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BEHAVIOUR OF SOME ISOLATED AND CONJUGATED UNSATURATED COMPOUNDS, ARENES AND AROMATIC HETEROCYCLES IN A Ni-Al/NaOH REDUCING SYSTEM

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Abstract: In this paper we present the results of some experiments in which substrates representing various unsaturated and aromatic systems were tested in reduction reactions with Ni-Al alloy in aqueous NaOH and we highlight the relationships between the structure and the reactivity of the investigated compounds. We have found that unsaturated compounds containing isolated double bonds carbon-carbon and polynuclear condensed ring aromatics present an advanced inertness to the reduction process by the aluminum component of the Ni-Al/NaOH system.

Unlike them, unsaturated compounds with C=C conjugated bonds are very reactive to the Ni-Al/NaOH system, 1,4 reduction processes being facilitated, behaviour attributed to the polar nature of the conjugated systems. The heterocyclic compounds have a higher reactivity than their homologues carbocyclic compounds.

Keywords: *aromatic compounds, GC-MS, Ni-Al alloy, reduction reaction, unsaturated compounds*

INTRODUCTION

The reduction method using Ni-Al alloy/NaOH is an intensively investigated topic [1-2], especially for its practical interest, being distinguished from heterogeneous catalysis with hydrogen and Raney nickel particularly through its technical simplicity and robustness [3-4], through mild reaction conditions [5] and the interaction with the environment and, last but not least, through the performing of reactions in water as solvent [5-7]. To these advantages there were gradually added various results reported in literature regarding selectivity and good yields for the reduction of various classes of organic compounds [8-9].

Our preliminary experiments [10-13] and the literature data [14-16] prove the concomitant existence of two possibilities of reduction reaction offered by the Ni-Al/NaOH system: heterogeneous catalysis and intermediate formation of some organoaluminic compounds, from which the most important reductive activity seems to be directly generated by the aluminum atoms.

The details of this mechanism are particularly important for an efficient exploitation of real interest preparative reactions and are still unknown at present. For this reason, the present research was focused mainly on the study of the direct action of the aluminum component from the Ni-Al/NaOH system on the organic compounds of different classes. For this purpose we worked with a substantial excess (5-10 times) of Ni-Al alloy that has allowed maintaining the composition and morphology of the solid reactant phase relatively constant and at the same time has placed the whole reactivity study in the favorable field for the mechanism reduction type where aluminum is the key reagent.

The arguments that led to the assumption that the main source of reduction in the Ni-Al/NaOH system originates in the aluminum atoms has been supplied by experiments performed with Ni-Al alloys with controlled content of aluminum [12] and some literature data [14-15].

In present paper, by using organic compounds from different classes as reducible substrates, we followed the reactions course by the structural and compositional analysis of intermediate and final products (including secondary products formed in lower proportions) to deduce the real course of the entire reduction process and to collect sufficient data for the subsequent of its mechanism. We have chosen GC-MS as a method of analysis, because is a rapid method that offers qualitative analysis about all the products in a mixture [17-18].

MATERIALS AND METHODS

General procedure: A 20 wt% aq NaOH solution was added dropwise to a mixture of substrate (specified quantities in Table 1) dissolved in dioxane or dioxane and ethanol and Raney Ni-Al alloy 50:50 wt% (Merck) within 15 minutes. The reaction mixture was stirred with heating for the appropriate time indicated in Table 1. The reaction progress was monitored by TLC using a mixture of ethyl acetate and petroleum ether as eluent. Then, the mixture was cooled to room temperature and filtered through Celite. The filtrate was neutralized with hydrogen chloride, extracted with diethyl ether (3 x 15 mL) and the organic layer was dried over anhydrous magnesium sulphate. The solvent was evaporated at normal pressure.

Apparatus: The composition of the mixture was determined by gas chromatography using a Carlo Erba HRGC 5300 instrument equipped with capillary column DB-1 type (10-30 m) and FID detector in temperature programmed regime. The structure of products was established by GC-MS using an Agilent 6890N gas chromatograph coupled to an Agilent 5975 mass spectrometer. The NMR spectra were recorded with a Bruker Advance DRX 400 spectrometer in $CDCl_3$.

Table 1. *Reduction of compounds* ***1-10*** *using Ni-Al alloy in aqueous NaOH*

Substrate		Reaction conditions					Products no.	Conversion* [%]
		Substr. [mmoles]	Ni-Al [mg]	Reaction media	T [°C]	Time [h]		
1	Unsaturated vegetable oils	2 g	1600	20 mL NaOH 20% 5 mL dioxane	90	9	no reaction	
2	Crotonic acid	5	360	5 mL NaOH 20%	50	5	**2a**	85
							2	15
3	Cinnamic acid	5	360	5 mL NaOH 20%	50	9	**3a**	90
							3	10
4	Naphthalene	3	800	10 mL NaOH 20% 5 mL dioxane 5 mL EtOH	80	15	no reaction	
5	Anthracene	3	800	10 mL NaOH 20% 5 mL dioxane 5 mL EtOH	80	15	no reaction	
		3	800	10 mL NaOH 20% 5 mL dioxane 5 mL EtOH	50 under sonication	15	**5a**	2
							5b	1
							5	97
6	Phenantrene	3	800	10 mL NaOH 20% 5 mL dioxane	90	16	**6a**	0,3
							6b	0,7
							6c	0,8
							6	98
7	2-Naphthol	3.5	800	10 mL NaOH 20% 5 mL dioxane 5 mL EtOH	80	15	**7a**	11
							7b	8
							7c	1
							7	80
8	3,3'-Dimethyl-2,2'-bipyridine	1.5	800	10 mL NaOH 20% 5mL dioxane 10mL EtOH	90	7	**8a**	7
							8	93
9	2-Methyl-quinoline	5	800	10 mL NaOH 20% 5 mL dioxane	70	12	**9a**	2
							9	98
10	4-Methyl-quinoline	5	800	10 mL NaOH 20% 5 mL dioxane	70	12	**10a**	3
							10	97

* Measured by GC

GC-MS analysis indicated formation of following reduction products identified by mass spectral and ^{1}H-NMR data:

Reduction of crotonic acid (2):
Butyric acid, 2a, m/z (%) = 89 (4) $[M+1]^{+}$, 88 (63) $[M]^{+\cdot}$, 87 (4) $[M-1]^{+}$, 71 (55) $[C_4H_7O]^{+}$, 60 (100) $[C_2H_4O]^{+}$; 45 (40) $[CO_2H]^{+}$
^{1}H-NMR: 0.96 ppm, t, 3H (CH_3); 1,61 ppm, m, 2H (CH_2 poz. β); 2.23 ppm, t, 2H (CH_2 poz. α); 10.52 ppm, s, 1H (COOH)

Reduction of cinnamic acid (3):
3-Phenylpropionic acid, 3a, m/z (%) = 151 (1) $[M+1]^{+}$, 150 (7) $[M]^{+\cdot}$, 149 (55) $[M-1]^{+}$, 133 (4) $[C_9H_9O]^{+}$, 105 (35) $[C_8H_9]^{+}$; 104 (100) $[C_8H_8]^{+}$, 103 (18) $[C_8H_7]^{+}$, 91 (83) $[C_7H_7]^{+}$, 77 (10) $[C_6H_5]^{+}$, 65 (14) $[C_5H_5]^{+}$, 45 (13) $[CO_2H]^{+}$
^{1}H-NMR: 2.67 ppm, t, 2H (CH_2 poz. α); 2.95 ppm, t, 2H (CH_2 poz. β); 7.26 ppm, m, 5H (C_6H_5); 10.51 ppm, s, 1H (COOH).

Reduction of naphthalene, 4. Only unreacted starting material was identified by GC-MS method.

Reduction of anthracene, 5, under sonication
1,2-Dihydroanthracene, **5a**, m/z (%) = 181 (15) $[M+1]^{+}$, 180 (100) $[M]^{+\cdot}$, 179 (92) $[M-1]^{+}$, 178 (75) $[M-2H]^{+}$, 165 (24) $[C_{13}H_9]^{+}$, 141 (12) $[C_{11}H_9]^{+}$, 94 (34) $[C_7H_{10}]^{+}$, 55 (15) $[C_4H_7]^{+}$
1,2,3,4-Tetrahydroanthracene, **5b**, m/z (%) = 183 (19) $[M+1]^{+}$, 182 (100) $[M]^{+\cdot}$, 181(21) $[M-1]^{+}$, 167 (38) $[C_{13}H_{11}]^{+}$, 166 (17) $[C_{13}H_{10}]^{+}$, 165 (31) $[C_{13}H_9]^{+}$, 141 (34) $[C_{11}H_9]^{+}$

Reduction of phenanthrene, 6
3,4-Dihydrophenanthrene, **6a**, m/z (%) = 181 (14) $[M+1]^{+}$, 180 (100) $[M]^{+\cdot}$, 179 (66) $[M-1]^{+}$, 165 (28) $[M-CH_3]^{+}$, 139 (4) $[C_{11}H_7]^{+}$, 89 (15) $[C_7H_5]^{+}$, 51 (1) $[C_4H_3]^{+}$
1,2,3,4-Hexahydrophenanthrene, ***cis***, **6b** and ***trans***, **6c**, m/z (%) = 183 (15) $[M+1]^{+}$, 182 (100) $[M]^{+\cdot}$, 167 (24) $[M-CH_3]^{+}$, 154 (44) $[C_{12}H_{10}]^{+}$, 141 (29) $[C_{11}H_9]^{+}$, 76 (4) $[C_6H_4]^{+}$

Reduction of 2-naphthol, 7
3,4-Benzocyclohexanol, **7a**, m/z (%) = 149 (8) $[M+1]^{+}$, 148 (100) $[M]^{+\cdot}$, 147 (23) $[M-1]^{+}$, 92 (7) $[C_7H_8]^{+}$, 91 (19) $[C_7H_7]^{+}$, 77 (6) $[C_5H_5]^{+}$, 65 (12) $[C_5H_5]^{+}$, 51 (2) $[C_4H_3]^{+}$, 39 (1) $[C_3H_3]^{+}$
Naphthalene, **7b**, m/z (%) = 129 (11) $[M+1]^{+}$, 128 (100) $[M]^{+\cdot}$, 127 (11) $[M-1]^{+}$, 102 (7) $[C_8H_6]^{+}$, 77 (3) $[C_5H_5]^{+}$, 51 (3) $[C_4H_3]^{+}$
1,2,3,4-Tetrahydronaphthalene, **7c**, m/z (%) = 133 (15) $[M+1]^{+}$, 132 (68) $[M]^{+\cdot}$, 131 (15) $[M-1]^{+}$, 104 (100) $[C_8H_8]^{+}$, 91 (33) $[C_7H_7]^{+}$, 65 (4) $[C_5H_5]^{+}$

Reduction of 3,3'-dimethyl-2,2'-bipyridine, 8
3,3'-Dimethyl-2-(2-piperidyl)-pirydine, 8a, m/z (%) = 190 (3) $[M]^{+}$, 120 (100) $[C_8H_{10}N]^{+}$, 70 (4) $[C_4H_8N]^{+}$

Reduction of 2-methylquinoline, 9

2-Methyl-1,2,3,4-tetrahydroquinoline, **9a**, m/z (%) = 147 (39) $[M]^{+\cdot}$, 132 (100) $[C_9H_{10}N]^+$, 117 (16) $[C_8H_7N]^+$, 91 (27) $[C_7H_7]^+$, 77 (6) $[C_6H_5]^+$, 65 (11) $[C_5H_5]^+$

Reduction of 4-methylquinoline, 10

4-Methyl-1,2,3,4-tetrahydroquinoline, **10a**, m/z (%) = 147 (56) $[M]^{+\cdot}$, 132 (100) $[C_9H_{10}N]^+$, 117 (20) $[C_8H_7N]^+$, 77 (6) $[C_6H_5]^+$

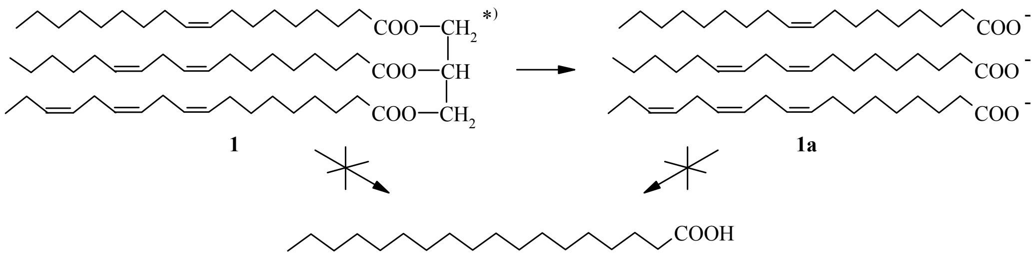
RESULTS AND DISCUSSION

Reduction of compounds containing carbon-carbon isolated double bonds

The reduction issue of reducible compounds containing only C=C isolated double bonds by Ni-Al alloy in base is interesting because such a structure presents the lowest polarity and therefore is the least suitable for a mechanism by direct electron transfer or any mechanism involving ionic or highly polarized intermediates.

As polar substrates of this type we selected five types of vegetable oils characterized by different content of unsaturated fatty acids (mainly oleic, linoleic, linolenic), all of them containing C=C isolated double bonds and mostly with *cis* configuration.

The chosen system allows for a quantitative determination of the reduction process with good accuracy by ^{1}H-NMR investigation of unsaturated proton signal intensities [19-21]. The details of this method and the experimental data have been presented in one of our previous works [11]. In this paper we present only the conclusions of this reduction experiment as shown in Figure 1.



*) - Schematic representation for unsaturated acids of vegetable oils

Figure 1. *Action of Ni-Al/NaOH system on unsaturated fatty acids of vegetable oils*

As is presented in Figure 1, our attempts to reduce all types of vegetable oils containing unsaturated acids with isolated double bonds in the Ni-Al/NaOH system prove the absence of any hydrogenation process. This result is in accordance with literature data: alkenes with C=C isolate bonds are considered generally unreactive to the Ni-Al reducing system both in basic medium and in formic acid [1]. However, there are reported some exceptions such as cyclooctatetraene, whose reduction by Ni-Al/NaOH stops at cyclooctene as final product, while catalytic hydrogenation using H_2/Ni-Raney leads to cyclooctane [1], thereby suggesting a difference of mechanism between the two hydrogenation modes.

Reduction of compounds containing carbon-carbon conjugated double bonds

In contrast to the inertness of alkenes with C=C isolated double bonds, there is a much higher reactivity of unsaturated systems with C=C conjugated double bonds. Figure 2 presents the results for the reduction of *α,β*-unsaturated carboxylic compounds, resulting almost total conversions in the hydrogenation of C=C conjugated double links carried out under mild reaction.

$$H_3C-CH=CH-COOH \longrightarrow H_3C-CH_2-CH_2-COOH$$

2 **2a**

$$H_5C_6-CH=CH-COOH \longrightarrow H_5C_6-CH_2-CH_2-COOH$$

3 **3a**

Figure 2. *Reduction of α,β-unsaturated carboxylic compounds*

Similar cases of easy and high conversions reduction using the Ni-Al/NaOH system have been reported in literature for *α,β*-unsaturated compounds including cinnamic acid derivatives substituted on the aromatic ring, cyclohexylidene-acetic acid or benzylideneacetone [1]. Related cases have been reported for *α,β*-unsaturated aldehydes [22-25].

Thus, doubles links from the conjugated systems (particularly *α,β*-unsaturated carboxyl and carbonyl compounds) show a much higher reactivity than isolated alkenes. The most likely explanation of this behaviour consists in the significant higher polarity of the above mentioned systems that allows a better adaptation of the asset contribution of electrons from aluminum atoms as reducing agent.

Reduction of aromatic compounds with condensed ring

In this paper we have studied the reduction by the Ni-Al/NaOH system of naphthalene, anthracene, phenanthrene and β-naphthol as representatives for the class of aromatic compounds with condensed ring; the results are presented in Figure 3.

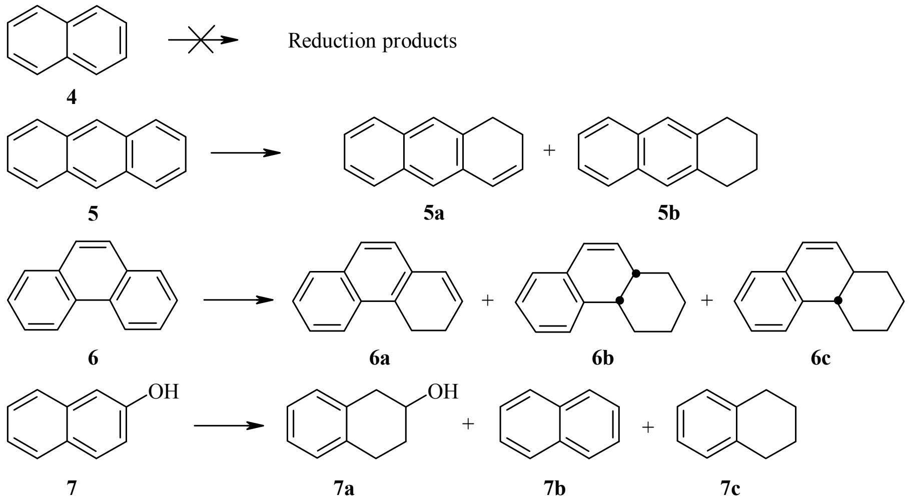


Figure 3. *Reduction of aromatic compounds with condensed ring*

The structures of 1,2-dihydroanthracene for compound **5a** and 1,2,3,4-tetrahydroanthracene for compound **5b** respectively derive from the fragmentation mechanisms shown in Figure 4.

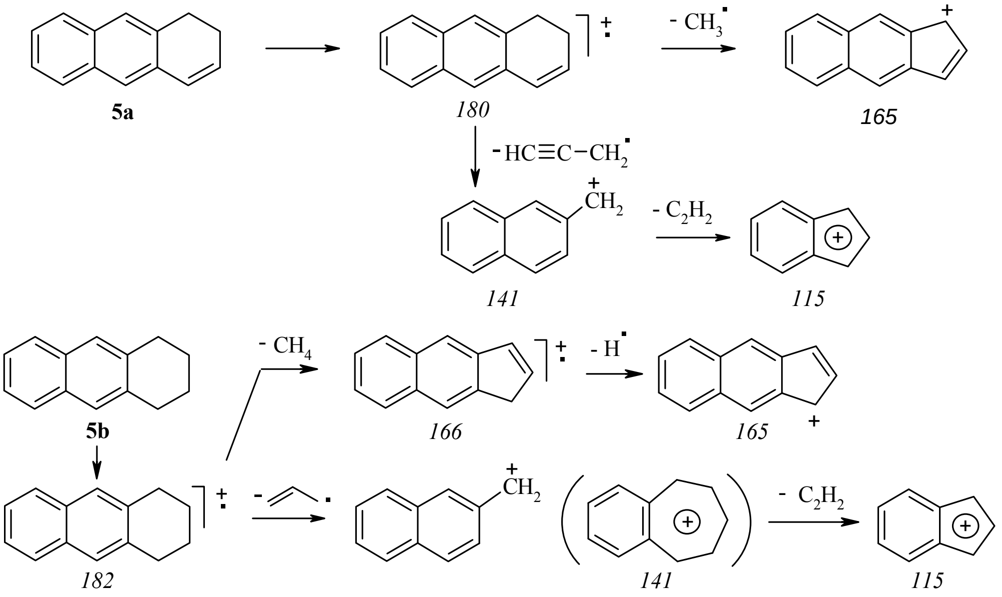


Figure 4. *Mass fragmentation pathways of compounds* ***5a*** *and* ***5b***

The structure of di- and tetrahydrogenated compounds with hydrogenation locating on the marginal ring (unusually, especially for a dihydroderivative) is supported by the fragmentation $m/z = 180 \rightarrow 165$ Da for the dihydroderivative **5a** and $m/z = 182 \rightarrow 166 \rightarrow 165$ Da for tetrahydroderivative **5b**.

A similar situation exists in the case of reducing products of phenanthrene, composed from hexahydroderivatives diastereoisomers **6b** and **6c**, where there is a correlation between the corresponding mass spectra and the fragmentation mechanism (Figure 5).

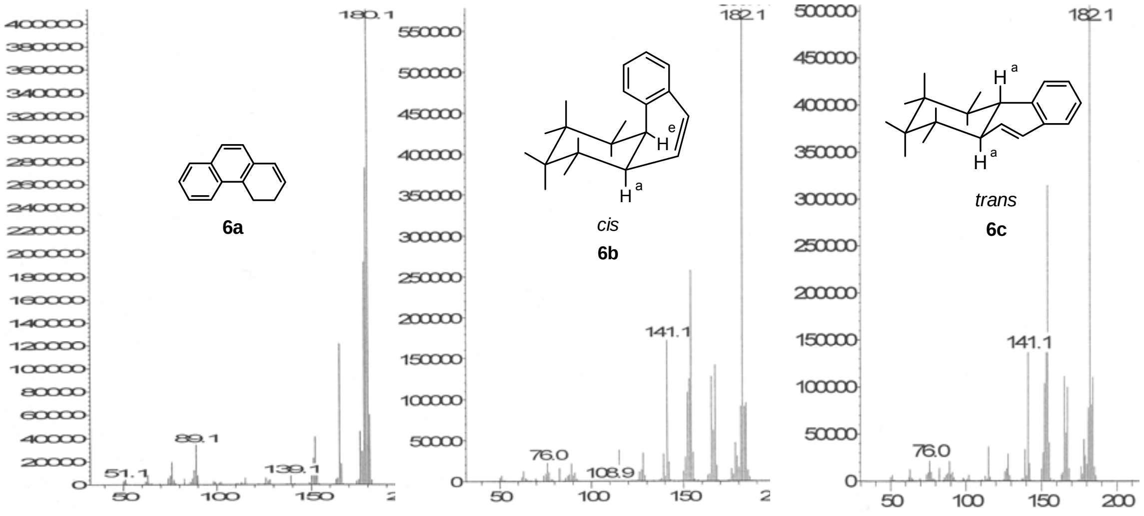


Figure 5. *Mass spectra of compounds* ***6a-6c*** *with assigned structures; cis configuration (**6b**) and trans configuration (**6c**) tentatively assigned*

Another reduction product of **6** has a molecular formula corresponding to dihydrophenanthrene, the most likely being the 3,4-dihydrophenanthrene, **6a**, as suggested by MS peak assignment.

In the case of the main reduction product of 2-naphthol, which is a tetrahydroderivative, the question which arises is in which of the aromatic rings of naphthalene hydrogenation occurs. Figure 6 on rationalizing of experimental mass spectrum shows that there are several fragments derived from a benzene ring which contains an OH substituent. The compound **7a** has the structure of 3,4-benzocyclohexanol, fact which is agreement with other results described in literature [1].

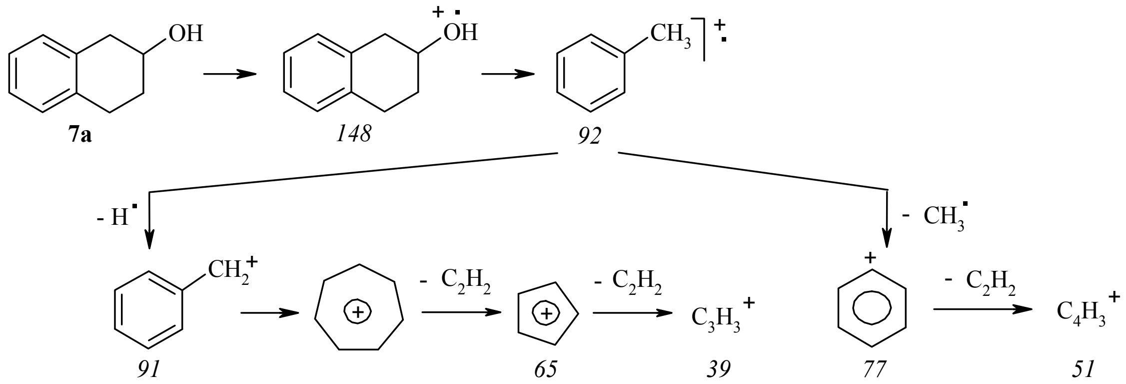


Figure 6. *Mass fragmentation pathways of compounds* ***7a***

Experimental results show a very low reactivity of these aromatic substrates, even with an excess of metal: naphthalene does not react at all, anthracene reacts only under ultrasonic field and conversions are very low. This is surprising because it was expected that, under the action of the metal reducing reagent, the 9,10-dihydroderivatives of anthracene or phenanthrene would have been easily achieved, knowing how easily these polynuclear systems lead to dihydroderivatives by reduction with metals and proton donors. The rationalization that we propose for this behaviour is related to the sterical incompatibility of the rigid planar geometry of aromatic compound with the solid phase or, more likely, two aluminum atoms must have access to different positions of aromatic substrate (1,4 at naphthalene and 9,10 at anthracene).

This interpretation is supported by the structure of the hydrogenation product, both phenanthrene and especially anthracene where the substrates do not show any tendency of reduction in the *meso* positions but aim at marginal positions (1,2 at anthracene and 3,4 at phenanthrene) suggesting that this approach is less sterically hindered. Unlike hydrocarbons, 2-naphthol presents a significantly higher reactivity, thus making possible the activation by transformation into tautomer with a *α,β*-unsaturated ketone structure that is a more reactive substrate (Figure 7).

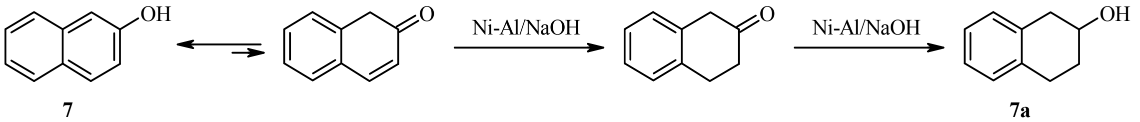


Figure 7. *Reduction of 2-naphthol by keto tautomer*

Reduction of heterocyclic aromatic compounds

The reduction reactions of heterocyclic aromatic compounds with isolated or condensed rings are shown in Figure 8.

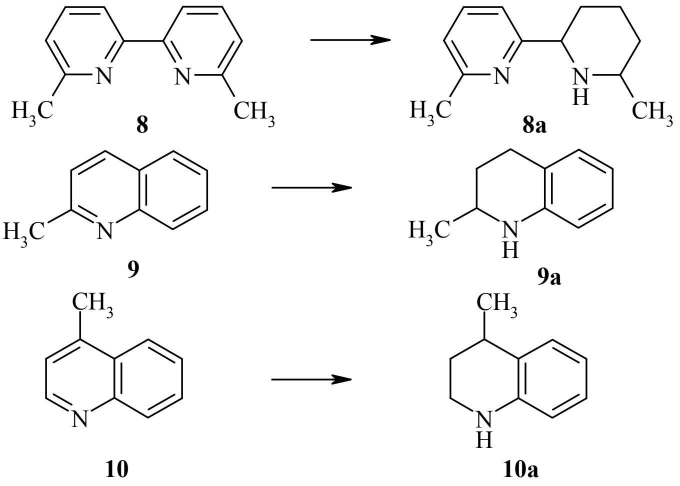


Figure 8. *Reduction of heterocyclic aromatic compounds*

For compound **8a** a structure of 1,2,3,4,5,6-hexahydroderivative is confirmed by identifying the corresponding fragment peak base of the 2,6-dimethylazatropylium cation for whose formation we suggest a rearrangement associated with fragmentation $m/z = 190 \rightarrow 120$ Da in Figure 9.

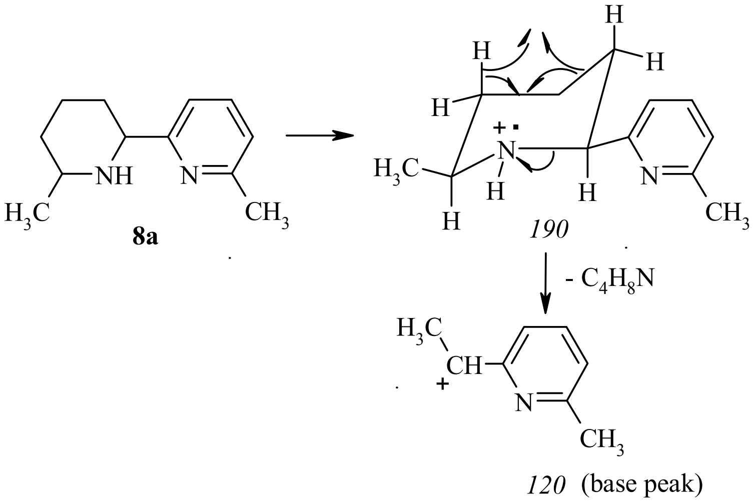


Figure 9. *Mass fragmentation pathways of compounds* ***8a***

The identification of 1,2,3,4-tetrahydroderivative structure for compound **9a** (and analogous compound **10a**) was based on the fragmentation mechanism proposed in Figure 10, in which there are highlighted the structures of the fragments with m/z = 65, 77 and 91 Da, demonstrating that the ring which does not react is benzene and therefore the heterocyclic aromatic ring is hydrogenated.

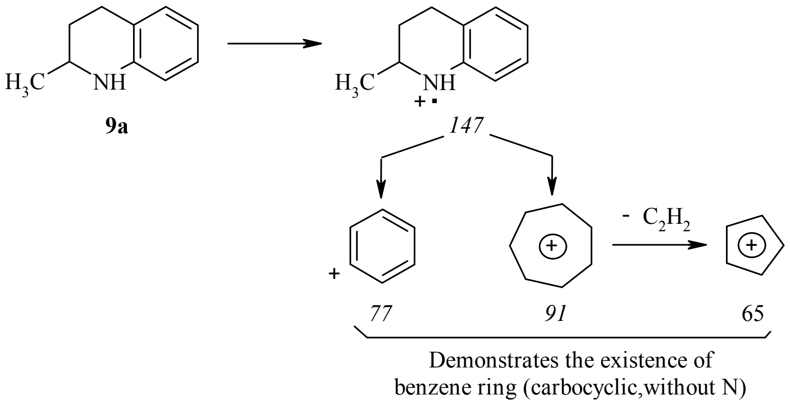


Figure 10. *Mass fragmentation pathways of compounds* ***9a***

We can observe that the reactivity of condensed heterocyclic systems is slightly higher than the corresponding carbocyclic systems, e.g. quinoline derivatives have small conversion while naphthalene does not react at all in the same conditions. Thus, the presence of heteroatoms increases reactivity in all cases, the heterocyclic ring being affected by hydrogenation.

The literature data concerning the reduction of 6-methylquinoline [26] confirms this observation. The aromatic isolated ring compounds (bipyridil type) shows a higher reactivity than the condensed ring, confirming the hypothesis of negative steric influence agreed above for carbocyclic polynuclear condensed systems. In this way, the results existing in literature on reducing of 3- and 4-methylpyridine and 2,2'-bipyridil confirm this behaviour. Under forced condition and extended reaction time a 68% conversion is reported in the complete hydrogenation of 2-phenylpyridine to 2-cyclohexylpiperidine [26].

CONCLUSIONS

The unsaturated compounds with conjugated carbon-carbon double bonds are highly reactive to the Ni-Al/NaOH system and 1,4 reduction reactions are facilitated.

Unlike unsaturated compounds with conjugated carbon-carbon double bonds, the unsaturated compounds containing isolated carbon-carbon double bonds, such as oleic acid, linoleic and linolenic acids from vegetable oils present advanced inertness to reduction by nickel-aluminum alloy in base.

The polynuclear condensed arenes (naphthalene, anthracene, phenanthrene) have a very low reactivity towards Ni-Al/NaOH because of the steric restrictions in the direct contact within between the solid phase organic substrate and the Ni-Al alloy. Reductions that occur (to a small extent) imply marginal positions (1,2).

The heterocyclic compounds present a higher reactivity than their carbocyclic analogues and are involved the ring containing heteroatom.

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