

Selective catalytic hydrogenation of unsaturated derivatives of nitrobenzene in alcoholic media

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Abstract

The catalytic hydrogenation of nitrobenzylic ethers (4-nitrobenzylallylether and 4-nitrobenzylcrotylether) into the corresponding unsaturated amines, in ethanolic solutions containing different concentrations of KOH, was investigated. Platinum catalysts supported on graphite were used. Increasing selectivities were obtained with increasing KOH concentrations, the basicity of the solution affecting more the hydrogenation rate of C=C bonds than that of the –NO₂ group. However, the formation of dimer intermediates which are difficult to hydrogenate restricts the yields in unsaturated amines. The selectivity in 4-aminobenzylcrotylether is higher (64%) than the selectivity in 4-aminobenzylallylether (50%). The steric effect and/or the electronic donor effect of the methyl group could account for this result. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic hydrogenation; Selectivity; Nitrobenzene; Carbon double bond (C=C); Platinum catalysts

1. Introduction

Primary amines with an unsaturated lateral chain are widely used as intermediate compounds in organic synthesis. They are known as enzyme inhibitors, such as dopamine β-hydroxylase [1–5], in the purpose to improve the cardiac rhythm and the arterial pressure. They are prepared generally by a multi-step synthesis involving protection of the amine group [6].

Another method consists in the selective reduction of the corresponding nitro compound in amine. This method, which is interesting for industrial applications, presents the problem of selectivity, since several unsaturated groups (such as C=C, NO₂ and benzenic ring) can be competitively reduced. The selective catalytic hydrogenation can be an attractive and elegant method, allowing to use only one preparation step and experimental conditions being milder and less polluting than the classical methods of organic synthesis.

However, the selective catalytic hydrogenation of the –NO₂ group, in the presence of C=C (or C≡C) groups, is very difficult to

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achieve [7] and only few works were devoted to this subject in the literature [7–9]. Indeed, it is known that the hydrogenation of an $-\text{NO}_2$ aromatic group is possible generally in the presence of other unsaturated groups (with Ni or Pd catalysts) with the exception of $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ groups [7].

There are only some exceptional cases involving molecules with a special steric crowding near the $\text{C}=\text{C}$ (or $\text{C}\equiv\text{C}$) bond, which hinders the contact between this function and the catalyst surface [10–13]. This behaviour led Onopchenko et al. [14] to protect the acetylene portion of (3-nitrophenyl) acetylene by a blocking bulky group (as the dimethyl carbinol). These authors succeeded, by this method, to hydrogenate selectively the NO_2 group of this compound, with ruthenium catalysts, and to obtain high yields of the corresponding unsaturated amine. Cobalt polysulfide and ruthenium sulfide catalysts were also used to achieve this selective catalytic hydrogenation, which, however, competes with the hydration of the acetylene group and also with condensation reactions [15].

Blout and Silverman [16] could hydrogenate nitrocinnamic acid esters in aminocinnamic acid esters with Raney nickel catalysts (at 20–30°C and under 2–3 atmospheres of hydrogen), but the reduction of $\text{C}=\text{C}$ occurs also after the reduction of the nitro group. Moreover, the presence of impurities in the nitro compounds causes a poisoning of nickel or noble metal catalysts (mainly at high temperatures) and a loss of selectivity [16].

Braden et al. [17] obtained interesting results with cobalt sulfide catalysts. Numerous nitro compounds (as, for example, nitrostyrenes and dinitrostilbenes, etc.) were selectively hydrogenated at temperatures 20–140°C and with 5–150 bars of hydrogen.

Baik et al. [18] used enzymatic catalysis in order to hydrogenate selectively the *ortho*- and the *para*-nitrophenylallylether in the corresponding unsaturated amines in a hydroalcoholic basic solution at 80°C.

In the present work, the selective hydrogenation of the 4-nitrobenzylallylether and of the 4-nitrobenzylcrotylether in their corresponding unsaturated amines was investigated. As it has been shown, in a previous preliminary study [19], the selective hydrogenation of nitrobenzene, carried out in competition with the hydrogenation of benzylallylether and also of benzylcrotylether, was favoured in basic ethanolic solutions, when in acid solutions, the $\text{C}=\text{C}$ bond was more easily hydrogenated. For this reason, the selective hydrogenation of these compounds was studied in function of the basicity of the solutions.

2. Experimental

The platinum catalysts, used in this work, were prepared by impregnation of pure granular graphite (Lonza KS-15), of a specific area equal to 14 m^2/g , with an aqueous solution of chloroplatinic acid (0.2–5%) and by reduction at 573 K. The graphite support was pretreated in a hydrogen stream at 1273 K and in the air at 573 K [20]. The obtained Pt/graphite catalysts were characterized in situ by cyclic voltammetry and also by hydrogen chemisorption (by pulsed chromatography) and by transmission electron microscopy [19].

A glass cell was used for their characterization by cyclic voltammetry. This cell, used also as reactor for the hydrogenation reactions, has five holes allowing to introduce three electrodes (working, counter and reference electrodes) and also the inlet and outlet of gases (N_2 or H_2) [21,22]. The granular Pt/graphite catalyst (200 mg) was deposited on a glass frit; it was stirred and maintained in suspension during the hydrogenation reaction by a counter current hydrogen flow (of a rate: 180 ml/min).

The hydrogenation experiments were carried out in an alcoholic solution (95% ethanol) of different basicities obtained by addition of KOH, with small concentrations in organic com-

Table 1
Characterization of Pt/graphite catalysts by cyclic voltammetry

Metal loading (% Pt/gr)	0.2	0.5	1	2	3	5
Metallic surface area (cm ² /g)	2130	3070	7110	8710	11 400	12 000
Dispersion (%)	34	20.5	22	17	12	8
	30 ^a	20 ^a	22 ^a	20 ^a	12 ^a	6 ^a
Metal particle size (nm)	2.5	4	3.9	5	7	10

^aDispersion measured by hydrogen chemisorption (by pulsed chromatography).

pound (10^{-3} M), $p(\text{H}_2) = 1$ atm and generally at 299 K.

Most of the organic compounds used in this work were synthesized. The nitrobenzylethers ($\text{NO}_2\text{C}_6\text{H}_4\text{OR}$, with $\text{R} = (\text{CH}_2=\text{CHCH}_2)$ and $(\text{CH}_3\text{CH}=\text{CHCH}_2)$) were prepared by reaction of nitrobenzylbromide with the corresponding unsaturated alcohol ($\text{CH}_2=\text{CHCH}_2\text{OH}$ and $\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$), according to the method of Cookson and Wallis [23].

The same method was used for the preparation of the corresponding saturated ethers (nitrobenzylpropylether and nitrobenzylcrotylether), the reacting alcohols being $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.

The aminobenzylethers were prepared by reduction of the corresponding nitrobenzylethers. Different chemical reduction systems were tested, but only the system $\text{Fe}-\text{FeSO}_4-\text{H}_2\text{O}$ resulted to a selective reduction of the nitro group with yields equal to 75% [24].

The progress of the reaction was followed by HPLC (Waters 486) using a Bondapak C18 column, with a 50:50 methanol–water eluent and a UV detector, allowing the detection of benzenic compounds.

The reaction rates were divided by the real active surface area of platinum leading to the intrinsic activity of this catalyst.

The initial selectivities of different reaction products, reported in Tables 2 and 3, are defined as the ratios of formation rates of these products to the consumption rate of the reactant at $t = 0$. The maximum selectivities in unsaturated anilines indicate the maximum quantities of produced anilines divided by the corresponding quantity of converted reactants. They were obtained generally at different conversions of the organic reactant, equal to about 70–80% for the 4-nitrobenzylallylether and 100% for the 4-nitrobenzylcrotylether.

3. Results

3.1. Selective hydrogenation of 4-nitrobenzylallylether in 4-aminobenzylallylether

The hydrogenation of 4-nitrobenzylallylether ($C = 1.25 \times 10^{-3}$ M, $p(\text{H}_2) = 1$ atm) was carried out at 299 K in alcoholic basic solutions of different compositions (95% $\text{C}_2\text{H}_5\text{OH} + x$ M

Table 2
Evolution of the intrinsic activity of platinum catalysts (in $\text{mol min}^{-1} \text{cm}^{-2}$), in hydrogenation of 4-nitrobenzylallylether, as a function of KOH concentration and catalyst dispersion

Dispersion of platinum (%)	95% $\text{C}_2\text{H}_5\text{OH}$	10^{-3} M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$	10^{-2} M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$	10^{-1} M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$
34	4.4×10^{-9}	3×10^{-9}	23×10^{-10}	18×10^{-10}
20.5	3×10^{-9}	1.6×10^{-9}	10×10^{-10}	7×10^{-10}
22	2.4×10^{-9}	1.5×10^{-9}	7.5×10^{-10}	3.9×10^{-10}
17	1.6×10^{-9}	1.4×10^{-9}	7×10^{-10}	6×10^{-10}
12	1×10^{-9}	0.7×10^{-9}	5×10^{-10}	3×10^{-10}
8	1×10^{-9}	0.1×10^{-9}	4×10^{-10}	2.4×10^{-10}

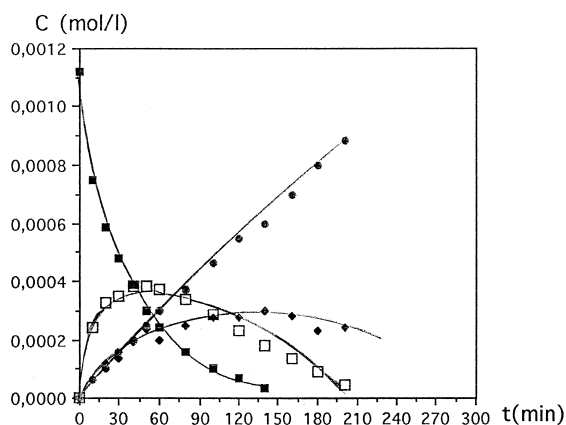


Fig. 1. Hydrogenation of 4-nitrobenzylallylether in 95% ethanol. Catalyst: 0.5% Pt/graphite. ■ 4-nitrobenzylallylether, ◆ 4-hydroxylaminobenzylpropylether, □ 4-nitrobenzylpropylether, ● 4-aminobenzylpropylether.

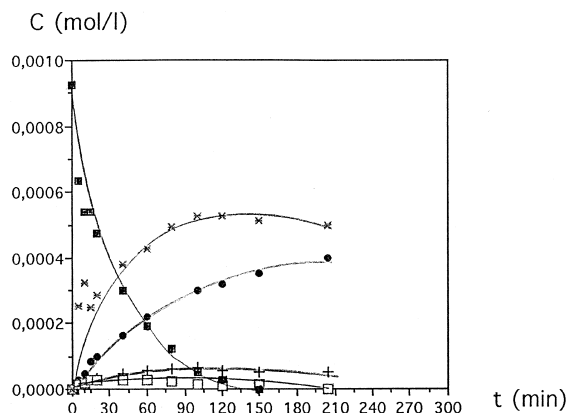


Fig. 2. Hydrogenation of 4-nitrobenzylallylether in 95% ethanol + 10^{-2} M KOH. Catalyst: 0.5% Pt/graphite. ■ 4-nitrobenzylallylether, □ 4-nitrobenzylpropylether, + 4-aminobenzylallylether, ● 4-aminobenzylpropylether, * heavy products.

KOH with $0 \leq x \leq 0.1$) using different catalysts prepared by impregnation of different platinum amounts (0.2–5%). These catalysts were characterized in situ by cyclic voltammetry [22,25] and by gas phase chemisorption of hydrogen and oxygen following the method of pulsed chromatography [26]. Different metal dispersions were obtained ranging between 34% and 8% (Table 1 and Ref. [19]).

The obtained results, regrouped in Table 2, show that the intrinsic rate of conversion of 4-nitrobenzylallylether increases with increasing platinum dispersion. Besides, it can be remarked

(Table 2) that the intrinsic reaction rate decreases with increasing KOH concentration. This variation of the reaction rate can be ascribed to the presence of two functional groups (the $-\text{NO}_2$ group and the double bond $\text{C}=\text{C}$) in the molecule of this compound, which are hydrogenated with different reaction rates both decreasing with increasing basicity, as it was found in a previous work [19]. Moreover, as in the case of nitrobenzene [19], at quite high KOH concentration ($x \geq 10^{-2}$ M), the formation of heavy products (different dimers) causes an inhibition of the catalyst.

Table 3

Evolution of the selectivity in hydrogenation of 4-nitrobenzylallylether as a function of KOH concentration

Reaction media	95% $\text{C}_2\text{H}_5\text{OH}$	10^{-3} M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$	10^{-2} M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$	10^{-1} M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$	1 M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$
Initial selectivity of 4-hydroxylaminobenzylpropylether (%)	30	0	0	0	0
Initial selectivity of 4-aminobenzylallylether (%)	0	0	6.6	26	35
Initial selectivity of 4-nitrobenzylpropylether (%)	45	39	11	6	4.4
Initial selectivity in 4-aminobenzylpropylether (%)	25	40	43	21	12
Initial selectivity in heavy products (%)	0	21	35	47	48.6
Maximum selectivity in 4-aminobenzylallylether ^a (%)	0	0	7	39	50

^aThe selectivity is maximum at conversions of the organic reactant equal to 70–80%.

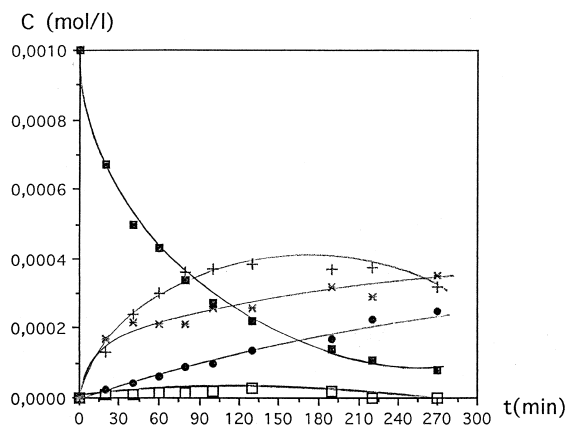


Fig. 3. Hydrogenation of 4-nitrobenzylallylether in 95% ethanol + M KOH. Catalyst: 0.5% Pt/graphite. ■ 4-nitrobenzylallylether, □ 4-nitrobenzylpropylether, ● 4-aminobenzylpropylether, + 4-aminobenzylallylether, * heavy products.

A study of the selective hydrogenation of 4-nitrobenzylallylether in 4-aminobenzylallylether as a function of KOH concentration, with a 0.5% Pt/graphite catalyst (dispersion of 20.5%), was carried out. It has been found that, at concentrations $0 \leq C_{\text{KOH}} < 10^{-3}$ M, the C=C bond is selectively hydrogenated (Fig. 1, Table 3). On the other hand, at KOH concentrations $C_{\text{KOH}} \geq 10^{-2}$ M, the selective hydrogenation of NO_2 group becomes more important and increases with increasing basicity of the solution (Table 3, Figs. 2 and 3). Consequently, in these conditions, the 4-aminobenzylallylether is formed with different selectivities depending on

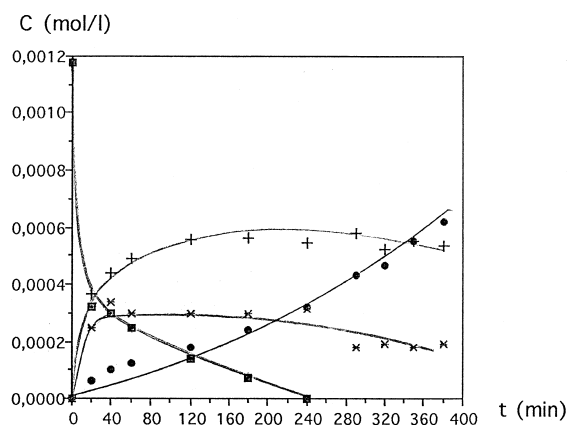


Fig. 4. Hydrogenation of 4-nitrobenzylcrotylether in 95% ethanol + 10^{-2} M KOH. Catalyst: 0.5% Pt/graphite. ■ 4-nitrobenzylcrotylether, + 4-aminobenzylcrotylether, ● 4-aminobenzylbutylether, * heavy products.

the basicity of the solution, the maximum selectivity $S = 50\%$ being obtained in a molar KOH solution (Table 3).

However, this selectivity is limited by the formation of heavy products, which increases also with the basicity of the solution and can attain 49% (Figs. 2 and 3, Table 3). The heavy products represent the sum of diazotated dimers: derivatives of azobenzene, azoxybenzene and hydrazobenzene, as in the case of nitrobenzene [19]. It should be remarked that the same evolution of the selectivity with the basicity of the solution was found in the case of the simple and competitive hydrogenation of nitrobenzene [19].

Table 4

Evolution of the selectivity in hydrogenation of 4-nitrobenzylcrotylether as a function of KOH concentration

Reaction media	95% $\text{C}_2\text{H}_5\text{OH}$	10^{-3} M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$	10^{-2} M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$	10^{-1} M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$	1 M KOH, 95% $\text{C}_2\text{H}_5\text{OH}$
Initial selectivity in 4-hydroxylaminobenzylbutylether (%)	11	0	0	0	0
Initial selectivity in 4-aminobenzylcrotylether	0	23	27	44	54.6
Initial selectivity in 4-nitrobenzylbutylether (%)	52.4	7	0	0	0
Initial selectivity in 4-aminobenzylbutylether (%)	37	23	18	12	4.5
Initial selectivity in heavy products (%)	0	47	55	44	40.9
Maximum selectivity in 4-aminobenzylcrotylether ^a (%)	0	53	49	63.5	64

^aThe selectivity is maximum at conversions of the organic reactant equal to 90–100%.

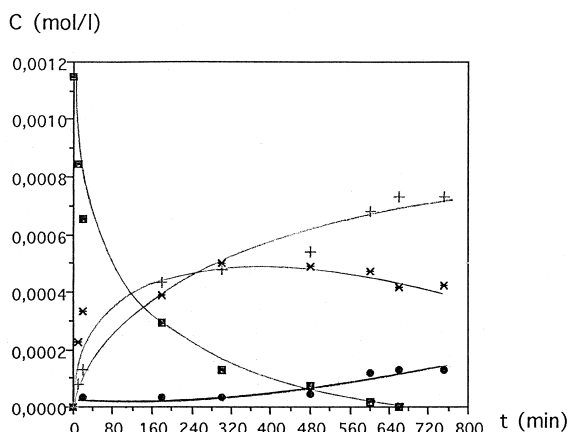


Fig. 5. Hydrogenation of 4-nitrobenzylcrotylether in 95% ethanol + M KOH. Catalyst: 0.5% Pt/graphite. ■ 4-nitrobenzylcrotylether, + 4-aminobenzylcrotylether, ● 4-aminobenzylbutylether, * heavy products.

The low selectivity in unsaturated amine can be explained by the slow hydrogenation and/or the poison effect of these dimer intermediate products [19,27–30].

3.2. Selective hydrogenation of 4-nitrobenzylcrotylether in 4-aminobenzylcrotylether

The hydrogenation of 4-nitrobenzylcrotylether ($C = 1.25 \times 10^{-3}$ M, $p(\text{H}_2) = 1$ atm) was studied in the same experimental conditions as those used previously in the case of 4-nitrobenzylallylether ($T = 299$ K, 95% $\text{C}_2\text{H}_5\text{OH} + x$ M KOH with $0 \leq x \leq 1$), with 0.5% Pt/graphite catalysts.

In this case also, as in the case of 4-nitrobenzylallylether, with increasing KOH concentrations, the hydrogenation of NO_2 group is favoured in comparison with the hydrogenation of $\text{C}=\text{C}$ bond (Table 4, Figs. 4 and 5). However, higher selectivities in 4-aminobenzylcrotylether than in 4-aminobenzylallylether were obtained (Tables 3 and 4).

4. Discussion

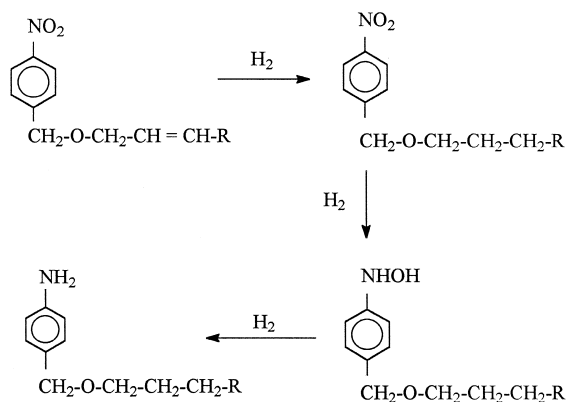
This study concerning the selective hydrogenation of nitrobenzylallylethers in the corre-

sponding unsaturated amines, follows a preliminary study of the competitive hydrogenation between the nitrobenzene and the benzylic allylethers [19]. The results of this last study indicated that the selectivity in competitive hydrogenations of $\text{C}=\text{C}$ and NO_2 groups depends on the pH of the solution: in an acid solution, the double bond, $\text{C}=\text{C}$, is more easily hydrogenated than the NO_2 group, whereas in an alkaline solution, the reactivity of both groups decreases. However, the hydrogenation rate of NO_2 group decreases to a lesser degree than that of the $\text{C}=\text{C}$ bond leading to a higher selectivity in aniline [19].

As a consequence of these previous results, the hydrogenation of nitrobenzylic allylethers was studied mainly in basic alcoholic solutions, after some experiments had been carried out in acidic and neutral solutions, which confirmed the above-mentioned preliminary results.

Indeed, in neutral and acid solutions, the reaction Scheme 1 can be proposed, with $\text{R} = \text{H}$ or CH_3 .

In basic alcoholic solutions, the obtained results show clearly that with increasing basicity of the solution, the selectivity in unsaturated aniline is improved. This pH effect is the consequence of a different decrease of hydrogenation rates of $\text{C}=\text{C}$ and $-\text{NO}_2$ groups with increasing basicity of the solution, the first one decreasing more strongly than the second one, as in the



Scheme 1.

Table 5

Comparative study of the hydrogenation rates of nitrobenzene, allylbenzylether and crotylbenzylether with a 0.5% Pt/graphite catalyst

Reaction media	Cat. activity in hydrogenation of nitrobenzene (mol min ⁻¹ cm ⁻²),	Cat. activity in hydrogenation of crotylbenzylether (mol min ⁻¹ cm ⁻²),	Cat. activity in hydrogenation allylbenzylether (mol min ⁻¹ cm ⁻²),	A ₁ /A ₂	A ₁ /A ₃
	A ₁	A ₂	A ₃		
5 × 10 ⁻³ M H ₂ SO ₄ , 95% C ₂ H ₅ OH	10 × 10 ⁻⁹	15 × 10 ⁻⁹	37.5 × 10 ⁻⁹	0.7	0.27
95% C ₂ H ₅ OH	5 × 10 ⁻⁹	1.7 × 10 ⁻⁹	14.5 × 10 ⁻⁹	2.9	0.34
10 ⁻³ M KOH, 95% C ₂ H ₅ OH	4 × 10 ⁻⁹	0.7 × 10 ⁻⁹	10 × 10 ⁻⁹	6	0.4
10 ⁻² M KOH, 95% C ₂ H ₅ OH	3 × 10 ⁻⁹	0.3 × 10 ⁻⁹	5 × 10 ⁻⁹	11	0.6
10 ⁻¹ M KOH, 95% C ₂ H ₅ OH	2 × 10 ⁻⁹	0	2 × 10 ⁻⁹	–	1
1 M KOH, 95% C ₂ H ₅ OH	1.9 × 10 ⁻⁹	0	1.7 × 10 ⁻⁹	–	1

case of competitive hydrogenations (Table 5 and Ref. [19]).

Moreover, it should be emphasized that the basic solutions favour the formation of different dimers (of the type of azoxybenzene, azobenzene and hydrazobenzene) which should be strongly adsorbed and act as poisons of the catalyst. Besides, the hydrogenation rate of hydrazobenzene is very slow and becomes equal to zero in strongly basic solutions (10⁻¹ M and 1 M KOH) [19].

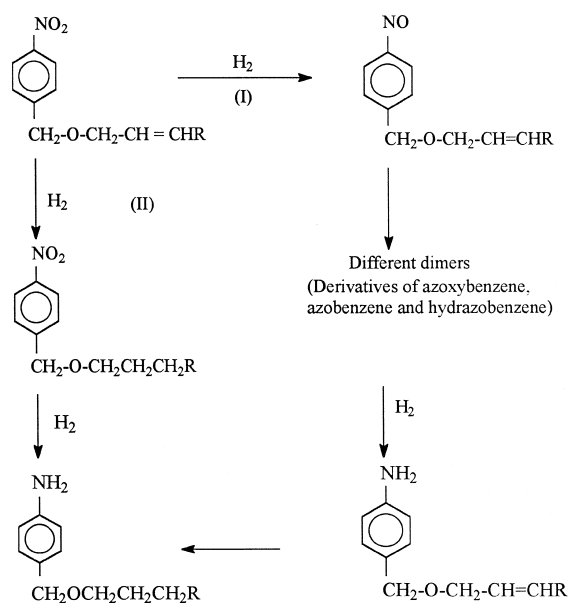
An important decrease of the hydrogenation rate of C=C bond with increasing pH was also reported in the literature [31] and can be ascribed to the presence of OH⁻ in the double layer or to poorly abundant weakly bound hydrogen species, which would be active for this reaction in alkaline solutions [32].

The higher selectivities in *p*-aminobenzylcrotylether (*S* = 64%) than in *p*-aminoallylbenzylether (*S* = 50%), obtained in solutions with *C*_{KOH} ≥ 10⁻³ M can be explained by the much lower reactivity of the crotyl group (-CH₂CH=CHCH₃) as compared with that of the allyl group (-CH₂CH=CH₂) (Table 5 and Ref. [19]). Indeed, in 10⁻³ M KOH and 10⁻² M KOH ethanolic solutions, the hydrogenation rate of benzylcrotylether is more than 10 times lower than that of benzylallylether (Table 5 and Ref. [19]). Furthermore, in 10⁻¹ M KOH and 1 M KOH solutions, the benzylcrotylether is no more hydrogenable, whereas the benzylallylether can still be hydrogenated with a quite measurable hydrogenation rate (Table 5 and Ref. [19]).

The steric effect and/or the inductive electron donor effect of the group -CH₃ could account for this low reactivity of the crotyl group.

In basic solutions, the reaction can be summarized as in Scheme 2 with R = H or CH₃, the way I being preponderant. The way II occurs in a minor extent (almost 4%) only for R = H (in the case of 4-nitrobenzylallylether; Table 3).

In conclusion, the obtained results point out that the hydrogenation rate of -NO₂ group is as high as that of the C=C group leading generally to low internal selectivities in unsaturated



Scheme 2.

amines. When the C=C bond is sterically crowded by the presence of different bulky groups, the selectivity is improved in agreement with the literature [10–14].

Another way of improving the selectivity is to use basic solutions inducing a stronger decrease of the hydrogenation rate of C=C bonds than that of NO₂ groups. However, the selectivity in unsaturated amines is again limited by the formation, following a complex mechanism, of intermediate dimers (derivatives of azobenzene, azoxybenzene and hydrazobenzene) which are difficult to hydrogenate.

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