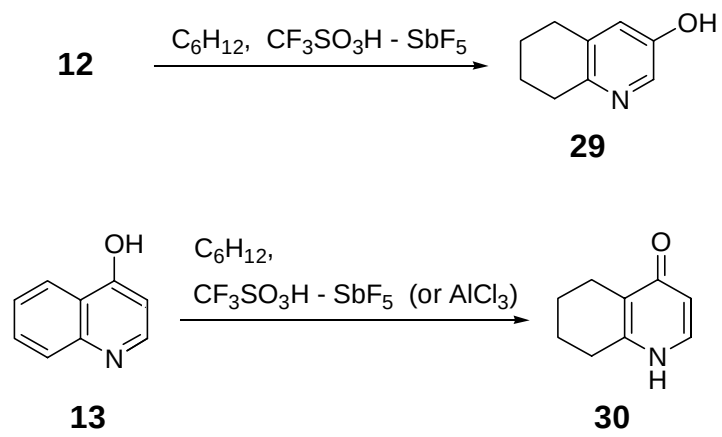
Compound (**13**) reacts slowly with benzene in the presence of $AlCl_3$ as well as $AlBr_3$, but reacted readily (for 4 h at 25 ^oC) in the presence of HBr-$AlBr_3$ to give a mixture of *cis* and *trans*-5,7-diphenyl-5,6,7,8-tetrahydro-4(1*H*)-quinolinone (**34**) in 82% yield (Scheme 6). The mechanism of this reaction including generation of dications (**26**) or (**27**) (or analogous complexes with $AlBr_3$) is considered similar to that described in Scheme 5.

Scheme 3

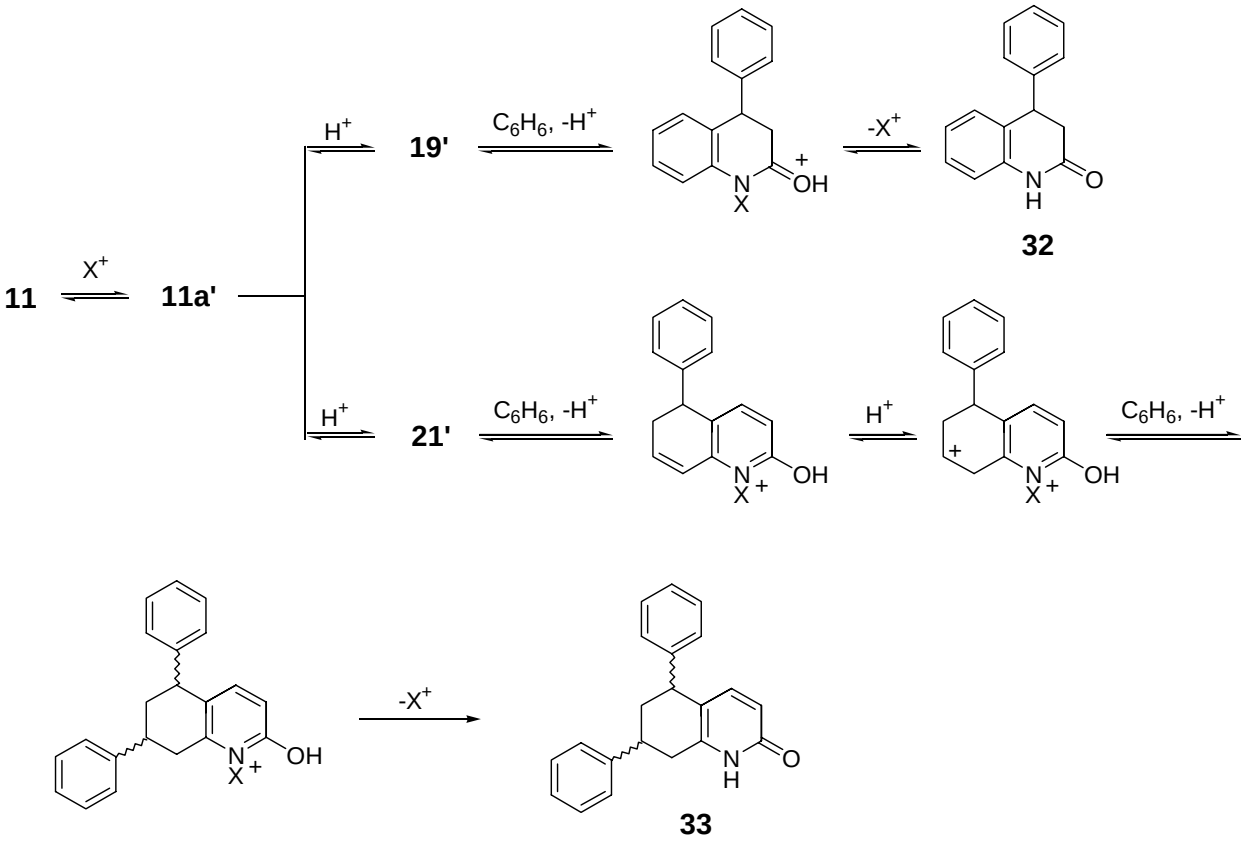


X = H or $Al_nCl_{3n}^-$

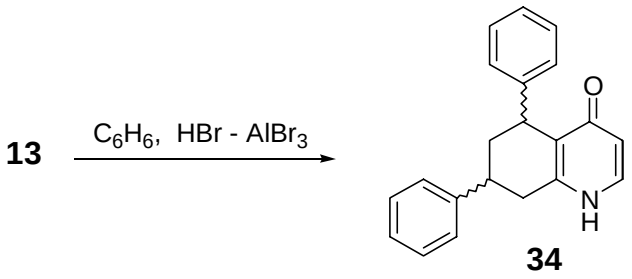
Scheme 4



Scheme 5



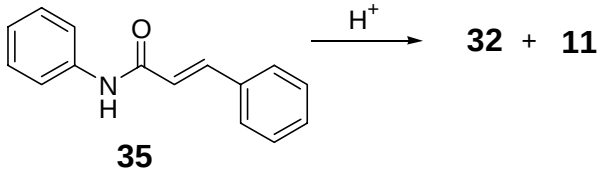
Scheme 6



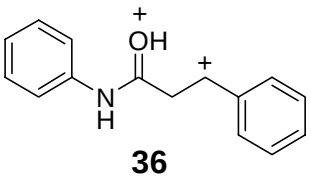
Compound (**12**), however, does not react with benzene in the presence of aluminum halides.[16] The lack of reactivity of **12** either towards benzene or cyclohexane in the presence of aluminum halides can be explained by the decrease in concentration of reactive dications (**22**-**24**) due to the favorable formation of **16** (or analogous complexes). This is in agreement with the similar behavior found for **11** and isomeric 1- and 3-isoquinolinols[1] the involving dications such as **19**, **5** and **8**.

It must be mentioned that product (**32**), which is formed upon reaction of **11** with benzene in low yield (Scheme 5), have been previously obtained in good yield by high-temperature (130 ^{o}C) polyphosphoric acid-catalyzed cyclization of cinnamanilide (**35**) (Scheme 7).[17] The reaction was accompanied by the formation of **11** as a byproduct. Compound (**11**) was obtained as a major product when the reaction was carried out with $AlCl_3$ at 100 ^{o}C.[18] The formation of **11** was explained by the direct elimination of benzene from **35**.[17] Now it is obvious that **11** is produced due to the elimination of benzene from **32** according to a reversible reaction shown in Scheme 5.

Scheme 7



We have also investigated the cyclization of (**35**) in triflic acid, a less acidic medium, in which the elimination of benzene from **32** will be less likely. Indeed, product (**32**) was obtained in 82 % yield over 5 h period at room temperature.[19] It seems reasonable that mechanism of the reaction includes generation of *O*,*C*-diprotonated dication (**36**) followed by its intramolecular cyclization. Dication (**36**) can be regarded as an analog of the dication (**19**) as well as of the long living dications (**17**, **18)** and *O*,*C*-diprotonated dication (**37**), which has been derived from protonation of 4-phenyl-3-buten-2-one in HF-SbF_5(1:1)-SO_2ClF acid system.[20]



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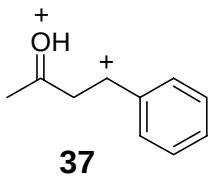

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CONCLUSION

In summary, we have found that quinolinols (**11-13**) undergo selective ionic hydrogenation with cyclohexane and condense with benzene in strong acid media to give respective products (**28-34**). The experimental results can be explained by participation of *N*,*C*-diprotonated dications (**19-27**) (or analogous complexes with aluminum halides) as key superelectrophilic intermediates. These intermediates, according to theoretical estimations, possess electrophilicity comparable with that of dications (**5-10**). However, the reactivity of **11-13** are less than that of 1- and 3-isoquinolinols.[1] This is due to the relatively lower stabilities of dications (**19-27**) when compared to that of dications (**5-10**) and is in accord with their computed relative energies.

In general, the ability of isomeric quinolinols and isoquinolinols to undergo activation in the presence of strongly acidic agents through the formation of dicationic intermediates makes it possible for the latter to act as a novel heterocylic synthons and extends the applicability Friedel-Crafts type reactions in the field of heterocyclic compounds.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz superconducting NMR spectrometer. HRMS spectra were measured at the Southern California Mass Spectrometry Facility at the University of California at Riverside. Triflic acid, aluminum halides and compounds (**11-15**) were purchased from suppliers and used as received. Cinnamanilide (**35**) was obtained by reaction of cinnamoyl chloride with aniline. Antimony pentafluoride was distilled under argon. Elevated temperature reactions were carried out in 15 mL pressure tubes.

Procedure for the Protonation of 11-15 was similar to that for isomeric quinolinols and isoquinolinols as previously reported.[2a]

5,6,7,8-Tetrahydro-2(1*H*)-quinolinone (28).

To a stirred solution of **11** (0.02 g, 0.14 mmol) in CF_3SO_3H (1.2 g, 8 mmol) was added SbF_5 (1 g, 4.6 mmol) at rt. After the addition of cyclohexane (0.1 g, 1.2 mmol) the reaction mixture was stirred and then

was kept at 25 ^{o}C over a 20 h period. Then the mixture was poured over several grams of ice. The resulting mixture was neutralized with 10% NH_4OH solution, washed with water and extracted with $CHCl_3$. The organic phase was dried over anhydrous $MgSO_4$. After concentration *in vacuo* the residue was purified by silica gel column chromatography with $CHCl_3$, $CHCl_3$ – acetone to give crystalline product (**28**) (0.017 g, 83%): mp 202-203 ^{o}C (lit.,[21] mp 205-206 ^{o}C). ^{1}H NMR ($CDCl_3$) δ 1.7-1.85 (m, 4H), 2.47 (t, *J* 6.3 Hz, 2H), 2.67 (t, *J* 6.3 Hz, 2H), 6.36 (d, *J* 9 Hz, 1H), 7.17 (d, *J* 9 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 21.5, 22.5, 26, 26.7, 114.4, 116.8, 143, 143.8, 164.9.

5,6,7,8-Tetrahydro-3(1*H*)-quinolinol (29).

To a stirred solution of **12** (0.06 g, 0.4 mmol) in CF_3SO_3H (2.4 g, 16 mmol) was added SbF_5 (1.4 g, 6.5 mmol) at rt. After the addition of cyclohexane (0.5 mL) the reaction mixture was stirred at 25 ^{o}C for 30 h. Then the mixture was poured over several grams of ice. The resulting mixture was neutralized with 10% NH_4OH solution, washed with water and extracted with $CHCl_3$. The organic phase was dried over anhydrous $MgSO_4$. After concentration *in vacuo* the organic phase was separated by silica gel column chromatography with benzene-acetone (3:1) to obtain the crystalline product **29** (0.045 g, 72%): mp 198-199 ^{o}C (acetone). ^{1}H NMR ($CDCl_3$) δ 1.79 (br s, 4H), 2.72 (br s, 4H), 7.78 (s, 1H), 7.98 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 21.9, 22.1, 22.8, 26.3, 130.8, 134.9, 136.5, 138.4, 153.8. HRMS $C_9H_{11}NO$ calcd 149.0841, found 149.0847.

5,6,7,8-Tetrahydro-4(1*H*)-quinolinone (30).

Method a. To a stirred solution of **13** (0.02 g, 0.2 mmol) in CF_3SO_3H (1.2 g, 8 mmol) at room temperature was added SbF_5 (1 g, 4.6 mmol). After the addition of cyclohexane (0.1 g, 1.2 mmol) the reaction mixture was stirred and then kept at 25 ^{o}C for 2 h. Then the reaction mixture was poured over several grams of ice. The resulting mixture was neutralized with 10% NH_4OH solution, washed with water and extracted with $CHCl_3$ (15×3 mL). The organic phase was dried over anhydrous $MgSO_4$. Concentration *in vacuo* provided the crystalline product (**30**) (0.019 g, 92%): mp 206-207 ^{o}C (acetone) (lit.,[22] mp 200-210 ^{o}C). ^{1}H NMR (DMSO-d_6) δ 1.5-1.7 (m, 4H), 2.25 (t, *J* 6.7 Hz, 2H), 2.49 (t, *J* 6.7 Hz, 2H), 5.92 (d, *J* 8 Hz, 1H), 7.46 (d, *J* 8 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ 21.5, 21.6, 21.7, 26.4, 112.9, 123.3, 135.9, 144.5, 176.8.

Method b. A mixture of **13** (0.1 g, 0.7 mmol), $AlCl_3$ (0.7 g, 5.2 mmol) and cyclohexane (4 mL) was stirred at 90 ^{o}C for 48 h and after workup described above gave **30** (0.071 g, 69%).

3,4-Dihydro-2(1*H*)-quinolinone (31).

To a suspension of $AlCl_3$ (0.68 g, 5 mmol) in cyclohexane (2 mL) was added **11** (0.1 g, 0.7 mmol). The resulting mixture was stirred at 90 ^oC for 24 h, followed by cooling the mixture was poured over several grams of ice and extracted with $CHCl_3$. The organic phase was washed with water, then dried ($MgSO_4$) and concentrated. The crude material was washed with hexanes. The solid residue[23] (0.1 g) was recrystallized from benzene to provide the product (**31**) (0.081 g, 80%): mp 166-167 ^oC (ethanol) (lit.,[24] mp 167-168 ^oC). ^1H NMR ($CDCl_3$) δ 2.64 (t, *J* 7.4 Hz, 2H), 2.97 (t, *J* 7.4 Hz, 2H), 6.81 (d, *J* 8.5 Hz, 1H), 6.98 (t, *J* 8.5 Hz, 1H), 7.17 (m, 2H), 8.8 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 25.2, 30.7, 115.4, 123.1, 123.6, 127.5, 128, 137.2, 171.9.

4-Phenyl-3,4-dihydro-2(1*H*)-quinolinone (32).

Method a. To a solution of $AlBr_3$ (1.35 g, 5 mmol) in benzene (3 mL) was added **11** (0.145 g, 1 mmol). The resulting solution was kept stirred at 25 ^oC for 24 h, then poured over ice and extracted with $CHCl_3$. The organic phase was washed with water, dried ($MgSO_4$) and concentrated to provide a mixture of **11**/**32**/**33** (~15:1:1), which was separated by silica gel column chromatography with $CHCl_3$ to obtain crystalline product (**32**) (0.011 g, 5%): mp 177-178 ^oC ($CHCl_3$), (lit.,[17] mp 178 ^oC). ^1H NMR ($CDCl_3$) δ 2.93 (m, 2H), 4.3 (t, *J* 8.3 Hz, 1H), 6.85-7 (m, 3H), 7.2-7.4 (m, 6H), 8.8 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 38.4, 42, 115.7, 123.4, 126.7, 127.2, 127.8, 128, 128,4, 128.9, 137, 141.4, 170.8.

Method b. Cinnamanilide (**35**) (1 g, 4.5 mmol) was dissolved in triflic acid (5 g, 33.3 mmol). The resulting solution was kept stirred at 20 ^oC for 5 h, and then poured over ice. Precipitated material was filtered of, washed with water and dried. The subsequent chromatographic purification (silica gel, $CHCl_3$) gave **32** (0.82 g, 82%).

5,7-Diphenyl-5,6,7,8-tetrahydro-2(1*H*)-quinolinone (33).

To a solution of $AlBr_3$ (1.33 g, 5 mmol) in benzene (2.5 mL) was added **11** (0.145 g, 1 mmol). The mixture was stirred at 25 ^oC for 250 h and then poured over ice and extracted with $CHCl_3$. The organic phase was dried ($MgSO_4$) and concentrated. The residue was separated by silica gel column chromatography with benzene-acetone (3:1) to obtain the crystalline product (**33**) (0.096 g, 32%) as a mixture of *cis* and *trans* isomers (~2:1). HRMS $C_{21}H_{19}NO$ calcd 301.1467, found 301.1465. Recrystallization of the mixture from acetone gave pure *cis*-**33**: mp 305-307 ^oC. ^1H NMR ($CDCl_3$) δ 1.97 (q, *J* 12.2 Hz, 1H), 2.28-2.38 (m, 1H), 2.9-3.2 (m, 3H), 3.97 (dd, *J* 12.2, 6 Hz, 1H), 6.29 (d, *J* 9.4 Hz, 1H), 6.97 (d, *J* 9.4 Hz, 1H), 7.12-7.35 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 35.4, 40.1, 41.1, 44.8, 117.1, 117.3, 126.7, 126.8, 126.9, 128.3, 128.6, 128.8, 143.3, 143.4, 144.1, 144.8, 164.9.

trans-**33**[25]: ^1H NMR ($CDCl_3$) δ 2.12 (dt, *J* 13.6, 4.2 Hz, 1H), 2.36 (dd, *J* 13.6, 5.6 Hz, 1H), 2.8-3.2 (m,

3H), 4.05 (dd, *J* 5.6, 4.2 Hz, 1H), 6.38 (d, *J* 9.4 Hz, 1H), 7.08 (d, *J* 9.4 Hz, 1H), 7.1-7.35 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 34, 34.2, 38.4, 41.6, 115.4, 117,7, 126.5, 126.6, 127, 128.4, 128.5, 128.6, 143.3, 143.7, 144.2, 145.1, 165.2.

5,7-Diphenyl-5,6,7,8-tetrahydro-4(1*H*)-quinolinone (34).

To a solution of $AlBr_3$ (1.33 g, 5 mmol) in benzene (2.5 mL) was added **13** (0.145 g, 1 mmol). The resulting solution was saturated with gaseous HBr (0.16 g, 2 mmol) and stirred at 25 ^{o}C for 4 h, then poured over ice. The quenched reaction mixture was treated with CH_2Cl_2 (2 mL) followed by ether (15 mL) and stirred for 1 h. The precipitated white powder was filtered off, washed with water and ether and dried to give the product (**34)** (0.247 g, 82%) as a mixture of *cis* and *trans* isomers (~1:2, respectively). HRMS $C_{21}H_{19}NO$ calcd 301.1467, found 301.1464. Recrystallization of the mixture from acetone gave pure *trans*-**34**: mp 291-293 ^{o}C. ^{1}H NMR (DMSO-d_6) δ 1.98 (d, *J* 14 Hz, 1H), 2.37 (td, *J* 14, 5.7 Hz, 1H), 2.9-3.4 (m, 3H), 4.47 (d, *J* 5.7 Hz, 1H), 7.05-7.4 (m, 11H), 8.47 (d, *J* 7.4 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ 32.6, 34.5, 36.8, 37.5, 110.8, 123.3, 126.3, 126.7, 126.8, 127.7, 128.2, 128.6, 140.9, 143.7, 143.9, 152.5, 169.8.

cis-**34**[25]: ^{1}H NMR (DMSO-d_6) δ 1.85 (q, *J* 13.4 Hz, 1H), 2.3-2.4 (m, 1H), 2.9-3.4 (m, 3H), 4.28 (dd, *J* 13.4, 8.4 Hz, 1H), 6.95 (d, *J* 7.4 Hz, 1H), 7.15-7.4 (m, 10H), 8.39 (d, *J* 7.4 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ 35.1, 38.5, 41.1, 41.3, 111.4, 124.5, 126.1, 126.7, 126.8, 127.1, 128.3,128.6, 140.2, 143.7, 145.5, 153.1, 170.2.

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REFERENCES AND NOTES

1. Chemistry in Superacids. Part 65. For part 64, See G. Rasul, G. K. S. Prakash, and G. A. Olah, *J. Phys. Chem.*, A, in press.

2. (a) K. Yu. Koltunov, G. K. S. Prakash, G. Rasul, and G. A. Olah, *J. Org. Chem.*, 2002, **67**, 4330. (b) K. Yu. Koltunov, G. K. S. Prakash, G. Rasul, and G. A. Olah, *J. Org. Chem.*, 2002, **67**, 8943. (c) K. Yu. Koltunov, G. K. S. Prakash, G. Rasul, and G. A. Olah, *Tetrahedron*, 2002, **58**, 5423. (d) K. Yu. Koltunov and I. B. Repinskaya, *Russ. J. Org. Chem.*, 2000, **36**, 446. (e) K. Yu. Koltunov and I. B. Repinskaya, *Russ. J. Org. Chem.*, 2002, **38**, 437.

3. G. A. Olah, *Angew. Chem., Int. Ed. Engl*., 1993, **32**, 767.

4. For a low-temperature generation of substituted ethylene dications bearing electron-donating groups such as an aryl, a hydroxy, a methoxy and a *N,N*-dihydroxyamino groups or for their reactions with arenes, see (a) G. A. Olah and A. M. White, *J. Am. Chem. Soc*., 1967, **89**, 4752. (b) G. A. Olah and M. Calin, *J. Am. Chem. Soc*., 1968, **90**, 4672. (c) G. A. Olah, J. L. Grant, and P. W. Westerman, *J. Org. Chem.*, 1975, **40**, 2102. (d) T. Ohwada and K. Shudo, *J. Am. Chem. Soc*., 1988, **110**, 1862. (e) T. Ohwada and K. Shudo, *J. Org. Chem.*, 1989, **54**, 5227, and the references cited therein. (f) T. Yamazaki, S. Saito, T. Ohwada, and K. Shudo, *Tetrahedron Lett.*, 1995, **36**, 5749. (h) D. A. Klumpp, K. Y. Yeung, G. K. S. Prakash, and G. A. Olah, *J. Org. Chem.*, 1998, **63**, 4481. (g) D. A. Klumpp, S. Lau, M. Garza, G. V. Sanchez, B. Schick, and K. Kantardjieff, *J. Org. Chem.*, 1999**, 64**, 7635.

5. I. B. Repinskaya, K. Yu. Koltunov, M. M. Shakirov, and V. A. Koptyug, *J. Org. Chem., USSR.* 1992, **28**, 785.

6. Dications (**19**-**27**) were preferred based on the participation of the non-bonded electron pairs of both heteroatoms in charge delocalization (with the exception of **24**). Favorable formation of dications (**20**, **21**, **26** and **27**) also conforms to positional selectivity of electrophilic substitution reactions of **11** and **13** in strong acids (hydrogen-deuterium exchange, nitration, etc.) to give 6- and 8-substituted 2- and 4-quinolones, see, for example: (a) R. M. Welch, A. R. Brown, and A. P. Phillips, Eur. Patent 1990, 356230. (b) A. R. Katritzky, B. Terem, E. V. Scriven, S. Clementi, and H. O. Tarhan, *J. Chem. Soc., Perkin Trans. II*, 1975, 1600. The possibility of additional *N*-protonation of **11a-13a** to give the Corresponding *N,N*-diprotonated dications was not considered to be kinetically favorable. See, for example, the discussion on that subject for 1- and 2-isoquinolinols: Ref. 2b.

7. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, R. E. Daniels, K. N. Kudin, M. C. Strain, O. Farcas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelly, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkarra, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Jonson, W. Chen, M. W. Wong, J. L. Andres, C. M. Gonzalez, M. Head-Gordon, and J. A. Pople, Gaussian 98 Revision A.5); Gaussian, Inc., Pittsburgh, PA, 1998.

8. T. Ziegler, *Chem. Rev*., 1991, **91**, 651.

9. Becke's three parameter hybrid method using the LYP correlation functional: (a) A. D. Becke, *J. Chem.*

Phys., 1993, **98**, 5648. (b) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785. (c) P. J. Stephens, F. J. Devlin, C. F. Chabalovski, and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.

10. W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory*; Wiley–Interscience: New-York, 1986.
11. A. E. Reed, L. A. Curtiss, and F. Wienhold, *Chem. Rev*., 1988, **88**, 899.
12. Similar property was found, previously, for LUMO and LUMO+1 of dications (**18**) (X = OR), and is recognized to be due to the inversion of these orbitals as a result of change in substituents X= H, Cl, CH_3 and C_6H_5 by OR. See: K. Yu. Koltunov, I. B. Repinskaya, M. M. Shakirov, and L. N. Shchegoleva, *Russ. J. Org. Chem.*, 1994**, 30**, 88.
13. Preferred electrophilic centers were chosen according to the largest values either of $c_{\bullet}^{2}$ and $q_{\bullet}$, see, for example, Ref. 2a and 2b.
14. Under the reaction conditions cyclohexane exists in an equilibrium with methylcyclopentane, see: C. D. Nenitzescu and R. Cantuniari, *Chem. Ber.*, 1933, **66**, 1097.
15. Conversion of **11** was ~50%. The reaction conditions were not optimized. However, prolonged reaction time or saturation of the reaction mixture with gaseous HBr considerably accelerates the reaction and causes subsequent dehydrogenation of **33** to give 5,7-diphenyl-7,8-dihydro-2(1*H*)-quinolinone as a major product. This is similar to the analogous reaction of 1-isoquinolinol with benzene in HBr-$AlBr_3$. See Ref. 2b.
16. However, **12** after 40 h of the reaction in HBr-$AlBr_3$ at 25 ^{o}C gave in 10% conversion a complex reaction mixture.
17. K. M. Johnston, *Tetrahedron*, 1968, **24**, 5595, and the references cited therein.
18. J. Colonge and R. Chambard, *Bull. Chem. Soc. Fr.*, 1953. 982.
19. The reaction mixture did not contain compound (**11)**. A single byproduct (~15%) of the reaction corresponds to the condensation of **35** with phenyl group of product (**32**).
20. K. Yu. Koltunov and I. B. Repinskaya, *Russ. J. Org. Chem.*, 1994, **30**, 97.
21. A. I. Meyers and G. Garcia-Munoz, *J. Org. Chem.*, 1964, **29**, 1435.
22. G. Salbeck, German Patent, Hoechst AG, DE 2426851, 1976.
23. As a mixture of **31**/**28** (95:5).
24. A. P. Venkov and S. M. Statkova-Abeghe, *Tetrahedron*, 1996, **52**, 1451.
25. The data are taken from the spectra of mixture of the *cis* and *trans* isomers.