

## A GREEN APPROACH FOR THE SELECTIVE REDUCTION OF AROMATIC CARBONYL COMPOUNDS USING RANEY Ni-AL ALLOY

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**Abstract:** Given the significant environmental risk associated with the use of organic solvents and catalysts in the classic reduction reaction catalysts, we are interested in adapting the reaction medium and in developing an eco-friendly methodology for the synthesis of corresponding alcohols in reasonably yields. In this study, the reduction of some aromatic carbonyl compounds with Ni-Al alloy in aqueous alkaline medium was carried out in two versions: with 20 wt% aq NaOH and with 1 wt% aq NaOH without organic solvent. The structures of the reaction products are rigorously proven by gas chromatography-mass spectrometry (GC-MS). There was observed an increase of the reduction reaction rate when we used 1 wt% aq NaOH without addition of organic solvent. For a good part of the studied substrates high conversion and selectivity were achieved by employing mild reaction conditions, minimal environmental pollution and simple work up procedure, foreshadowing yields above 90 % and representing candidates for convenient preparative applications.

**Keywords:** *acetophenones, aqueous reduction, GC-MS, substituted benzaldehydes*

## INTRODUCTION

Aromatic carbonyl compounds are receiving considerable attention due to their importance as versatile intermediates in the construction of biologically active structural motifs, as well as to their status of main constituents of many natural products [1 – 3]. Although the Ni-Al alloy in aqueous alkaline solution reducing system type has been tested for a wide range of products, a systematic study of their relative reactivity has not yet been carried out. It is obvious that the reactivity of organic compounds towards the reduction reactions depends on the organic functions present in the molecule, as well as on the steric characteristics [4]. In addition, during the attack on Ni-Al alloy with an aqueous solution of NaOH, there is a change of nanometer dimensions of the cavities created by the elimination of the aluminium atom from the network alloy [1, 5 – 7] simultaneously with the modification of the relationship between the reduction through electrons transfer from aluminium and the catalytic reduction on nickel [8, 9]. These effects will lead to changes in interaction with various organic substrates with structural and/or stereo differences [10].

Various kinds of research that use methanol, ethanol, *i*-propanol, tetrahydrofuran *etc.* as co-solvent or reaction medium for reduction reaction has been reported [8, 10 – 12]. So, we are interested in adapting the reaction medium and in developing an eco-friendly methodology for the synthesis of corresponding alcohols in reasonable yields [13 – 14]. We aimed also to investigate the stereochemical aspects and to determine the structure-reactivity relationships in the reduction of carbonyl compounds with different degrees of steric hindrance in an aqueous medium and in the absence of the organic co-solvent.

## MATERIALS AND METHODS

Nickel-aluminium alloy composition Ni 50 wt% and Al 50 wt% was purchased from the company Merck as powder for the preparation of Raney nickel for synthesis. Other chemicals were commercially available as pure chemicals.

### GC-MS measurements

The structure of products was established by GC-MS using an Agilent 6890N gas chromatograph coupled to an Agilent 5975 mass spectrometer. The working parameters are: column DB-5MS, 30 m x 0.25 mm ID, 0.25  $\mu\text{m}$ , injector temperature 300  $^{\circ}\text{C}$ , flow rate 1.2  $\text{mL}\cdot\text{min}^{-1}$ , hydrogen carrier gas, 1 mL injection solution sample, temperature program 40-250  $^{\circ}\text{C}$ , hold time 10 minutes at 250  $^{\circ}\text{C}$ , quadrupole MS to interface the MS with electron impact ionization (EI), ionization potential 70 eV, range scan  $m/z = 30-400$ . Injected solutions were prepared in  $\text{CH}_2\text{Cl}_2$  high purity (0.2  $\mu\text{L}$  sample / 200  $\mu\text{L}$   $\text{CH}_2\text{Cl}_2$ ).

### Reduction experiments

*Typical procedure for method i:* In a two neck round-bottomed flask equipped with a magnetic stirrer and reflux condenser was placed the substrate (5 mmol) dissolved in 1,4-dioxane (5 mL) and Raney Ni-Al alloy 50 : 50 wt% (15 mmol, 800 mg). A 20 wt%

aq NaOH solution (10 mL) was added dropwise to the mixture within 15 minutes. The reaction mixture was stirred at 70 °C until for an appropriate time until the consumption of starting material. The reaction progress was monitored by TLC (eluent, ethyl acetate : petroleum ether - 8 : 2). 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 dried over anhydrous magnesium sulphate. After the evaporation of solvent at normal pressure, the resulting crude material was analyzed by GC-MS.

The method *ii* are in accordance with method *i*, except that 20 mL of 1 % wt% aq. NaOH were used and no added dioxane or any solvents.

## RESULTS AND DISCUSSION

To highlight the main reactions that take place in the presence of the Ni-Al/NaOH reducing system and of the relative influence of the substrate structure on the share of reduction products, there were chosen series of aldehydes **1-8** and ketones **9-11** (Table 1). The molar ratio of reagents was chosen so as to ensure a large excess of reducing agent (in aluminium equivalents): the amount Ni-Al alloy used provide an excess of 5-10 times than the stoichiometric amount required. We have opted for a large excess of the reducing agent to provide a relatively constant composition and morphology of the reactive solid phase during reaction and to place the entire reactivity study performed in this paper in a favourable field of the mechanism type in which aluminium (reactive metal) is the key reduction reagent. Arguments that led to the assumption that the main source of reduction in the Ni-Al/NaOH system comes from aluminium atoms were provided by our other experiments performed with Ni-Al alloys with controlled content of aluminium [15, 16].

**Table 1.** Reduction of aromatic carbonyl compounds **1-11** using Ni-Al / NaOH system

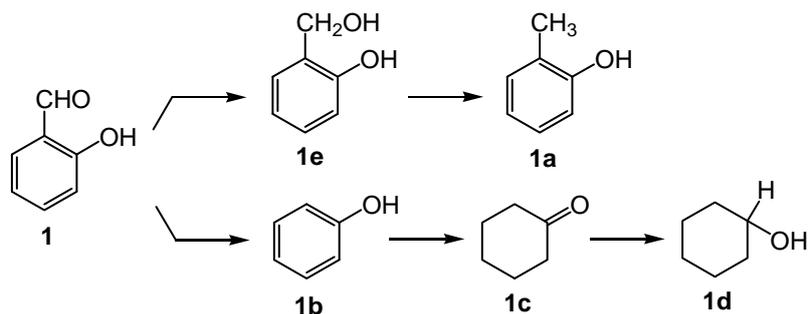
Substrate		Reaction condition	Reaction time [h]	Reduction products, Yield <sup>a</sup> [%]				
				a	b	c	d	e
<b>1</b>	Salicylaldehyde	<i>i</i>	1	82	2	5	3	-
		<i>ii</i>	5	28	27	-	-	39
<b>2</b>	4-Dimethylamino-benzaldehyde	<i>i</i>	9	24	1	6	-	-
		<i>ii</i>	1	55	37	4	2	-
<b>3</b>	3-Hydroxybenzaldehyde	<i>i</i>	1	96	1	2	-	-
<b>4</b>	3-Methoxybenzaldehyde	<i>i</i>	4	96	-	-	-	-
<b>5</b>	2,5-Dimethoxybenzaldehyde	<i>i</i>	11	44	-	-	-	-
<b>6</b>	Terephthalic aldehyde	<i>i</i>	2	4	93	3	-	-
<b>7</b>	3-Nitrobenzaldehyde	<i>i</i>	7	36	6	29	26	-
<b>8</b>	Cinnamaldehyde	<i>i</i>	2	25	55	3	-	-
		<i>ii</i>	2	7	87	2	-	-
<b>9</b>	Acetophenone	<i>i</i>	5	45	35	20	-	-
<b>10</b>	4-Ethylacetophenone	<i>i</i>	72	94	-	-	-	-
<b>11</b>	4-Chloroacetophenone	<i>i</i>	72	47	49	1	-	-

*i* – 5 mmol substrate, 5 mL dioxane, 800 mg Ni-Al alloy, 10 mL of 20 wt% aq NaOH

*ii* – 5 mmol substrate, 800 mg Ni-Al alloy, 20 mL of 1 wt% aq NaOH

<sup>a</sup>Measured by GC

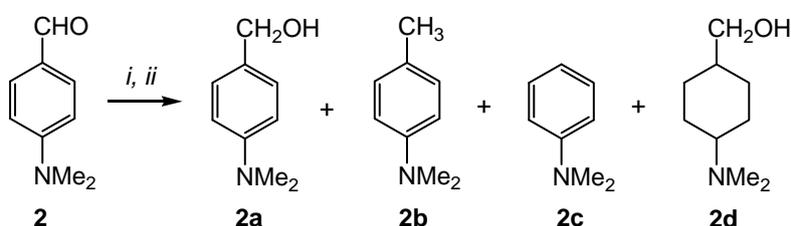




**Figure 3.** Reaction sequences of salicylaldehyde selective reduction

Thus, the main route of reduction leads successively to **1e** and then **1a** products. The formation of the total reduction carbonyl group ( $\text{CHO} \rightarrow \text{CH}_3$ ) was observed in other cases both in aldehydes [12, 17 – 19] and in ketones [20 – 22]. At higher temperatures or longer in reaction times it tends to become the main product, with the selectivity for preparative interest [21]. According to our previous work [15, 16, 23, 24] and literature data [1, 25], the total reduction of carbonyl group is facilitated by their vicinity of an aromatic ring. An unexpected secondary reaction, reflecting reductive cleavage of a less polar C-C bond, but observed for other aromatic carbonyl compounds, consists in the reductive elimination of the formyl group (products **1b**, **1c**, **1d**) and those coming from other substituted benzaldehydes as it will be seen further (products **2c**, **3c**, **6c**). As shown in the proportion in which these products occur, it follows that, most probably, they may be generated directly from the aldehyde and not from intermediates which suffered reductions. Unexpectedly, between the products of phenolic ring we can find cyclohexanone **1c**, which prevails over cyclohexanol **1d**. This proves that cyclohexanone is the primary product isolated in the reduction of the phenolic ring. A possible explanation for this progress of reaction could be the involvement in the reduction of a ketone tautomeric form, case also recorded in the literature [26].

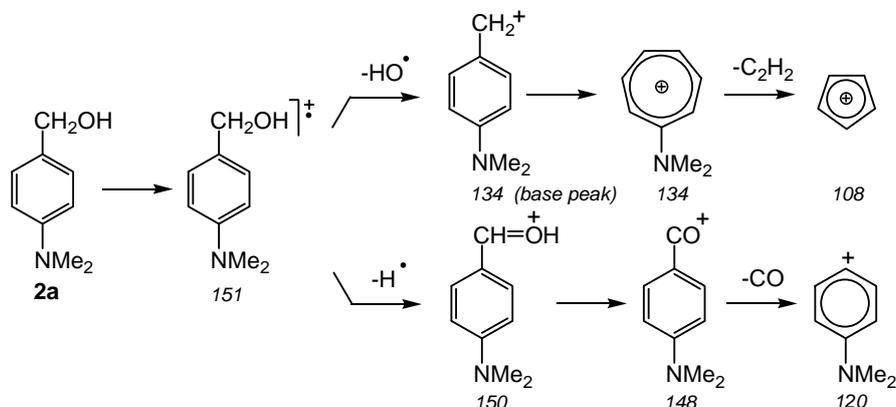
**The reduction of 4-dimethylaminobenzaldehyde 2** is described in Figure 4 and it reflects the same type of products distribution as in the case of salicylaldehyde reduction. The reduction of compound **2** was also performed for different concentrations of alkaline solution, noting the same increase in reaction rate when using 1 wt% aq NaOH.



**Figure 4.** Reduction of 4-dimethylaminobenzaldehyde using Ni-Al/NaOH

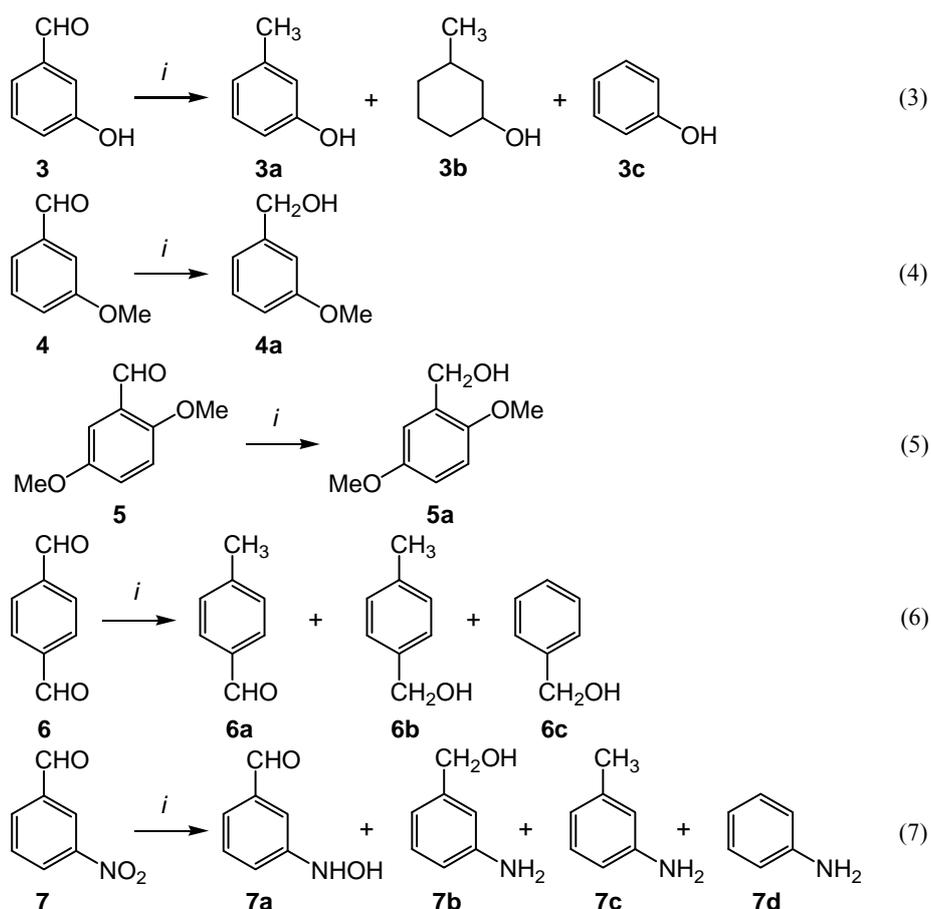
It is possible that the differences observed should be related to the solubility and diffusion of reagents and products in the area of solid phase. This interpretation is supported by the increase of the reaction rate when the reduction is carried out in ultrasounds field [27].

The structures of the products from Figure 4 have been rigorously proven by GC-MS. We mention here just the perfect concordance of peaks in the mass spectrum of the main product **2a** with the fragmentation mechanism proposed in Figure 5.



**Figure 5.** Mass fragmentation of compound **2a**

The reduction of substituted benzaldehydes **3-7** was performed only in standard conditions (20 wt% aq NaOH) and the results are shown in Figure 6.



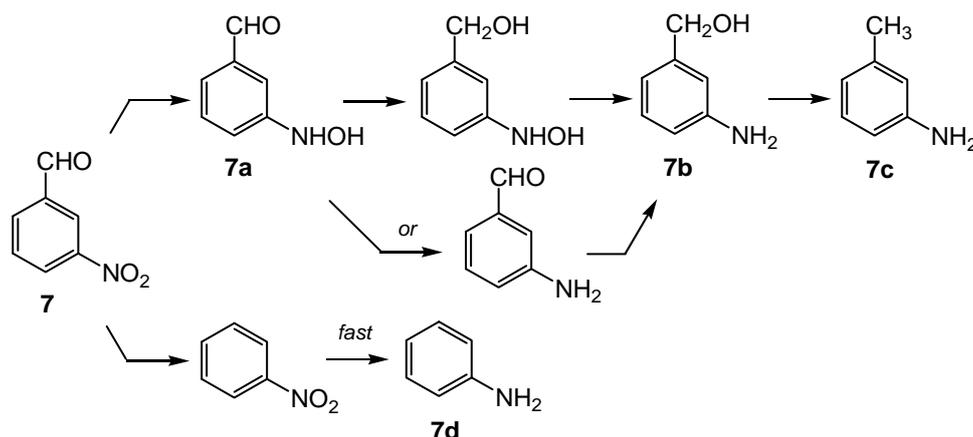
**Figure 6.** Reduction of compounds **3-7** using Ni-Al/NaOH

The experiment results described in Figure 6 show the very selective course of reactions (3), (4) and (6) offering a main product with an almost quantitative yield (93-96 %), being valuable as preparative methods. Reaction (5) also shows a very high selectivity, but conversion is lower. The increase of reaction time and/or the temperature could probably improve the preparative value.

Even if the reaction conditions are not fully comparable, we can broadly see the reactivity dependence on the nature of substituent. Thus, the electron-attracting substituents increase the selectivity (eg. CHO group of substrate **6**) and the repulsive-electron substituents reduce the reactivity (eg. 2,5-dimethoxy groups of substrate **5**). This observation is in agreement with an ionic mechanism (concentration of negative charge in the transition state).

For the reduction product (**6b**) of terephthalic aldehyde is difficult to predict the structure because one of the formyl groups is reduced to methylol and other to methyl with a selectivity of 93 %.

In the case of compound **7** a moment is caught in the development of a complex reductive process, which is still unfinished. There are products for intermediate and final reduction of both functions: -NHOH and -NH<sub>2</sub> (from -NO<sub>2</sub>) and -CH<sub>2</sub>-OH, -CH<sub>3</sub> and -H (from -CH=O). The most probable sequence of reactions responsible for the formation of these products is proposed in Figure 7.

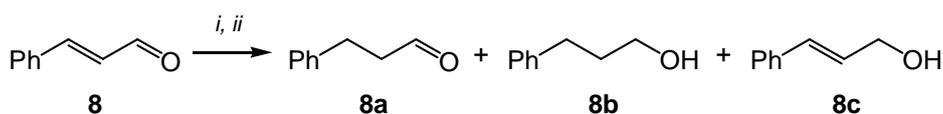


**Figure 7.** Reaction sequences of 3-nitrobenzaldehyde selective reduction

Therefore, the reduction of 3-nitrobenzaldehyde leads to several products in similar proportions, especially due to different stages of reduction of carbonyl group: reductive elimination, reduction at benzyl alcohol and methyl; in turn the nitro group implies, as intermediate stage, forming the derivative hydroxylamine. For these reasons, the studied reduction procedure leaves little hope for preparative applications.

### Reduction of cinnamaldehyde **8**

In the case of cinnamaldehyde **8** the competition between the reductions in positions 1,4 and 1,2 is targeted. The results presented in Figure 8 show without doubt that 1,4-reduction prevails on 1,2-reduction, the proportion having been between 80 : 3 and 94 : 2 as shown by the conversion ratio (**8a** + **8b**) / **8c**.

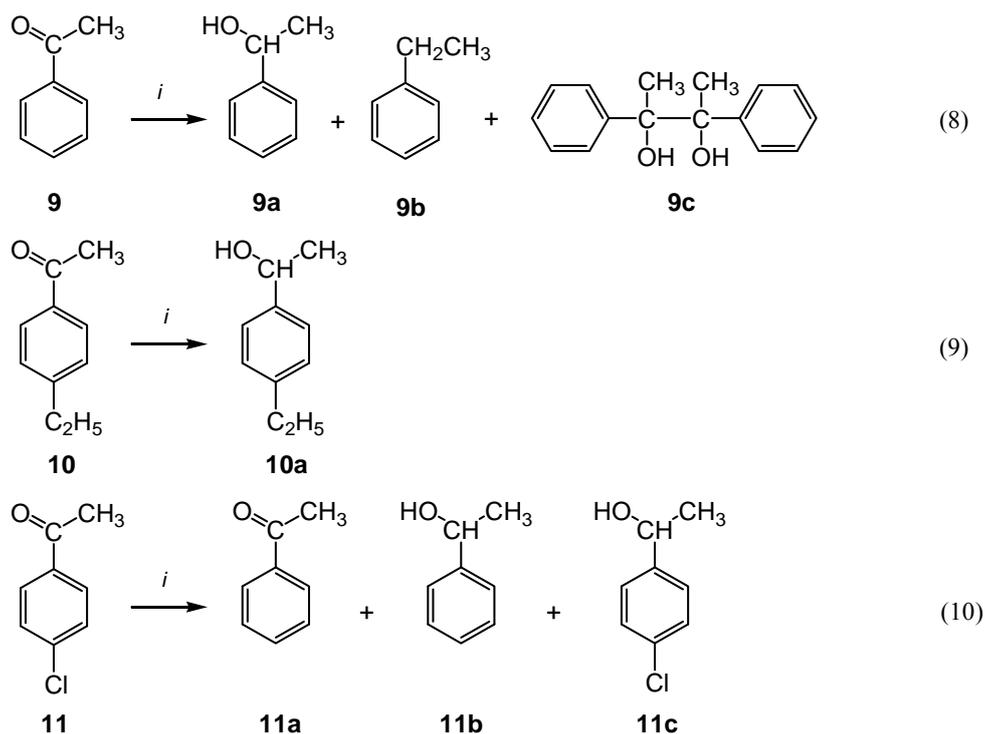


**Figure 8.** Reduction of cinnamaldehyde using Ni-Al/NaOH system

After the 1,4-reduction occurred with the formation of 3-phenylpropanal **8a**, the reduction process of aldehyde group continues so that at a longer reaction time, or dilution conditions (1 wt% aq NaOH) where reduction occurs rapidly, the selectivity in 3-phenylpropanol **8b** could reach 87-94 %.

**The reductions of compounds 9-11** are shown in Figure 9.

The possibility of formation of several types of products is highlighted: the corresponding secondary alcohol **9a**, the complete reduction product of carbonyl group **9b** and pinacolic coupling products **9c**. However, in some cases, subsequent reactions can be prevented by controlling reaction time and raising the selectivity towards preparative interest values (94 % for ketone **10**). From the composition of the crude reaction product shown in Figure 9, reaction (10), it results that the reduction processes of carbonyl group and the reductive elimination of halogen are simultaneously, with a higher rate for dehalogenation.



**Figure 9.** Reduction of compounds **9-11** using Ni-Al/NaOH

Although the reductive dehalogenation is faster than the reduction of carbonyl group, the reaction is not selective enough to expect efficient preparative applications but for the final reduction product **11b**. In this case there are not detected reduction products at aromatic ring or secondary benzyl alcohol function.

### **Spectral data**

GC-MS analysis indicated formation of following reduction products identified by mass spectral data:

#### **Reduction of salicylaldehyde 1:**

*o*-Cresol, **1a**, GC (R.T., min): 11.381; MS (m/z, (relative abundance, %)): 108 ( $M^+$ , 100), 107 (M-1, 87), 91 ( $C_7H_7$ , 24), 77 ( $C_6H_5$ , 38), 65 ( $C_5H_5$ , 4), 51 ( $C_4H_3$ , 1).

Phenol, **1b**, GC (R.T., min): 9.052; MS (m/z, (relative abundance, %)): 94 ( $M^+$ , 100), 66 ( $C_5H_6$ , 31), 40 ( $C_3H_4$ , 16).

Cyclohexanone, **1c**, GC (R.T., min): 6.442; MS (m/z, (relative abundance, %)): 98 ( $M^+$ , 51), 83 ( $C_5H_7O$ , 12), 70 ( $C_4H_6O$ , 32), 55 ( $C_4H_7$ , 100), 42 ( $C_2H_2O$ , 63).

Cyclohexanol, **1d**, GC (R.T., min): 6.180; MS (m/z, (relative abundance, %)): 100 ( $M^+$ , 2), 83 ( $C_6H_{11}$ , 52), 67 ( $C_5H_7$ , 29), 57 ( $C_4H_9$ , 100).

2-Hydroxybenzylic alcohol, **1e**, GC (R.T., min): 17.530; MS (m/z, (relative abundance, %)): 124 ( $M^+$ , 25), 107 (M-OH, 21), 106 (M- $H_2O$ , 55), 78 ( $C_6H_6$ , 100), 77 ( $C_6H_5$ , 36), 51 ( $C_4H_3$ , 22).

#### **Reduction of 4-dimethylaminobenzaldehyde 2:**

4-(*N,N*-dimethylamino)-benzylic alcohol, **2a**, GC (R.T., min): 22.710; MS (m/z, (relative abundance, %)): 151 ( $M^+$ , 50), 150 (M-1, 31), 148 ( $C_9H_{10}ON$ , 24), 134 ( $C_9H_{12}N$ , 100), 120 ( $C_8H_{10}N$ , 16), 108 ( $C_7H_{10}N$ , 10), 77 ( $C_6H_5$ , 14).

4-Methyl-(*N,N*-dimethylaniline), **2b**, GC (R.T., min): 15.157; MS (m/z, (relative abundance, %)): 135 ( $M^+$ , 68), 134 (M-1, 100), 119 (M- $CH_3$ , 14), 91 ( $C_7H_7$ , 21) [ $C_7H_7$ ] $^+$ , 65 ( $C_5H_5$ , 9).

*N,N*-Dimethylaniline, **2c**, GC (R.T., min): 12.409; MS (m/z, (relative abundance, %)): 121 ( $M^+$ , 75), 120 (M-1, 100), 77 ( $C_6H_5$ , 25), 51 ( $C_4H_3$ , 13).

1-(*N,N*-Dimethylaminocyclohexane)-methanol, **2d**, GC (R.T., min): 18.634, 19.357 (*cis* + *trans*); MS (m/z, (relative abundance, %)): 151 ( $M^+$ , 13), 126 (M- $CH_2OH$ , 2), 84 ( $C_6H_{12}$ , 100), 69 ( $C_5H_9$ , 36), 44 (N( $CH_3$ ) $_2$ , 13).

#### **Reduction of 3-hydroxybenzaldehyde 3:**

*m*-Cresol, **3a**, GC (R.T., min): 12.024; MS (m/z, (relative abundance, %)): 108 ( $M^+$ , 100), 107 (M-1, 94), 79 ( $C_6H_5+2H$ , 37), 77 ( $C_6H_5$ , 35), 51 ( $C_4H_3$ , 11).

3-Methylcyclohexanol, **3b**, GC (R.T., min): 7.880; MS (m/z, (relative abundance, %)): 114 ( $M^+$ , 2), 97 (M-OH, 53), 81 ( $C_6H_9$ , 77), 71 ( $C_5H_{11}$ , 100), 44 ( $C_2H_4O$ , 44).

Phenol, **3c**, GC (R.T., min): 9.047; MS (m/z, (relative abundance, %)): 94 ( $M^+$ , 100), 66 ( $C_5H_6$ , 29), 44 ( $CH_2CHOH$ , 12).

#### **Reduction of 3-methoxybenzaldehyde 4:**

3-Methoxybenzylic alcohol, **4a**, GC (R.T., min): 18.371; MS (m/z, (relative abundance, %)): 138 ( $M^+$ , 100), 137 (M-1, 29), 109 ( $C_6H_5O_2$ , 64), 94 ( $C_6H_7O$ , 29), 91 ( $C_7H_7$ , 14), 77 ( $C_6H_5$ , 50), 51 ( $C_4H_3$ , 14).

#### **Reduction of 2,5-dimethoxybenzaldehyde 5:**

2,5-Dimethoxybenzylic alcohol, **5a**, GC (R.T., min): 23.822; MS (m/z, (relative abundance, %)): 168 ( $M^+$ , 100), 153 (M- $CH_3$ , 22), 137 (M- $OCH_3$ , 30), 110 (M- $CO(CH_3)_2$ , 26), 106 (M-2( $OCH_3$ ), 14), 65 ( $C_5H_5$ , 29).

#### **Reduction of terephthalaldehyde 6:**

4-Methylbenzaldehyde, **6a**, GC (R.T., min): 12.134; MS (m/z, (relative abundance, %)): 120 ( $M^+$ , 86), 119 (M-1, 100), 105 (M- $CH_3$ , 1), 91 ( $C_7H_7$ , 95), 65 ( $C_5H_5$ , 26).

*4-Methylbenzyl alcohol, 6b*, GC (R.T., min): 13.741; MS (m/z, (relative abundance, %)): 122 ( $M^+$ , 90), 107 (M-CH<sub>3</sub>, 100), 93 (C<sub>7</sub>H<sub>7</sub>+2H, 44), 91 (C<sub>7</sub>H<sub>7</sub>, 75), 79 (C<sub>6</sub>H<sub>5</sub>+2H, 72), 77 (C<sub>6</sub>H<sub>5</sub>, 65), 65 (C<sub>5</sub>H<sub>5</sub>, 25), 51 (C<sub>4</sub>H<sub>3</sub>, 16).

*Benzyl alcohol, 6c*, GC (R.T., min): 10.679; MS (m/z, (relative abundance, %)): 108 ( $M^+$ , 80), 107 (M-1, 57), 91 (C<sub>7</sub>H<sub>7</sub>, 17), 79 (C<sub>6</sub>H<sub>5</sub>+2H, 100), 77 (C<sub>6</sub>H<sub>5</sub>, 70), 51 (C<sub>4</sub>H<sub>3</sub>, 29), 44 (C<sub>2</sub>H<sub>4</sub>O, 21).

**Reduction of 3-nitrobenzaldehyde 7:**

*3-Hydroxyaminobenzaldehyde, 7a*, GC (R.T., min): 15.162; MS (m/z, (relative abundance, %)): 136 (M-1, 7), 134 (C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>N, 100), 119 (C<sub>7</sub>H<sub>5</sub>ON, 15), 91 (C<sub>7</sub>H<sub>7</sub>, 21).

*3-Aminobenzyl alcohol, 7b*, GC (R.T., min): 19.860; MS (m/z, (relative abundance, %)): 123 ( $M^+$ , 100), 106 (M-OH, 28), 94 (C<sub>6</sub>H<sub>8</sub>, 94), 77 (C<sub>6</sub>H<sub>5</sub>, 70), 65 (C<sub>5</sub>H<sub>5</sub>, 24), 44 (C<sub>2</sub>H<sub>4</sub>O, 18).

*3-Methylaniline, 7c*, GC (R.T., min): 12.041; MS (m/z, (relative abundance, %)): 107 ( $M^+$ , 94), 106 (M-1, 100), 91 (C<sub>7</sub>H<sub>7</sub>, 4), 77 (C<sub>6</sub>H<sub>5</sub>, 20), 51 (C<sub>4</sub>H<sub>3</sub>, 6).

*Aniline, 7d*, GC (R.T., min): 8.942; MS (m/z, (relative abundance, %)): 93 ( $M^+$ , 100), 66 (C<sub>5</sub>H<sub>6</sub>, 33), 40 (C<sub>3</sub>H<sub>4</sub>, 5).

**Reduction of cinnamaldehyde 8:**

*3-Phenylpropanal, 8a*, GC (R.T., min): 14.604; MS (m/z, (relative abundance, %)): 134 ( $M^+$ , 53), 92 (C<sub>7</sub>H<sub>8</sub>, 72), 91 (C<sub>7</sub>H<sub>7</sub>, 100), 78 (C<sub>6</sub>H<sub>6</sub>, 52), 77 (C<sub>6</sub>H<sub>5</sub>, 31), 44 (CH<sub>2</sub>CHO, 27).

*3-Phenylpropanol, 8b*, GC (R.T., min): 16.561; MS (m/z, (relative abundance, %)): 136 ( $M^+$ , 28), 118 (M-H<sub>2</sub>O, 56), 117 (C<sub>9</sub>H<sub>9</sub>, 100), 92 (C<sub>7</sub>H<sub>8</sub>, 44), 91 (C<sub>7</sub>H<sub>7</sub>, 92), 77 (C<sub>6</sub>H<sub>5</sub>, 10), 65 (C<sub>5</sub>H<sub>5</sub>, 17).

*1-Phenyl-1-propen-3-ol, 8c*, GC (R.T., min): 18.650; MS (m/z, (relative abundance, %)): 134 ( $M^+$ , 54), 117 (M-OH, 57), 103 (M-CH<sub>2</sub>OH, 50), 92 (C<sub>7</sub>H<sub>8</sub>, 83), 91 (C<sub>7</sub>H<sub>7</sub>, 82), 78 (C<sub>6</sub>H<sub>6</sub>, 61), 77 (C<sub>6</sub>H<sub>5</sub>, 54), 51 (C<sub>4</sub>H<sub>3</sub>, 1), 44 (C<sub>2</sub>H<sub>4</sub>O, 100).

**Reduction of acetophenone 9:**

*1-Phenylethanol, 9a*, GC (R.T., min): 11.660; MS (m/z, (relative abundance, %)): 122 ( $M^+$ , 34), 107 (M-CH<sub>3</sub>, 100), 105 (M-OH, 38), 79 (C<sub>6</sub>H<sub>5</sub>+2H, 95), 77 (C<sub>6</sub>H<sub>5</sub>, 71), 51 (C<sub>4</sub>H<sub>3</sub>, 29).

*Ethylbenzene, 9b*, GC (R.T., min): 13.818; MS (m/z, (relative abundance, %)): 106 ( $M^+$ , 30), 91 (C<sub>7</sub>H<sub>7</sub>, 100), 77 (C<sub>6</sub>H<sub>5</sub>, 9), 65 (C<sub>5</sub>H<sub>5</sub>, 12), 51 (C<sub>4</sub>H<sub>3</sub>, 11).

*2,3-Diphenyl-2,3-butanediol, 9c*, GC (R.T., min): 22.199; MS (m/z, (relative abundance, %)): 121 (C<sub>8</sub>H<sub>9</sub>O, 100), 106 (C<sub>7</sub>H<sub>6</sub>O, 16), 44 (C<sub>2</sub>H<sub>4</sub>O, 63).

**Reduction of 4-ethylacetophenone 10:**

*1-(4-Ethylphenyl)-ethanol, 10a*, GC (R.T., min): 17.327; MS (m/z, (relative abundance, %)): 150 ( $M^+$ , 8), 132 (M-OH, 42), 117 (C<sub>9</sub>H<sub>9</sub>, 100), 79 (C<sub>6</sub>H<sub>5</sub>+2H, 33), 43 (C<sub>3</sub>H<sub>7</sub>, 11).

**Reduction of 4-chloroacetophenone 11:**

*Acetophenone, 11a*, GC (R.T., min): 11.762; MS (m/z, (relative abundance, %)): 120 ( $M^+$ , 40), 105 (M-CH<sub>3</sub>, 100), 77 (C<sub>6</sub>H<sub>5</sub>, 81), 51 (C<sub>4</sub>H<sub>3</sub>, 28).

*1-Phenylethanol, 11b*, GC (R.T., min): 11.661; MS (m/z, (relative abundance, %)): 122 ( $M^+$ , 34), 107 (M-CH<sub>3</sub>, 100), 105 (M-OH, 38), 79 (C<sub>6</sub>H<sub>5</sub>+2H, 95), 77 (C<sub>6</sub>H<sub>5</sub>, 71), 51 (C<sub>4</sub>H<sub>3</sub>, 29).

*1-(4-Chlorophenyl)-ethanol, 11c*, GC (R.T., min): 17.395; MS (m/z, (relative abundance, %)): 156 ( $M^+$ , 22), 141 (M-CH<sub>3</sub>( $M^+$ ), 100), 112 (C<sub>6</sub>H<sub>5</sub>Cl, 29), 103 (C<sub>6</sub>H<sub>6</sub>OCl, 29), 77 (C<sub>6</sub>H<sub>5</sub>( $M^+$ ), 83), 44 (C<sub>2</sub>H<sub>4</sub>O, 39).

## CONCLUSIONS

The conventional reduction reaction of aromatic aldehydes and ketones with Ni-Al alloy requires longer reaction times for the completion of the reaction. In contrast, there was observed an increase of the reduction reaction rate when we used 1 wt% aq NaOH without addition of co-solvent.

For aromatic carbonyl compounds, three types of reduction reactions, apparently independent, have been reported: reduction of carbonyl group to alcohol, reductive elimination of the carbonyl group (formyl, acetyl) and total hydrogenation of aromatic ring. The last two processes occur with relatively low rates, the latter being likely to occur by 1,4-reduction of tautomeric forms (for phenolic substrates) or by heterogeneous catalysis.

For a large part of the studied substrates (salicylaldehyde, 3-hydroxybenzaldehyde, 3-methoxybenzaldehyde, terephthalaldehyde, 4-ethylacetophenone) high conversions and selectivities were obtained by using 1 wt% aq NaOH without addition of co-solvent, envisaging yields more than 90% and accounting candidates for convenient preparative applications.

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