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Superelectrophilic activation of 1-nitronaphthalene in the presence of aluminum chloride. Reactions with benzene and cyclohexane⁺

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1-Nitronaphthalene smoothly reacts with benzene and undergoes selective reduction with cyclohexane in the presence of aluminum chloride to give 2,4,4-triphenyl-3,4-dihydronaphthalen-1(2H)-one oxime and 5,6,7,8-tetrahydro-1-naphthylamine, respectively. The mechanistic aspects of these and related reactions are discussed on the basis of DFT, providing insight into the protonation behavior of 1-nitronaphthalene coordinated to AlCl₃.

Diprotonation of nitroarenes, nitroalkenes and aci-nitroalkanes in liquid superacids is an efficient approach to involve them in Friedel-Crafts type transformations leading to a large variety of useful derivatives.¹ However, apart from the usual difficulties encountered in handling vast amounts of Brønsted superacids, an often-observed drawback of such reactions is the lack of their selectivity. 1-Nitronaphthalene (1), for instance, reacts with benzene in a 30-fold molar excess of triflic acid ($H_0 = -14$) for 2 h at 0–5 °C to afford a mixture of 2-phenyl-, 4-phenyl- and 3,4-diphenyl-1-naphthylamines in about 50% overall yield.² The parent nitrobenzene (2) reacts with benzene similarly, but even less satisfactorily, to give a mixture of mono-, di- and triphenylated anilines, wherein the conversion is poor (<20% for 48 h at 80 °C) and the yields are moderate.3 The key intermediates of these reactions were recognized to be superelectrophilic^{1c} O,O-diprotonated forms 3 and 4 (Scheme 1), despite the whole mechanism not being known.

On the other hand, it is known that readily available and easy to use Lewis acids, such as AlCl₃, can mediate reactions proceeding *via* dicationic superelectrophiles no less effectively than liquid superacids.⁴ Moreover, in some cases this leads to a change in the reaction pathway.⁵ In this connection, it is noteworthy that in addition to a strong Lewis acidity, a catalytic amount of protic superacid, HAl_nCl_{4n} or $H_2O-Al_nCl_{3n}$ ($H_o \approx -18$), is normally present in such reaction media due to the *in situ* reaction between the excess of AlCl₃ and traces of water in the starting materials.⁶ Besides, the proton acidity could increase further if water is generated as a co-product in the course of reaction.

Given the above results, we report herein experimental and theoretical (DFT) studies on superelectrophilic activation of 1 in the presence of $AlCl_3$. This approach provides a new and selective reaction of 1 with benzene, as well as with cyclohexane, another weak nucleophile. Similar reactions of the parent compound 2 and 1-naphthylamine have also been briefly examined for the purpose of comparison.

When reacted with benzene in the presence of a 5-fold molar excess of $AlCl_3$, **1** was completely converted into triphenylated oxime **5** and tetracyclic oxime **6** just within 30 min at 25 °C (Scheme 2). After which, the major product **5** was easily isolated in 60% yield by crystallization. Upon prolonging the reaction time for up to 7 days, compound **6**, in its turn, becomes the major product which can also be isolated by means of crystallization. It is apparent that under the applied conditions oxime **5** is a kinetically preferred product, while the formation of oxime **6** is mainly a result of thermodynamically controlled electrophilic transalkylation. Clearly, the elimination of water during the conversion of **1** into **5** strongly increases the proton acidity of the reaction medium, which

[†] Electronic supplementary information (ESI) available: Experimental and computational details and NMR spectra of all compounds (PDF). See DOI: 10.1039/ c8ob02653j



 $\mbox{Scheme 1}$ $\mbox{Proposed direction of diprotonation of nitroarenes 1 and 2 in triflic acid. <math display="inline">^{2,3}$

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 $\label{eq:scheme 2} \begin{array}{ll} \mbox{Reaction of 1} \mbox{ with benzene. The molar percentage of products 5 and 6 is given based on 1H NMR spectroscopic data.} \end{array}$

also promotes the ultimate production of **6**. Indeed, we have shown that compound **5** itself is practically not converted into **6** in the presence of aluminum chloride. However, **5** reacts with benzene and aluminum chloride for 10 days at room temperature to give **6**, provided there is prior saturation of the reaction mixture with gaseous HCl.

Notably, the structures of 5 and 6 are determined unambiguously by NMR (ESI[†]). It is noteworthy that the upfield shifted signal at $\delta_{\rm H} = 6.59$ ppm corresponded to the H5 protons of oxime 5 in the ¹H NMR spectrum. According to our conformational analysis, H5 resides in the shielding cone of one of the phenyl groups of the *gem*-diphenyl moiety in the most stable conformation of 5 (ESI[†]). Remarkable also is an unusual hindered rotation of the phenyl group in 6 at room temperature. The ¹H and ¹³C NMR spectra of 6 contain broad signals of hydrogen and carbon *ortho*-atoms of the phenyl group. The estimated NMR rotational barrier ($\Delta G^{\text{#}}$ at $-5 \,^{\circ}\text{C}$) is 11.6 kcal mol⁻¹, which coincides with the value calculated by DFT/PBE/ $\Lambda 1^7$ (ESI[†]).

Furthermore, the reaction of **1** with cyclohexane catalyzed by a five- to eight-fold molar excess of $AlCl_3$ for a few hours at 100–110 °C resulted in the formation of 5,6,7,8-tetrahydro-1naphthylamine (7) (Scheme 3). Under the reaction conditions cyclohexane exists in equilibrium with methylcyclopentane. Both alkanes are able to react with strong electrophiles as hydride donors and thereby release isomeric cations $C_6H_{11}^+$. The latter reacts further with excess of cyclohexane/methylcyclopentane to give dicycloalkanes $C_6H_{11}-C_6H_{11}$ ultimately.⁸

The reaction of **2** with benzene in the presence of $AlCl_3$ appeared to be similar to that mediated by triflic acid,³ leading to a complex mixture consisting mainly of mono-, di- and triphenylated anilines (GC-MS data). In contrast, the reaction of **2** with cyclohexane is rather more selective, making it possible to obtain 4-chloroaniline (**8**) in good isolated yield (Scheme 4).

It should be noted that a 4–8 fold molar excess of aluminum chloride is not essential and a decrease in the loading is possible. This, however, slows down the reactions, and the use



Scheme 3 Reaction of 1 with cyclohexane



Scheme 4 Reactions of 2 with benzene and cyclohexane.

of less than a 2-fold molar excess of AlCl_3 completely suppresses them.

According to spectroscopic and theoretical studies, aluminum chloride coordinates with only one oxygen atom of nitro compounds regardless of the reagent ratio.⁹ Our DFT calculations also show that the coordination of each oxygen atom in **1** with $AlCl_3$ is quite unfavorable (by 4.5 kcal mol⁻¹) compared to monocoordination of **1** with Al_2Cl_6 (ESI[†]).¹⁰ Hence, in the presence of several equivalents of $AlCl_3$, **1** can exist as *O*-monocoordinated species, which may undergo catalytic protonation to form a number of isomeric superelectrophiles **9**.

Depending on the balance between the stability (concentration in the reaction media) and reactivity, intermediates **9** could give the corresponding products with the nucleophiles. In order to estimate the relative stabilities, electrophilicities, and positions of electrophilic centers for the most feasible model structures **9a–h**, we have calculated their relative energies, the energies of the lowest unoccupied molecular orbital (ϵ_{LUMO}), the squares of the coefficients of carbon atoms at the LUMO of electrophilic centers (c.²) and the atomic charges (q.) localized at carbon atoms (Table 1).

The computed relative energies of isomers **9** showed the following favorable order of formation : $9a \gg 9h > 9e > 9g > 9f >$ 9d > 9c > 9b, corresponding to the protonation of the *O*-coordinated **1** at the vacant oxygen atom, followed by the positions 8, 5, 7, 6, 4, 3, and 2. The significant values of both c.² and q. predict electrophilic reaction centers to be C4 or C2 and C5 or C7 for **9a** and **9h**, respectively. Similarly, one can easily predict electrophilic centers for other isomers, which however can be excluded from mechanistic considerations as they are relatively too unstable.

From all these observations, it is possible to propose a plausible mechanism for the reaction of **1** with benzene involving an initial intermediacy of **9a**' (Scheme 5). It should be commented on that another key intermediate formed in the reaction, dicationic species **10**, is responsible for the production of either of the resulting structures **11** and **12**, which are transformed into oximes **5** and **6** after quenching with water.

The reaction of **1** with cyclohexane may, in principle, proceed *via* three alternative pathways. The first one involves the participation of intermediate **9h**, which can react with cyclohexane to give 5,6,7,8-tetrahydro-1-nitronaphthalene initially (by analogy with similar reactions of quinoline and

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Table 1 PBE/cc-pVDZ calculated energies of the LUMO (ε_{LUMO}), thesquare of the coefficients on carbon atoms at the LUMO (c_i^2), NBOcharges (q_i) and PBE/ Λ 1 relative energies of structures **9a**-h^a

Structure, ^{<i>b</i>} q . ^{<i>c</i>} and $(c$. ²) ^{<i>c</i>}	$\varepsilon_{ m LUMO}$, eV	Relative energy, kcal mol ⁻¹
Cl ₃ ĀI—O _{,+} ,OH		
N 0.14 (0.01) 0.15 (0.09) 9a 0.21 (0.11)	-9.12	0.0
Cl ₃ Al-O,+,O N 0.26 (0.15) H + H 0.20 (0.05) 9b	-9.66	28.3
Cl ₃ ĀI-O,+,O N 0.21 (0.04) 9c	-9.30	26.3
$CI_3AI - O_{+,O}$ $V_{+,O}$ 0.25 (0.24) 0.28 (0.18) 9d	-9.36	25.7
Cl ₃ Al-O,+,O N 0.29 (0.23) 0.28 (0.19) H H H 9e	-9.34	21.4
Cl ₃ Al-O,+,O 0.21 (0.06) H + 0.31 (0.27) 9f	-9.29	25.2
Cl ₃ Al-O,+,O 0.34 (0.20) H H + 9g 0.20 (0.05) Ol Al-O O	-9.32	23.6
0.29 (0.21) 0.24 (0.24) 9h	-8.83	15.1

^{*a*} The calculations were performed with thermochemical ΔG (298.15 K) and Grimme's D3(BJ) dispersion corrections.^{11 *b*} The data are provided for the most stable stereoisomers (see the ESI). ^{*c*} These parameters are shown for the most significant values of q_i and c_i^2 .

isoquinoline)¹² followed by the nitro group reduction. However, the latter step is not in line with the reaction of 2 with cyclohexane leading to the formation of chlorinecontaining product 8. It is more likely, therefore, that intermediate 9a' is again involved in the reaction as shown in Scheme 6. This pathway implies, *de facto*, the intermediacy of 1-naphthylamine, which undergoes ionic hydrogenation to give 7 (*cf.* ref. 12 and 13). A separate experiment showed that 1-naphthylamine was indeed converted into 7, provided there is prior saturation of the reaction mixture with gaseous HCl, but at a somewhat slower rate than 1 (ESI†). This is under-



Scheme 5 Proposed mechanism for the reaction of 1 with benzene.



Scneme 6 Proposed mechanism for the reaction of 1 with cyclohexane.

standable in view of the different self-determined proton acidities in these two reactions. And lastly, the reaction of **1** with cyclohexane can include the intermediate formation of 4-chloro-1-naphthylamine by analogy with the conversion of **2** into **8**. In contrast to **8**, 4-chloro-1-naphthylamine can easily lose the chlorine (as is the case with 4-chloro-1-naphthol)¹⁴ to give back 1-naphthylamine and thereby 7.

Finally, the reaction of 2 with cyclohexane proceeds probably *via* nucleophilic attack of Cl^- on intermediate 4' resulting in the formation of 4-chloronitrosobenzene coordinated to AlCl₃ followed by its reduction (Scheme 7).

In conclusion, an excess of aluminum chloride can be successfully used instead of triflic acid to mediate the reaction of **1** with benzene. The new approach alters the reaction pathway and affords oximes **5** and **6** in good yields. It is also shown



that nitroarenes 1 and 2 undergo selective reduction with cyclohexane in the presence of $AlCl_3$ to give aromatic amines 7 and 8. In all respects, it is seen that the key intermediacy of superelectrophilic *O*-protonated complexes of 1 and 2 with aluminum chloride (structures 9a' and 4', respectively) is the best rationale for the observed reactions.

Conflicts of interest

There are no conflicts to declare.

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