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Facile dehalogenation of halogenated anilines and their derivatives using Al-Ni alloy in alkaline aqueous solution

Research Article

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Abstract: This article describes the simple hydrodehalogenation of halogenated anilines and their derivatives by the action of Raney aluminium-nickel alloy in aqueous alkaline solution at room temperature. The reaction course was monitored by means of 1H nuclear magnetic resonance (NMR) spectroscopy and GC-MS spectra.

The effect of Al and Ni and the nature and quantity of the base for effective hydrodehalogenation were studied.

The possibility of lowering Al content more than 500 times and Ni content more than 10 times in the filtered mother liquor by a dehalogenation procedure was tested using precipitation.

The reduction method described was satisfactorily proved for dehalogenation of polyhalogenated anilines in the multiphase dimethoxymethane/aqueous NaOH/Al-Ni reaction mixture. Dehalogenation under multi-phase conditions was demonstrated for the preparation of *ortho*-alkylated anilines from simply available 2-substituted-4- chloroanilines.

Keywords: *Raney Al-Ni alloy • Ortho-alkylated anilines • Waste water treatment • Removal of metals • ICP-OES*

1. Introduction

The activation of the carbon-halogen bond in aromatic compounds is an important issue. In particular, the transformation of a C-X bond into a C-H bond (hydrodehalogenation reaction) is useful in organic synthesis for the elimination of an aromatic halogen after it has acted as a protecting and/or orienting group in aromatic electrophilic substitution [1-4,6-8].

Halogenated anilines (XANs) are essential building blocks in the production of organic fine chemicals including for example phenylurea herbicides, such as Bromuron (*N´*-(4-bromophenyl)-*N,N*-dimethylurea), Chlorotoluron (*N´*-(3-chloro-4-methylphenyl)-*N,N*-dimethylurea) or Monuron (*N´*-(4-chlorophenyl)-*N,N*-dimethylurea) (see Fig. 1) [5].

In addition, XANs are starting materials for the regioselective synthesis of 5- and/or 7-substituted quinolines and other heterocycles [4] and for the preparations of *ortho*-acylated- or *ortho*-alkylated 4-chloroanilines [6,7].

Water solubility of halogenated anilines depends on type, position and quantity of bonded halogen atoms [8]. The solubility of the monochlorinated anilines varies over a range of 0.02 to 0.04 mol XAN L^{-1} [8]. As a result, they are common impurities in waste water streams from chemical or pharmaceutical plants [9]. XANs are not easily biodegradable. Some flow unchanged through the wastewater treatment plant, while some are adsorbed on sewage [9].

Catalytic hydrogenation, reduction by using metals or metal hydrides as well as reductions with some nucleophilic neutral or anionic species (N_2H_4, *i*-PrO^-, $HCOONH_4$) have been used for the transformation of an aromatic C-X bond into a C-H bond [3,10-18]. Aryl chlorides and fluorides are markedly less reactive in comparison to the corresponding bromides and iodides and are rather resistant to chemical reduction, especially when substituted with electron-donating groups [11].

Lunn and Sansone found that Raney aluminium-nickel alloy is able to reduce a range of organic compounds in aqueous or methanolic KOH solutions [15,16]. Two

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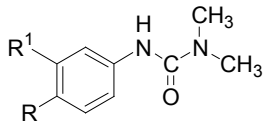


Bromuron: R= Br, R^1= H
Chlorotoluron: R= CH_3, R^1=Cl
Monuron: R = Cl, R^1= H

Figure 1. Examples of halogenophenylurea herbicides.

examples for reduction of halogenated biphenyls and tetrabromobisphenol A by the action of Al-Ni alloy in aqueous NaOH solution at a temperature of 90°C showed that these vigorous conditions brought about not only the dehalogenation but also hydrogenation of the aromatic system [17,18].

However, we have reported previously that the hydrodehalogenation of 4-halogenoanilines works well in alkaline aqueous solutions of EDTA buffer even at room temperature [19].

A common drawback of the methods that use metal reagents and/or catalysts lies in contamination of the reaction medium with the respective metals. However, there are many applicable methods for minimization of metal content in waste water, *e.g.* coagulation and hydroxide or sulphide induced precipitation [20,21].

Formed powdered nickel can simply be collected by filtration and recovered. Nickel salts are in great demand in the battery and accumulator industry [22], where significant experience with the recycling of nickel wastes exists.

In the following, the hydrodehalogenation of XANs at room temperature using aluminium nickel alloy in alkaline aqueous solution is described.

The aim of this report is to describe the application of Raney Al-Ni alloy to the simple hydrodehalogenation of various industrially important polyhalogenated anilines and their derivatives in alkaline aqueous solutions or organic solvent-aqueous NaOH multiphase mixtures at room temperature and atmospheric pressure.

2. Experimental Procedure

All operations were carried out in air at atmospheric pressure and room temperature. All XANs and their derivatives, aniline, $NaBH_4$, Al (powder, 200 mesh), Zn (powder, 100 mesh), Al-Ni alloy (50% Al + 50% Ni, Raney type, powder), Cu-Zn (70% Cu + 30% Zn, powder, 60 mesh), Cu-Sn alloy (H_2CuSn, spherical powder, 200 mesh), Ni foil (0.5 mm thickness), 10% Pd/C and all organic solvents used were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar) with a purity of at least 98% and used without further purification. All the chemicals used for the preparation of buffers were purchased from commercial suppliers in a p.a. quality. GC-MS analyses were performed on a GC-MS Shimadzu GCMS QP 2010 instrument equipped with a DB-XLB capillary column (30 m × 0.25 mm, 0.25 μm), operating at an energy of ionization of 70 eV [23]. The ^{1}H NMR spectroscopy of the $CDCl_3$ extract from the reaction mixture was used for rapid determination of the dehalogenation reaction. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 360 spectrometer. Additionally, the residues of Al-Ni alloy separated by decantation were also extracted with $CDCl_3$, and the extracts were analyzed in the same way, but no difference between the compositions of these two extracts was observed. The content of Al and Ni in the treated water solutions were determined on a GBC Integra XL ICP-OES (Inductively Coupled Plasma - Optical Emission Spectroscopy) spectrometer. The AOX (adsorbable organically bound halogens) analyses were performed according to the European ISO 9562 standard. 4-Bromo- and 4-chloroaniline stock solutions (0.01 M) were prepared at room temperature by dissolving appropriate solid 4-XAN in distilled water under overnight stirring. The preparation of buffer solutions was published elsewhere [19]. The following procedures represent the general method used for reduction of aqueous solutions of XANs:

2.1. Dehalogenation of 4-XAN in the buffered solutions

The reaction was carried out in a 250 mL two-necked, round-bottomed flask equipped with magnetic stirring and a thermometer. The outlet of the flask was fitted to a glass tube filled with granulated charcoal. The reaction flask was immersed into the water bath. The aqueous solution (0.01 M, 100 mL, 1 mmol) of 4-XAN was mixed together with the aqueous solution of 0.5 M edetane buffer (equimolar mixture of tetrasodium and trisodium salt of ethylenediamintetraacetic acid, 100 mL, pH=10.8) and the powder of aluminum-nickel alloy (0.135 g, 2.5 mmol of Al) was added (pH=10.8). The reaction mixture was stirred at 500 rpm for 14 hours at 25°C. The mixture was then filtered and the filtrates were extracted to the $CDCl_3$. ^{1}H NMR and GC-MS of this $CDCl_3$ extract indicated the conversion of XAN to the aniline.

2.2. Dehalogenation of XANs in the NaOH solutions

The reaction was carried out in a 250-mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was prepared by dissolution of XAN (1 mmol) in the aqueous NaOH solution (100 mL) (NaOH contents are listed in Tables 2 and 3). Powdered reduction agent (quantities are mentioned in Tables 2 and 3) was added in one portion to the reaction mixture under vigorous

stirring and the flask outlet was fitted to a glass tube filled with granulated charcoal. The reaction mixture was stirred at 500 rpm at a temperature of 25°C for 17 hours and filtered. A 30 mL aliquot of the filtrate was extracted with three portions of $CDCl_3$ (1×1 mL and 2×0.5 mL). The ^1H NMR and GC-MS spectra of this $CDCl_3$ extract indicate the conversion of XAN to aniline.

The above mentioned filtrate of the reaction mixture after dehalogenation (*solution 1*) contains 0.25-0.75 mg L^{-1} of AOX after reduction.

According to ICP-OES, *solution 1* typically contains 430-475 mg L^{-1} Al and 0.1 mg L^{-1} Ni.

Solution 1 was maintaned at pH 6.7-7.0 using a 24 wt.% aqueous solution of H_2SO_4 and the insoluble part was filtered off. The filtrate contained less than 0.05 mg L^{-1} of Al and less than 0.01 mg L^{-1} of Ni according to ICP-OES.

2.3. Dehalogenation of G-NH-Ar-X_n dissolved in organic solvent using Al-Ni in the NaOH solutions

The reaction was carried out in a 250-mL two-necked round-bottomed flask equipped with a magnetic stirrer and thermometer. The flask outlet was fitted to a glass tube filled with granulated charcoal. The reaction mixture was prepared by dissolution of G-NH-Ar-X_n (1 mmol) in an appropriate volume of organic solvent (see Tables 4 and 5) and addition of 1 M aqueous NaOH solution. Powdered aluminium-nickel alloy was added in one portion to the reaction mixture under vigorous stirring. The reaction mixture was stirred at 500 rpm at a temperature of 25°C for 17 hours and filtered. The filter cake was washed using 50 mL of dimethoxymethane (DMM). The filtrate was diluted with 50 mL of water and concentrated to ca.50 mL volume at diminished pressure, cooled to room temperature and extracted with $CDCl_3$ used in three portions (1×1 mL and 2×0.5 mL). ^1H NMR and GC-MS spectra of this $CDCl_3$ extract indicated the conversion of G-NH-Ar-X_n to the products.

2.4. Isolation of products from multiphase DMM-aq. NaOH reaction mixture

The spent Al-Ni alloy was washed with 20 mL of fresh DMM and the obtained filtrate was extracted twice with additional 25 mL portions of DMM. The combined organic phases were washed with 50 mL of water, filtered through a silica gel pad and evaporated to dryness. The residue was weighed and analyzed using ^1H, ^{13}C NMR and MS spectroscopy. The isolated diphenylamine [24], 2-benzylaniline [25], 2-trifluoromethylaniline [26] were previously reported and the spectral data of these products were in agreement with the data reported in literature.

3. Results and Discussion

3.1. Dehalogenation of XANs in buffered aqueous solutions

Initially, the reduction efficiency of Al-Ni in the dehalogenation of the model substrate 4-bromoaniline (4-BAN) was tested at the different pH values using EDTA buffers for alkaline and sulphate buffers for acidic values of the pH (Fig. 2). It was found earlier that hydrodehalogenation of halogenoaromatics proceeds only in the alkaline region [16]. We observed slow debromination of 4-BAN even in acidic conditions in sulphate buffer. However, this dehalogenation is accompanied by dissolution of the nickel sponge (according to the ICP-OES analyses of filtered reaction mixture).

The dehalogenation reaction of 4-BAN with Raney Al-Ni alloy works effectively at pH greater than 10 in edetane buffers. The hydrodebromination of 4-BAN is completed in less than 10 hours, when a slurry of added Al-Ni alloy powder in the saturated aqueous solution of the 4-BAN or 4-chloroaniline (4-CAN) and EDTA buffer is stirred vigorously. We observed that the dehalogenation rates of 4-BAN and 4-CAN are very similar using Al-Ni in the presence of EDTA buffer (pH = 10.9) [19]. However, using 0.5 M $KHCO_3/K_2CO_3$ buffer (pH=10.3) we observed that the dehalogenation was never completed, even after 48 hours. Subsequent ICP-OES analysis of Al content confirmed that the quantity of dissolved Al^{3+} is low in the case of the use of $KHCO_3/K_2CO_3$ buffer (slightly soluble $NaAl(OH)_2CO_3$ probably cover the Al-Ni surface) [27].

3.2. Effect of the nature of the base used

Based on the findings described above we decided to investigate the behaviour of the Al-Ni alloy in alkaline medium that did not contain a higher concentration of salts.

The dechlorination of 4-CAN in alkaline solutions other than aqueous NaOH was investigated using aqueous solutions of different bases (Table 1). It is noteworthy that the use of Raney Ni–Al alloy in aqueous NaOH or KOH solutions led to strongly reducing agents, comparatively stronger than using the alloy in other alkaline aqueous solutions under otherwise identical conditions [18]. Aniline was obtained selectively and

in 100% conversion using NaOH or KOH even after 15 minutes of reaction (Table 1, runs 10 and 11). In the case of adding 1 M aqueous solution of $NaHCO_3$ to the 100 mL of 1 M aqueous 4-CAN solution stirred together with 0.54 g of Al-Ni alloy, the dehalogenation does not proceed. Using 1M NaOAc aqueous solution, 91.2% of 4-CAN remained unreacted. The dechlorination was found to be incomplete when suspensions of $Mg(OH)_2$ were used. When performing the reaction in 1 M or 0.4 M NH_4OH, Na_2CO_3, K_3PO_4 or K_2CO_3 solutions, 4-CAN was completely converted to aniline (Table 1, entries 4-9). That is to say, the reducing ability of the Raney Al–Ni alloy exhibited upon addition of alkaline aqueous solutions follows the order: KOH = NaOH > K_2CO_3 = Na_2CO_3 = K_3PO_4 = NH_4OH > $Mg(OH)_2$ > NaOAc >> $NaHCO_3$.

3.3. Dehalogenation of XANs in aqueous NaOH solution: effect of the amount of the Al-Ni alloy and NaOH

Furthermore, we examined the course of dehalogenation of XANs in alkaline medium using NaOH as the base. When using NaOH solution, the dehalogenation was found to be completed even when 2.5 equivalents of Al in the form of Al-Ni alloy and 5 equivalents of NaOH were used and the reaction was performed at room temperature (Table 2, entries 1-3). When the amount of Al-Ni alloy was reduced (*e.g.* to 1.48 eq.), 12 mol% of 4-CAN remained unchanged. Similarly, when the quantity of NaOH was decreased (to 3 equivalents), the dechlorination became sluggish and 7% of 4-CAN remained unchanged.

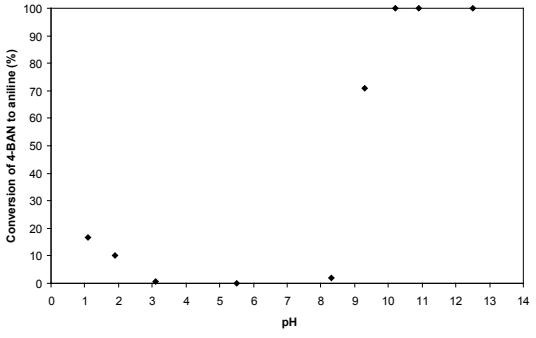


Figure 2. pH profile of the debromination reaction of 4-bromoaniline using Raney Al-Ni alloy as reductant.

3.4. Effect of the nature of the reduction agent in NaOH solution

The comparison of the reductive activity of commonly used powdered reduction agents (metals, alloys and $NaBH_4$) toward the 4-BAN and 4-CAN in 0.4 M NaOH solution can be seen in Table 3. As shown, we verified that powdered metals like Al, Mg or Zn and alloys like bronze (Cu-Sn) and brass (Cu-Zn) are not effective for the dehalogenation of XANs under the present conditions at room temperature (Table 3, entries 9-10).

This is in the agreement with the literature, because powdered Al, Mg or Zn work as reducing agents only under special conditions (*e.g.* under reflux in MeOH and application of specific reagents like ammonium formate) [28].

In contrast, interesting results were achieved using Devarda´s alloy in alkaline solution. However, Devarda´s alloy is efficient only as a debromination agent for 4-BAN, but it completely fails in case of 4-chloroaniline (4-CAN) dechlorination (Table 3, entries 11-12).

In order to develop a reducing system based on a Ni catalyst, the dechlorination of XAN using a combination of Al powder and metallic Ni or Ni^{2+} was studied. We established that the application of Al powder as a reduction agent was unsuccessful in the dehalogenation of XANs, even in the presence of nickel powder or decanted spent Al-Ni alloy (see Table 3, entries 1-5).

Table 1. Effects of the nature of the base (dissolved in 50 mL of water) in the dechlorination of 4-CAN (100 mL of 0.01 M aq. solution) at 25°C, magnetic stirring (500 rpm in 250 mL flask), reaction time: 17 h.

Entry	Al-Ni alloy (g)	Base	Conversion of 4-CAN to $PhNH_2$ (%)
1	0.54 g	$NaHCO_3$ (50 mmol)	0
2	0.54 g	NaOAc (50 mmol)	18.8
3	0.54 g	$Mg(OH)_2$ (50 mmol)[a]	74.7
4	0.54 g	NH_4OH (50 mmol)	100
5	0.54 g	Na_2CO_3 (50 mmol)	100
6	0.54 g	Na_2CO_3 (20 mmol)	100
7	0.54 g	K_2CO_3 (20 mmol)	100
8	0.54 g	K_3PO_4 (20 mmol)	100
9	0.54 g	NH_4OH (20 mmol)	100
10	0.54 g	NaOH (20 mmol)	100[b]
11	0.54 g	KOH (20 mmol)	100[b]

[a]*suspension of $Mg(OH)_2$ in reaction mixture*
[b]*reaction time: 15 minutes*

Table 2. Effect of the amount of Al-Ni and NaOH on the hydrodehalogenation of 1 mmol of XANs dissolved in 100 mL H_2O. Reaction conditions: 17 hours vigorous stirring at room temperature.

Entry	Halogenoaniline	Quantity of NaOH (g)	Quantity of Al-Ni (mmol of Al)	Conversion to aniline (%)
1	0.01M 4-BAN	0.4	0.270 g of Al/Ni (5)	100.0
2	0.01M 4-BAN	0.4	0.135 g of Al/Ni (2.5)	100.0
3	0.01M 4-BAN	0.2	0.135 g of Al/Ni (2.5)	100.0
4	0.01M 4-BAN	0.2	0.08 g of Al-Ni (1.48)	90.8
5	0.01M 4-CAN	0.8	0.270 g of Al/Ni (5)	100.0
6	0.01M 4-CAN	0.4	0.135 g of Al/Ni (2.5)	100.0
7	0.01M 4-CAN	0.2	0.135 g of Al/Ni (2.5)	100.0
8	0.01M 4-CAN	0.4	0.08 g of Al-Ni (1.48)	88.0
9	0.01M 4-CAN	0.12	0.135 g of Al-Ni (2.5)	93.0
10	0.01M 4-FAN	0.4	0.135 g of Al/Ni (2.5)	100.0
11	0.01M 4-FAN	0.2	0.135 g of Al/Ni (2.5)	100.0
12	0.01M 4-FAN	0.12	0.135 g of Al/Ni (2.5)	91.0
13	0.01M 4-FAN	0.2	0.080 g of Al/Ni (1.48)	71.7
14	0.01M 4-FAN	0.4	0.080 g of Al/Ni (1.48)	74.1

Table 3. Dehalogenation of 4-BAN or 4-CAN using different reduction agents (Reaction conditions: 0.01 M aq. solution of 4-XAN (100 mL) in 100 mL of 0.25 M aq. NaOH; reaction time 17 h; 10 mmol of reduction agent was used).

Entry	Reduction agent	Conversion to aniline
1[a,b]	Zn powder	0 %
2[a,b]	Al powder	0 %
3[a,b]	Mg powder	0 %
4[a,b]	$NaBH_4$	0 %
4[a,b]	Al powder + Ni powder (0.3 g)	0 %
5[a,b,c]	Al powder + spent Al-Ni alloy	0 %
6[a,b,d]	Al powder + Ni/C	100 %
7[a,b,e]	Al powder + Pd/C	100 %
8[a,d]	$NaBH_4$ + Ni powder	0 %
9[a,b]	Cu/Zn (70/30)	0 %
10[a,b]	H_2CuSn	0 %
11[a]	Devarda´s alloy (45%Al/50%Cu/5%Zn)	100 %
12[b]	Devarda´s alloy (45%Al/50%Cu/5%Zn)	0 %
13[a,b]	Raney Al-Ni alloy	100 %
14[b]	Al powder + $NiSO_4$ (10 mmol)	94.3 %

[a] *4-BAN used as substrate*
[b] *4-CAN used as substrate*
[c] *spent Al-Ni alloy after decantation of reaction mixture from entry 13 were re-used*
[d] *catalyst prepared according to Lipschutz [29]*
[e] *according to Janiak [30], XAN to catalyst molar ratio was 275:1*

In the case of using Al powder in the presence of $NiSO_4$ aqueous solution, 94.3 % of 4-CAN was reduced to aniline (the total amount of Al was kept at 0.54 g and 50 mL of 0.2 M aq $NiSO_4$ solution was added to the reaction mixture) (Table 3, run 14).

The effect of hydrogenation catalysts such as Ni or Pd on charcoal was examined using Al powder as a reducing agent (Table 3, entries 6-7). In both cases, a complete dechlorination of 4-CAN was observed. These results clearly show that the application of both aluminum and active hydrogenation catalyst (in-situ prepared nickel sponge or Pd supported on charcoal) is fundamental for the dehalogenation described.

Table 4. Dehalogenation in the mixture of aqueous NaOH/organic solvent system (Reaction conditions: 1 mmol of 4-bromo-2-chloroaniline dissolved in organic solvent + 30 mL of 1 M NaOH solution + 20 mL H_2O + 0.54 g of Al-Ni alloy, reaction time 17 hours).

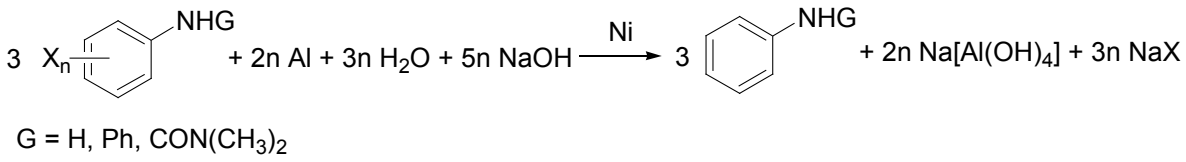
Entry	Organic solvent (mL)	Conversion to aniline (%)
1	THF (50)	77.15
2	EtOH (50)	100
3	$MeOCH_2CH_2OH$ (50)	83.3
4	*n*-BuOH (20)	mixture of compounds
5	BuOAc (20)	0
6	Et_2O (20)	31.6
7	methylal (20)	100
8	ethylal (20)	100

From the results described above, we propose that the reduction is initiated with the attack of the OH^- and water on the metallic Al with subsequent formation of $[Al(OH)_4]^-$ and H_2. Activated aluminium metal directly reduces Ni^{2+} to the finely divided metallic nickel catalyst. The hydrogen gas produced during the dissolution of Al adsorbed on activated hydrogenation catalyst (Ni sponge or Pd on charcoal) takes part in the subsequent dehalogenation reaction.

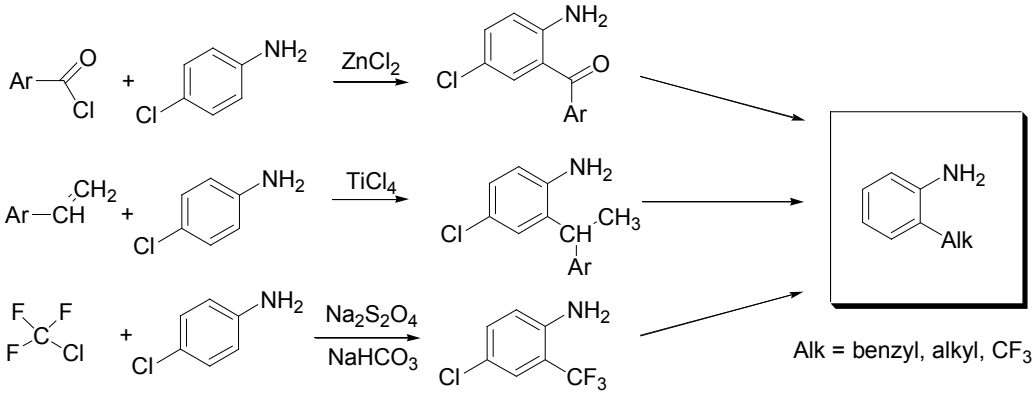
The dehalogenation of XANs and their derivatives is described in Scheme 1.

3.5. Dehalogenation of XANs in organic solvent-aqueous NaOH system

Moreover, dehalogenation in a multiphase reaction medium consisting of organic solvent/aqueous NaOH/Al-Ni was tested using water-insoluble 4-bromo-2-chloroaniline (BCAN).



Scheme 1. The dehalogenation of XANs and their derivatives using Al-Ni alloy.



Scheme 2. Preparation of 2-alkylated anilines using electrophilic aromatic substitution [6,7] and subsequent reduction.

Table 5. Reduction of different G-NH-Ar-X_n after 17 hours of stirring at room temperature in aqueous NaOH solution.

Entry	G-NH-Ar-X_n (mmol)	Quantity of NaOH[d] (g)	Quantity of Al-Ni (mmol of Al)	Conversion to aniline (%)
1	2,6-dichloroaniline (1)	1.2	0.54 g (10)	100
6[a]	2,4,5-trichloroaniline (1)	2.0	0.81 g (15)	100
7[a]	3,5-dichloroaniline (1)	1.2	0.54 g (10)	100
8[a]	2,3-dichloroaniline (1)	1.2	0.54 g (10)	100
9[a]	3-bromodiphenylamine (1)	0.8	0.27 g of Al/Ni (5)	100% of diphenylamine
10[a]	Monuron (4)	3.2	1.08 g (20)	100[b] (81%[e])
11[a]	Bromuron (4)	3.2	1.08 g (20)	100[b] (83%[e])
12[a]	Chlorotoluron (4)	3.2	1.08 g (20)	100[c] (72%[e])
13[a]	4-chloro-2-trifluoromethylaniline (1)	0.8	0.27 g of Al/Ni (5)	100% of o-trifluoro-methylaniline (89%[e])
14[a]	2-amino-5-chloro-2´ fluorobenzophenone, (1mmol)	3.2	1.08 g (20)	100% of 2-benzylaniline (78%[e])
15[a]	2-amino-5-chlorobenzophenone (1 mmol)	3.2	1.08 g (20)	100% of 2-benzylaniline (85%[e])

[a] *XAN dissolved in 20 mL of DMM*
[b] *N,N-dimethyl-N´-phenylurea as the product*
[c] *N,N-dimethyl-N´-(4-methylphenyl)urea as the product*
[d] *NaOH added during 1 h period as 1 M aqueous solution*
[e] *isolated yield*

Different solvents were investigated for the dehalogenation of water insoluble 4-bromo-2-chloroaniline (BCAN), such as ethanol, THF, methoxyethanol, *n*-butanol, butyl acetate, diethylether and two acetals, dimethoxymethane (DMM) and diethoxymethane (DEM).

BCAN is highly soluble in all tested solvents (1 mmol in 20 mL of solvent after a few minutes of stirring).

However, in the case of water-miscible solvents (EtOH, THF, methoxyethanol), a 1:1 ratio of solvent:aqueous NaOH solution was used to suppress precipitation of BCAN from the reaction mixture.

In EtOH and acetals, the dehalogenation occurred easily even at room temperature. In ethers (THF and Et_2O), the dehalogenation proceeded slowly, and even after 17 h of vigorous stirring, aniline and the starting BCAN were observed together (Table 4, entries 1,6). If butyl acetate was used, only unreacted BCAN was found in the reaction mixture. In *n*-BuOH, a mixture of compounds was formed. In methoxyethanol, the dehalogenation was found to be slower compared with the reactions run in EtOH, DEM or DMM.

In the acetals used, the dehalogenation occurred easily, and after overnight stirring only aniline was detected in the reaction mixture.

The main advantage in the use of water immiscible methylal or ethylal is the fact that their consumption in the described dehalogenation procedure is lower

compared with ethanol (no precipitation of BCAN after mixing with aq. NaOH).

From an applicability standpoint, methylal as a co-solvent especially represents a good choice for the following reasons: a) excellent solubility of XAN's in DMM; b) solubility of DMM in water is ca. 30 wt.% (better mass transfer); c) the boiling point of DMM, 42°C, enables simple distillation and recycling of DMM; d) contrary to usual ethers or DEM, DMM does not form explosive peroxides; e) DMM has an extremely low toxicity and ecotoxicity [31-33].

Based on the findings described above, we decided to investigate the behaviour of the Raney Al–Ni alloy in the mixture of DMM and aqueous NaOH for the dehalogenation of water-insoluble polyhalogenated anilines and their G-NH-Ar-X_n derivatives. For this purpose, we used industrially important halogenated ureas used as herbicides, such as Monuron (*N´*-(4-chlorophenyl)-*N,N*-dimethylurea), Bromuron (*N´*-(4-bromophenyl)-*N,N*-dimethylurea), Chlorotoluron (*N´*-(3-chloro-4-methylphenyl)-*N,N*-dimethylurea).

The molar ratios of the reactants used for the dehalogenation were Al : Ni : NaOH : G-NH-Ar-X_n = 5*n* : 2.3*n* : 20*n* : 1, the conversion to aniline (or appropriate aniline derivative) being 100 % in all cases (Table 5, entries 6-16).

Easily available *ortho*-acylated- or *ortho*-alkylated 4-chloroanilines [6,7] serve as starting materials for the simple preparation of *ortho*-alkylated-anilines used as intermediates for drug or pesticide synthesis. As a result, the efficiency of the dehalogenation method described above was proven using appropriate commercially available derivatives of XANs (2-amino-5-chlorobenzophenone, 2-trifluoromethyl-aniline).

4. Conclusions

In conclusion, we have reported a general method for dehalogenation of halogenated anilines and their derivatives using Al-Ni alloy in alkaline aqueous solutions at room temperature. Under these conditions, dimethoxymethane was shown to be a suitable green co-solvent for the dehalogenation of sparingly water-soluble XANs and their derivatives in a dimethoxymethane-aqueous NaOH-Al/Ni alloy multiphase reaction system. We successfully reduced aluminium and nickel from the effluents generated using neutralization. This simple method enables recovery of most of the Al and Ni from the water solution.

From the point of view of environmental protection, this process shows potential advantages in reducing the adverse impact of AOX dissolved in industrial effluents. We hope that this simple approach enables broader utilization of Al-Ni alloy as a cheap and commercially available dehalogenation agent applicable in aqueous or multi-phase reaction mixtures.

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