

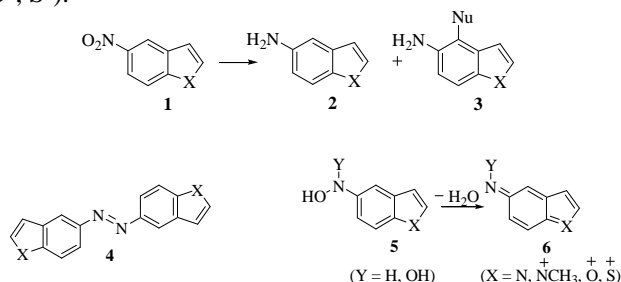
**ELECTROHYDROGENATION OF  
5-NITROINDOLES AND 5-NITROBENZOFURANE  
IN NEUTRAL AND BASIC HYDROALCOHOLIC  
SOLUTIONS AT RANEY METAL ELECTRODES**

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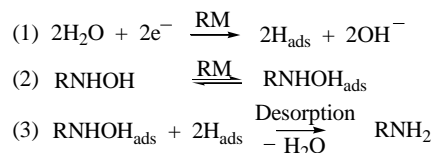
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We have shown that the electroreduction, of 5-nitroindole (**1**, X = NH), at Hg, in *basic* (KOH 0.15 M, pH > 13) and *acidic* (HCl, HBr, or H<sub>2</sub>SO<sub>4</sub> 0.15 M, pH = 0.3) aqueous alcoholic solutions gives aminoindole (**2**, X = NH) and the corresponding 4-substituted aminoindole **3** (X = NH) and in a ratio depending on nitroindole (**1**), the pH, and the nucleophile present in the medium.<sup>1</sup> Similarly, the electroreduction of 5-nitro-1-methylindole (**1**, X = NCH<sub>3</sub>), 5-nitrobenzofurane (**1**, X = O), and 5-nitrobenzothiophene (**1**, X = S), in *acidic* medium, also gives a mixture of the amine **2** (X = NCH<sub>3</sub>, O, or S) and of the corresponding 4-substituted derivative **3** (X = NCH<sub>3</sub>, O, or S).<sup>2,3</sup> However, in *basic* medium, the main product isolated from the electroreduction of 5-nitro-1-methylindole (**1**, X = NCH<sub>3</sub>), 5-nitrobenzofurane (**1**, X = O) and 5-nitrobenzothiophene (**1**, X = S) is the azo derivative **4**.<sup>2</sup> In *neutral* medium (pH = 6-7), only the amine **2** (X = NH) is obtained in a low yield.<sup>1</sup> It has been shown<sup>1,2</sup> that, both in *basic* and *acidic* medium for X = NH and in *acidic* medium for X = NCH<sub>3</sub>, O, and S, iminoquinonoids **6** (Y = OH or H) are intermediates in the formation of the amine **2** and the substituted derivative **3**. Iminoquinonoids **6** arise from base- or acid-catalysed dehydration of dihydroxylamines **5** (Y = OH) and/or hydroxylamines **5** (Y = H) respectively. Such dehydration is very slow in neutral medium. It is also very slow for X = NCH<sub>3</sub>, O, and S in basic medium since it cannot be base-catalysed and would give an iminoquinonoid cation **6** (X = <sup>+</sup>NCH<sub>3</sub>, O<sup>+</sup>, S<sup>+</sup>).



In this paper, the electrohydrogenation of 5-nitroindole (**1**, X = NH), 5-nitro-1-methylindole (**1**, X = NCH<sub>3</sub>) and 5-nitrobenzofurane (**1**, X = O) and 5-nitrobenzothiophene (**1**, X = S), at Raney metal electrodes (RM, M = Ni, Co, and Cu) in neutral and basic hydroalcoholic solutions is compared with the electroreduction at Hg. RM electrodes cannot be used for electrohydrogenations in acidic medium at pH = 0.3 (HX 0.15 M) because the electrodes are rapidly oxidized by water at such a low pH. Two mechanisms might operate in the electrohydrogenation of nitro compounds at large surface area (porous) RM electrodes: a classical electronation-protonation (EP) mechanism which involves reaction of the adsorbed nitro compound and of the adsorbed reduction intermediates with chemisorbed hydrogen (H<sub>ads</sub>) generated *in situ*, at the surface of the electrode, by reduction of water as illustrated by

equations (1) to (3) for the hydrogenolysis of an hydroxylamine intermediate.<sup>3</sup>



The electrohydrogenations at RM electrodes were carried out under controlled potential conditions at the so-called “zero-current potential” (E<sub>ZCP</sub>)<sup>3</sup> in EtOH/H<sub>2</sub>O 50/50 (v/v) or MeOH/H<sub>2</sub>O 95/5 (v/v) under *neutral* (AcONa 0.54 M/AcOH 0.54 M, pH = 6; E<sub>ZCP</sub> = -0.7 V vs. Ag/AgCl/Cl<sup>-</sup> with E<sub>ref</sub> = E<sub>SCE</sub>) and *basic* (KOH 0.15 M, pH > 13; E<sub>ZCP</sub> = -1.0 to -1.2 V) conditions. The best results were obtained in EtOH/H<sub>2</sub>O 50/50 and with RCu electrodes for both neutral and basic conditions. At RNi electrodes and in basic medium, 5-nitroindole (**1**, X = NH) gave 5-aminoindole (**2**, X = NH) and 5-aminoindoline (partial hydrogenation of the 2,6 double bond). With RCo electrodes, no hydrogenation of the double bond of **1** (X = NH) was observed but, in general, the yield of **2** (X = NH) was lower than that obtained with RCu electrodes and the results were less reproducible. The results of electrohydrogenation at RCu electrodes are shown in Table 1 for the *neutral* conditions and in Table 2 for the *basic* conditions. The yields of **2** are much higher than those obtained at a Hg electrode both in *neutral* medium (16% for X = NH<sup>1</sup>) and in *basic* medium (32% for X = NH,<sup>1</sup> 2% (27% of azo derivative **4**) for X = NCH<sub>3</sub>,<sup>2</sup> 10% (69% of **4**) for X = O,<sup>2</sup> 0% (78% of **4**) for X = S<sup>2</sup>). When the electrohydrogenation of 5-nitroindole (**1**, X = NH) was carried out at a RCu electrode in *basic* medium in the presence of PhSH in excess (3 eq.), 5-aminoindole (**2**, X = NH) and 4-thiophenyl-5-aminoindole (**3**, X = NH, Nu = PhS) were obtained in 48% and 41% yield respectively. At a Hg cathode, the electroreduction under similar conditions gave only 4-thiophenyl-5-aminoindole (**3**, X = NH, Nu = PhS) in a 59% yield.<sup>1</sup> The mechanism of formation of **2** and **3** will be discussed.

Table 1. Preparative electrolyses of **1** at RCu in neutral EtOH/H<sub>2</sub>O 50/50 (v/v) medium.

X	Amine <b>3</b> (%)
NH	73
NCH <sub>3</sub>	46
O	53-67
S	72-76

Table 2. Preparative electrolyses of **1** at RCu in basic EtOH/H<sub>2</sub>O 50/50 (v/v) medium.

X	Amine <b>3</b> (%)
NH	88
NCH <sub>3</sub>	34-64
O	72-76
S	79-85

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**References**

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