

**Figure 2.** Frontal chromatogram obtained with oak sawdust column (1.5 cm(i.d.) $\times$ 23 cm(L)). Sample solution: 10 ppm heavy metal ions in 0.05F ammonium acetate and 0.05F potassium sodium tartrate (pH 5.0).

were adsorbed more at the high pH range. However, the adsorption of Cr(VI) ion on the oak sawdust (Figure 1(A)) and that of Pb(II) ion on the bean stem particles (Figure 1(B)) were increased at the low pH range. It was thought that most of sawdusts were anionic in the high pH and neutral to cationic in the low pH, we couldn't explain the increase in adsorption of Pb(II) ion on the bean stem particles in the low pH. Nitrogen contents of various sawdusts and the  $K_d$  values of copper, cadmium, nickel, and lead ions on oak sawdust at pH 9.0 are given in Table 1. From the results of these experiments, it could be illustrated that the uptake of these heavy metal ions on the sawdusts is quantitative, the nitrogen content in the sawdust has no influence on the adsorption, and the removal of organic compounds in the sawdusts, such as alcohols and fats, by extraction with acetone or 1%-NaOH solution gave increased adsorption. Selectivities were a little different; oak has a selectivity on Cu(II) and Ni(II), pine on Cd(II), and alder on Pb(II). Therefore, among the sawdusts, the oak sawdust was a good adsorbent. The increasing order of  $K_d$  values on oak sawdust at pH 5.0 was Ni(II) $<$ Cd(II) $<$ Cu(II) $<$ Cr(VI) $<$ Fe(III) $<$ Pb(II) and at pH 9.0 was Cr(VI) $<$ Fe(III) $<$ Pb(II) $<$ Ni(II) $<$ Cd(II) $<$ Cu(II) (Figure 1(A)).

The  $K_d$  values for activated charcoal and natural zeolite were also measured to compare with those of sawdusts. In Table 1, the values on the activated charcoal were similar to those on oak sawdust, but those on the natural zeolite were smaller than those on the most of sawdusts.

To confirm the increasing order of  $K_d$  values of the heavy metal ions on the sawdusts and removal possibility on them in the industrial and laboratory waste water by the sawdust, it was examined whether the break through points of the heavy metal ions on a column packed with oak sawdust would be larger enough than the column's void volume (14 mL in this case) (Figure 2). Although the pH of the sample solution was the one (pH 5.0) in which the  $K_d$  values of

the metal ions were comparatively smaller than those at the higher pH, the break through points of them were large enough (Ni(II): 350 mL, Cd(II): 430 mL, Cu(II): 1,490 mL, and Pb(II): 3,300 mL) and the increasing order of the break through points was same as that of the  $K_d$  values. Therefore, it was thought to be possible that heavy metal ions in the industrial and laboratory waste water could be removed favorably by the sawdust column.

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## The Cathodic Reduction of N'-Phenyl-N-Alkyl-N-Nitrosoureas

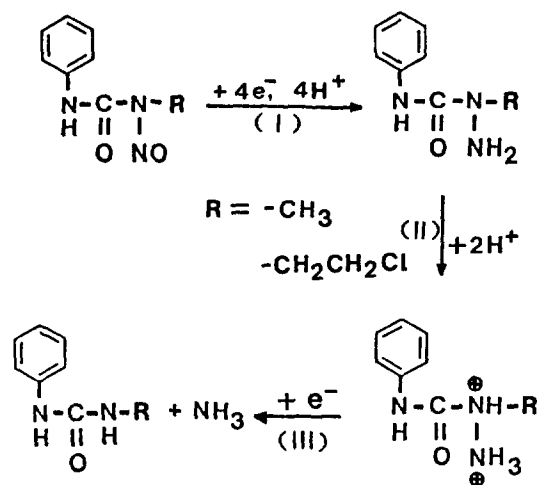
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There are many reports for the chemical syntheses and the biological applications<sup>1</sup> for N-nitrosourea analogues since Montgomery and coworkers<sup>2</sup> published papers, some of which can be used as the antitumor agents. However, there are no any reports for the electrochemical behaviors and the electrochemical reduction of N-alkyl-N-nitrosourea to N-alkyl aminourea or urea. On the other hand, as not like this compound the electrochemical synthesis and the investigation of electrochemical properties for the N-nitrosoamine analogues have been taken so much<sup>3</sup>, which is a carcinogen and a similar compound to N-nitrosourea.

Two electrode system have sometimes applied for the electrochemical synthesis of N-nitrosoamine analogues. However, in a certain case authors miss that the anodic products formed on counter electrode react often with the starting materials or the resultant products formed on cathode. This disturbs a specific reduction of reactants on cathode and often lead to the formation of unexpected if a two electrode system or a cell without liquid junction is used.



**Scheme 1.** Mechanism for the electrolysis of products 1 and 2.

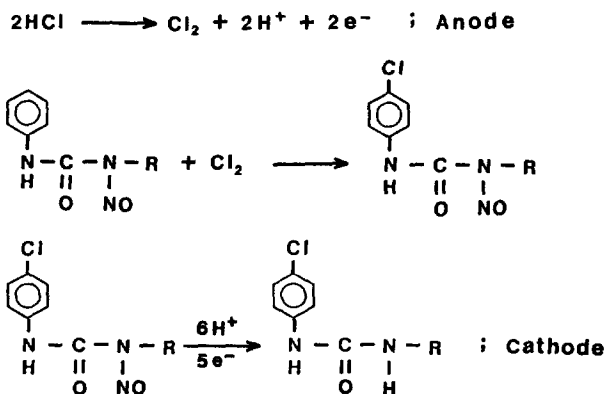
Thus, we have made the reduction of *N'*-phenyl-*N*-(2-chloroethyl)-*N*-nitrosourea **1** and *N'*-phenyl-*N*-methyl-*N*-nitrosourea **2** with the mercury pool electrode in (5 : 3) EtOH/4 N-HCl solution in order to provide a better understanding of the reduction paths in both case of employing a cell with and without liquid junction. We obtained the different reduction products employing a cell with and a cell without liquid junction between the counter electrode and working electrode, separately.

We synthesized *N'*-phenyl-*N*-Nitrosourea by using the previous methods<sup>4</sup>. The reaction of the derivatives of aniline in the dichloromethane solution and methyl isocyanate or 2-chloroethyl isocyanate led to *N*-phenyl-*N*-alkyl urea in a ice bath. *N'*-phenyl-*N*-alkyl-*N*-nitrosourea was prepared from the reaction of NaNO<sub>2</sub> with the above urea in HCOOH solution.

We thoroughly observed the polarographic behaviors of these compounds and then cathodically reduced these with the mercury pool electrode in a ice cooling bath. Compound **1** and **2** was separately reduced at -0.70 V and -0.80 V vs. Ag/AgCl electrode in the three electrode system, because the half-wave potential of **1** was -0.30 V and of **2** was -0.32 V vs. Ag/AgCl electrode in the medium of (5 : 3) EtOH/4 N-HCl. The resultant products of each compounds have been isolated by TLC and confirmed by means of mp, IR, NMR, mass spectra and/or elemental analysis<sup>5</sup>.

The number of participating electrons in the reduction process were 4.6 - 4.8 for all electrolysis using the cell with the liquid junction and without ones, respectively. We obtained the different compounds in each electrolysis of **1** and **2** employing the cell with and without liquid junction separately. On the electrolysis using the cell with liquid junction, the reduction products were *N'*-phenyl-*N*-(2-chloroethyl)-*N*-aminourea **3** and *N'*-phenyl-*N*-(2-chloroethyl)urea **4** as by-product for **1**, and *N'*-phenyl-*N*-methyl-*N*-aminourea **5** and *N'*-phenyl-*N*-methyl urea **6** for **2**. From the spectroscopic and coulometric data, we might suggest that the electrolysis products of **1** and **2** obtained using the cell with liquid junction have been produced by the following mechanism (Scheme 1).

Some different products were obtained in case of employ-



**Scheme 2.** Mechanism for formation of product **8** and **9**.

**Table 1.** Results from Electrolytic Reduction of *N*-nitrosoureas in (3 : 5) 4 N-HCl/EtOH at -0.7 V vs. for **1** and -0.8 V vs. Ag/AgCl Electrode for **2**

Compound	Method	Product with liquid junction (w/w%)	Product without liquid junction (w/w%)
1		3(78.2)	4(43.0)
		4(10.6)	8(15.0)
			7(25.0)
2		5( 3.5)	6(48.0)
		6(85.0)	9(32.0)

ing the cell without liquid junction. There are three kinds of products in this reaction. They are a compound **4**, *N'*-phenyl-*N*-(ethyl)-*N*-nitrosourea **7**, and *N'*-(*p*-chlorophenyl)-*N*-(2-chloroethyl) urea **8** for **1**, respectively. For the compound **2**, we obtained comparable results to the compound **1**. The reduction of **2** at -0.8 V vs. Ag/AgCl electrode led to *N'*-(*p*-chlorophenyl)-*N*-methylurea **9** as the major product and *N'*-phenyl-*N*-methyl urea **6** as the minor one. It is interesting that the compounds **8** and **9** are formed from the electroreductive reaction of *N'*-phenyl-*N*-alkyl-*N*-nitrosoureas under without liquid junction in HCl medium. The mechanism producing **8** and **9** will be proposed as follows; At first the generation of chlorine by anodic oxidation take place and then it is succeeded by attacking of chlorine to phenyl ring. After that the chlorinated species is formed on mercury electrode by the cathodic reduction (Scheme 2).

As shown in Table 1, the reaction in the cell with liquid junction is a selective method to prepare *N*-aminoureas from *N*-nitrosoureas, especially for compound **1**. The following could be a reason for selectivity; Such a reduction pathway of these compounds can be due to that the departure of NH<sub>3</sub> group at compound **1** is more difficult than compound **2** at step III (Scheme 1), since the electron withdrawing effect of a chloroethyl group is greater than a methyl group, consequently, the reaction was ended at step II for the compound **1**.

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- Selected data; **3**: mp. 113-115°C, IR (KBr); 3350, 3330 cm<sup>-1</sup> (-NH, s), 1640 cm<sup>-1</sup> (C=O), 1570 cm<sup>-1</sup> (-NH, b). <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ 3.5 (2H, s, -NH<sub>2</sub>), δ 3.7-3.8 (4H, m, -CH<sub>2</sub>CH<sub>2</sub>Cl), δ 7.0-7.2 (5H, m, -C<sub>6</sub>H<sub>5</sub>), δ 8.4-8.5 (1H, s, Ar-NH-). MS; m/z 213 (27%), 215 (M+2, 9%). Elemental analysis, Tound; C 51.25%, H 5.70%, N 18.74%. Calcd.; C 50.59%, H 5.66%, N 19.67%. **4**: mp. 123-125°C. IR; 3370 cm<sup>-1</sup> (-NH, s), 1640 cm<sup>-1</sup> (-NH, b). <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ 3.4-3.6 (4H, m, -CH<sub>2</sub>CH<sub>2</sub>Cl), δ 6.1-6.4 (1H, t, -NH-CH<sub>2</sub>-), δ 6.6-7.3 (5H, m, -C<sub>6</sub>H<sub>5</sub>), δ 8.30 (1H, s, Ar-NH-). **5**: IR; 3340, 3296 cm<sup>-1</sup> (-NH<sub>2</sub>, s) 1646 cm<sup>-1</sup> (C=O), 1586 cm<sup>-1</sup> (-NH, b), 1118 cm<sup>-1</sup> (C-N, s). <sup>1</sup>H-NMR (Acetone-D<sub>6</sub>); δ 3.77 (2H, s, -NH<sub>2</sub>, δ 6.87-7.47 (5H, m, C<sub>6</sub>H<sub>5</sub>-), δ 7.92 (1H, s, -NH). MS; m/z 165, 150 (M-CH<sub>3</sub>), 92 (M-C<sub>2</sub>H<sub>5</sub>N<sub>2</sub>O). **6**: mp. 145°C. IR; 3420 cm<sup>-1</sup> (-NH, s), 1650 cm<sup>-1</sup> (C=O), 1580 cm<sup>-1</sup> (-NH, b). <sup>1</sup>H-NMR (CDDl<sub>3</sub>), δ 5.69 (1H, s, -NH-), δ 7.17-7.60 (5H, m, -C<sub>6</sub>H<sub>5</sub>) δ 7.91 (1H, s, Ar-NH). MS; m/z 150, 93 (MC<sub>2</sub>H<sub>4</sub>NO). Elemental Analysis, found; C 63.32%, H 6.82%, N 18.13%, Calcd.; C 63.98%, H 6.71%, N 18.65%. **7**: mp. 80°C, <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ 1.15-1.40 (3H, t, -CH<sub>2</sub>CH<sub>3</sub>), δ 4.00-4.25 (2H, q, -CH<sub>2</sub>CH<sub>3</sub>) δ 7.02-7.21 (5H, m, C<sub>6</sub>H<sub>5</sub>-), δ 9.7-9.9 (1H, s, Ar-NH). IR; 3360 cm<sup>-1</sup> (-NH, s), 1705 cm<sup>-1</sup> (C=O), 1540 cm<sup>-1</sup> (-NH, b). **8**: mp. 154°C. IR; 3370 cm<sup>-1</sup> (-NH, s), 1630 cm<sup>-1</sup> (C=O), 1095 cm<sup>-1</sup> (-C<sub>6</sub>H<sub>5</sub>Cl, s), 795 cm<sup>-1</sup> (1,4 disubstituted benzene). <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ 3.66-4.20 (4H, m, CH<sub>2</sub>CH<sub>2</sub>Cl), δ 6.65 (1H, s, HN-CH<sub>2</sub>CH<sub>2</sub>Cl), δ 7.32-8.07 (4H, q, C<sub>6</sub>H<sub>5</sub>-), δ 9.21 (1H, s, Ar-NH). MS; m/z 234, 127 (M-C<sub>3</sub>H<sub>5</sub>NOCl, 20.5%), 129 (6.4%), 107 (M-C<sub>6</sub>H<sub>5</sub>N, 100%). **9**: mp. 204-205°C. IR; 3330, 3310 cm<sup>-1</sup> (-NH, s), 1645 cm<sup>-1</sup> (C=O), 1550 cm<sup>-1</sup> (-NH, b), 1092 cm<sup>-1</sup> (Ar-Cl), 837 cm<sup>-1</sup> (1,4-disubstituted

benzene). <sup>1</sup>H-NMR (CDCl<sub>3</sub>); δ 2.67-2.83 (3H, d, -CH<sub>3</sub>), δ 5.68 (1H, s, -NHC=O), δ 7.03-7.53 (4H, q, ArNH), δ 8.47 (1H, s, ArNH). MS; m/z 184, 127 (M-C<sub>2</sub>H<sub>4</sub>NO, 100%), 129 (33%).

### Nucleophilic Substitution Reactions of Benzyl bromides with N-Methylanilines in Methanol-Acetonitrile Mixtures

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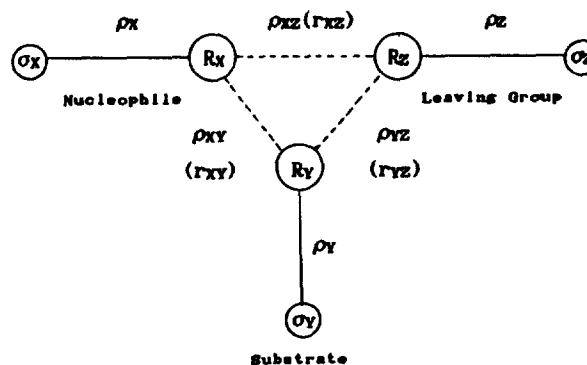
In our previous work, we have shown that benzyl derivatives react by a dissociative S<sub>N</sub>2 mechanism with a relatively loose transition state (TS)<sup>1</sup>. The cross-interaction constants between X-substituted nucleophiles and Z substituted leaving groups, ρ<sub>XZ</sub> (Scheme 1), in Eq. (1)<sup>2</sup> were negative<sup>1</sup> indicating that a stronger nucleophile (δσ<sub>X</sub><0) and a better leaving group (δσ<sub>Z</sub>>0) lead to a later TS<sup>2</sup> (δρ<sub>Z</sub>>0) and δρ<sub>X</sub><0, respectively in Eq. (2).

$$\log k_{ij}/k_{HH} = \rho_i \sigma_i + \rho_j \sigma_j + \rho_{ij} \sigma_i \sigma_j \quad (1)$$

where i, j = X, Y or Z

$$\rho_{XZ} = \frac{\partial^2 \log k_{XZ}}{\partial \sigma_X \partial \sigma_Z} = \frac{\partial \rho_Z}{\partial \sigma_X} = \frac{\partial \rho_X}{\partial \sigma_Z} \quad (2)$$

It has been reported that a typical dissociative S<sub>N</sub>2 process has relatively narrow range of the magnitude of ρ<sub>XY</sub> (0.6-0.8)<sup>1d</sup> suggesting a similar degree of bond formation is involved in the TS. In this work, we report the results of kinetic studies on the nucleophilic substitution reactions of benzyl bromides with N-methylanilines in methanol-acetonitrile mixtures at two temperatures of 45.0 and 55.0°C, Eq. (3).



Typical S<sub>N</sub>2 TS  
Scheme 1