

## Electroorganic Preparations

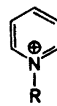
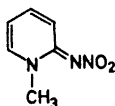
### XXXV. Reduction of Nitraminopyridines and Related Compounds

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2-, 3-, and 4-Nitraminopyridine and pyridine-1-nitroimide have been electrolyzed. 2-Nitraminopyridine yields in N hydrochloric acid a mixture of 2-aminopyridine and 2-hydrazinopyridine whereas 2-aminopyridine is the main product at pH 13. Pyridine-2-diazotate is reducible in alkaline solution to 2-aminopyridine. 1-Aminopyridinium iodide and pyridine-1-nitroimide are reduced to pyridine in a two-electron reduction.

Some nitramines have previously been investigated polarographically<sup>1-3</sup> and by classical electrolysis;<sup>4</sup> the pyridine nitramines show,<sup>5</sup> however, a polarographic behaviour somewhat different from that described for other primary nitramines,<sup>2</sup> so controlled potential reductions of these and related compounds have been made. The following compounds have been included: 2-Nitraminopyridine (Ia), the 3- and 4-isomers, 1,2-dihydro-1-methyl-2-nitroiminopyridine (IIa), pyridine-1-nitroimide (IIIa), 1-aminopyridinium iodide (IIIb), 2-hydrazinopyridine (Ic), and pyridine-2-diazotate (Ib).



Ia R = NHNO<sub>2</sub>  
 b R = N=NONa  
 c R = NHNH<sub>2</sub>  
 d R = NH<sub>2</sub>

IIa

IIIa R =  $\overline{\text{N}}-\text{NO}_2$   
 b R = NH<sub>2</sub>, I<sup>-</sup>

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## RESULTS

In Fig. 1 are depicted the half-wave potentials of 2-nitraminopyridine (Ia). In acid solution a pH-dependent wave is found which between pH 1.5 and 7 is followed by a small second wave. This second wave is followed by a pronounced maximum at a potential slightly more negative than that of 2-hydrazinopyridine (Ic). Between pH 9 and 11, the first wave of Ia is at increasing pH gradually replaced by a pH-independent wave appearing at a more negative potential in the manner generally found in a transition from a reduction of an acid to the reduction of the corresponding base. Ia is known to form an anion in alkaline solution.

Controlled potential reduction in 2 N hydrochloric acid of Ia at the potential of the first wave ( $n = 5.4 - 5.6 F/mol$ ) yielded a mixture of 2-hydrazinopyridine (Ic) (50–60 %) and 2-aminopyridine (Id) (40–50 %); besides Ic and Id, nitrogen was formed. The reaction mixture was analyzed for ammonium chloride and 2-chloropyridine, but neither of these compounds were detected.

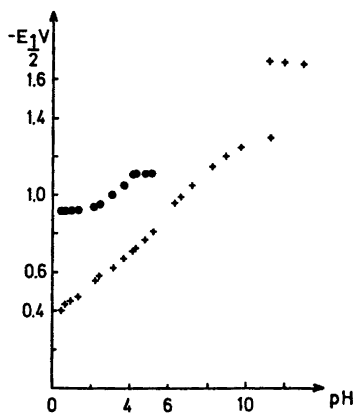


Fig. 1. Half-wave potentials (V vs. SCE) of 2-nitraminopyridine (Ia). +, 1st wave of Ia; ●, 2nd wave of Ia.

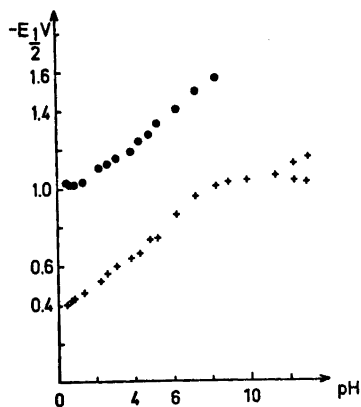


Fig. 2. Half-wave potentials (V vs. SCE) of 1,2-dihydro-1-methyl-2-nitroiminopyridine (IIa). +, 1st wave; ●, 2nd wave.

In 6 N hydrochloric acid a higher yield of Ic was found and this was also the case in acetate buffer. In alkaline solution the reduction consumed 4  $F/mol$ , and 2-aminopyridine was the main product; a small amount of Ic was formed. In a phosphate buffer, pH 11, more Ic was formed than at pH 13 although Id was the main product.

1,2-Dihydro-1-methyl-2-nitroiminopyridine (IIa) behaves in acid solution as does Ia; a pH-dependent wave followed at a more negative potential by a two-electron wave. At pH > 13 the wave splits into two waves (Fig. 2).

Controlled potential reduction of II in N hydrochloric acid containing 40 % ethanol consumed 5.6–5.7  $F/mol$ ; 2-hydrazino-1-methylpyridinium

chloride (IIc) was formed in about 75 % yield and 2-amino-1-methylpyridinium chloride (IIId) in about 25 % yield.

Reduction in alkaline solution at a potential of the limiting current of the composite wave yielded IIId in a four-electron reduction, although the limiting current of the polarographic wave of IIa is approximately the same in acid and alkaline solution. During the reduction a small anodic wave of IIc appeared; this wave disappeared towards the end of the reduction.

The two waves in alkaline solution are quite close to each other which makes a selective reduction difficult. Reduction at a potential of the lower half of the first wave produced a reducible unstable compound which might be a diazotate.

Pyridine-2-diazotate is stable enough for a polarographic investigation only at  $\text{pH} > 8$  (Fig. 3). At  $\text{pH} > 11.5$  the anion is the electroactive species; between  $\text{pH} 10$  and  $11.5$  a transition between a reduction of the anion and the species formed by recombination of the anion with a proton. The wave-height at  $\text{pH} 10$  and  $13$  is approximately the same, so the reducible species at  $\text{pH} 10$  is probably the undissociated diazohydroxide. At  $\text{pH} < 9$  a similar change to a reduction involving more protons begins, but the instability of the reducible compound at  $\text{pH} < 8$  makes the measurements uncertain. A possible explanation is that the protonation is followed by loss of water with formation of a diazonium ion which rapidly is attacked by a nucleophile with loss of nitrogen.

Controlled potential reduction of Ib at  $\text{pH} 13$  gave 2-aminopyridine in a two-electron reduction.

Reduction of 3-nitraminopyridine (IVa) in 6 N hydrochloric acid gave a nearly quantitative yield of 3-hydrazinopyridine (IVc) with only traces of 3-aminopyridine (IVd). In N hydrochloric acid the yield of 3-hydrazinopyridine

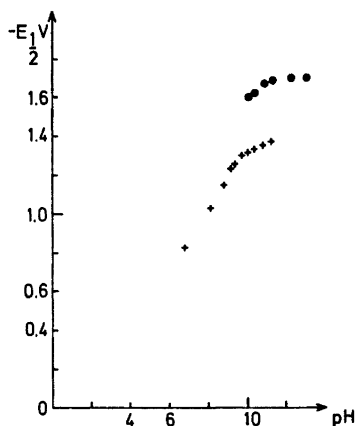


Fig. 3. Half-wave potentials (V vs. SCE) of sodium pyridine-2-isodiazotate (Ib). +, 1st wave; ●, 2nd wave.

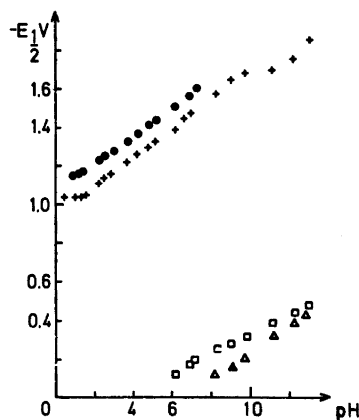


Fig. 4. Half-wave potentials (V vs. SCE) of 2-hydrazinopyridine (Ic) and 2-hydrazino-1-methylpyridinium dichloride (IIc). ●, cathodic wave of Ic; □, anodic wave of Ic; +, cathodic wave of IIc; Δ, anodic wave of IIc.

was about 55 %, and of 3-aminopyridine about 35 %. In alkaline solution the latter was the product.

Similar results were obtained in the reduction of 4-nitraminopyridine (V); in 6 N hydrochloric acid 4-hydrazinopyridine (Vc) was formed in high yield together with only traces of 4-aminopyridine (Vd); in N hydrochloric acid the hydrazine was formed in 45 % yield and the 4-aminopyridine in 25 % yield.

2-Hydrazinopyridine is reducible at  $\text{pH} < 8$ ; the potential is close to the decomposition potential of the medium; the electrode reaction is a two-electron reduction to 2-aminopyridine. The reduction potential of 2-hydrazino-1-methylpyridinium chloride (IIc) is about 0.1 V more positive (Fig. 4) than that of Ic, and it is reducible even at pH 13. Between pH 9.5 and 12 a transition takes place to the reduction of a species having one proton less.

The similarity of half-wave potentials of Ic and its 1-methyl derivative in acid solution suggests that the disappearance of the wave of Ic about pH 8 is caused by a diminishing in protonation of the pyridine nucleus.

The anodic wave of Ic is well developed at  $\text{pH} > 5.5$ , whereas that of the 1-methyl derivative is found at  $\text{pH} > 8$ . The height of the anodic wave at pH 13 is about twice that at  $\text{pH} < 7$  and corresponds to a four-electron oxidation. A preparative oxidation, however, gave  $n = 2$  which would indicate a branching in the reaction which leads to different results at the dropping mercury electrode and the mercury pool electrode.

A preparative oxidation of Ic at pH 13 gave an unknown yield of a compound reducible at  $-1.3$  V (SCE); reduction of this compound regenerated some Ic, but the over-all yield in the cycle was only about 25 %. The major product was pyridine.

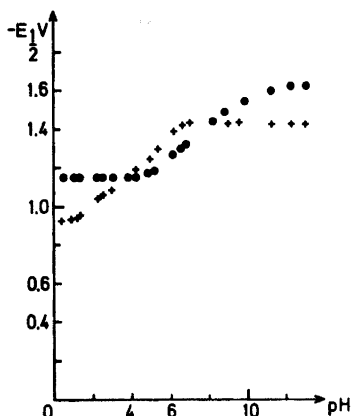


Fig. 5. Half-wave potentials (V vs. SCE) of 1-aminopyridinium iodide (IIIb) and 1-acetaminopyridine (IIIc). +, IIIb; ●, IIIc.

1-Aminopyridinium iodide (IIIb) is reducible from pH 0–14 (Fig. 5); at  $\text{pH} > 4$  a maximum is found which is especially developed in neutral and slightly alkaline solution. 1-Aminopyridinium nitrate shows no anodic wave. The dependence of  $E_{1/2}$  on pH suggests that at  $\text{pH} < 6$  a protonation takes place

prior to the electron transfer. The electrode reaction is a two-electron reduction to pyridine.

Pyridine-1-nitroimide (IIIa) is more easily reducible than IIIb, but more difficultly reducible than Ia. In acid and alkaline solution two waves are found; in acid solution the waves merge about pH 5 which is the  $pK$  of the compound. Reduction in acid solution at a potential of the first wave causes both waves to disappear and pyridine is formed in a two-electron reduction. The same is found in alkaline solution.

#### DISCUSSION

In the reduction of 2-nitraminopyridine in 2 N hydrochloric acid solution three products were isolated: 2-Hydrazinopyridine (50–60 % yield), 2-aminopyridine (40–50 %), and nitrogen (35–45 %); ammonium chloride and 2-chloropyridine were not detected, although two or three methods were tried for each compound.

The formation of 2-hydrazinopyridine is expected from the electrochemical reduction of other nitramines<sup>1–4</sup> and the chemical reduction of 4-nitraminopyridine,<sup>6</sup> but the presence of a fair amount of 2-aminopyridine needs an explanation.

The reduction of 2-nitraminopyridine is performed at a potential ( $\sim -0.5$  V *vs.* SCE) which is considerably more positive than that required for the further reduction of Ic to Id; the overall electron consumption would in case of reduction of Ic to Ie be about 7 (50 % amine) instead of  $n = 5.4 - 5.6$  found experimentally, and if a catalytic evolution of hydrogen took place simultaneously, a still higher  $n$ -value would be expected. These considerations together with the absence of ammonium chloride make it unlikely that 2-aminopyridine under these conditions is formed by reduction of 2-hydrazinopyridine.

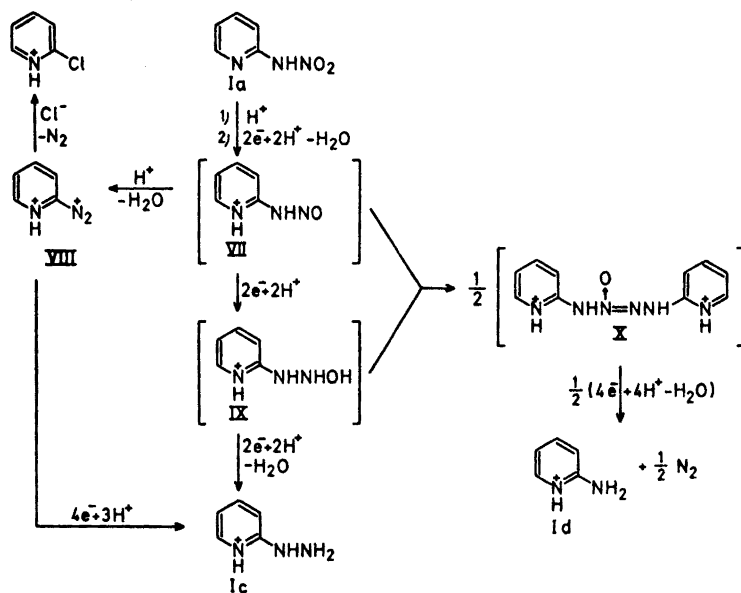
The absence of 2-chloropyridine (yield < 2 %) makes it unlikely that the diazonium ion is an intermediate in the reduction, as the 2-pyridinediazonium ion is known to react rapidly with chloride ions. 4-Chloropyridine is found as a side product in the reduction of 4-nitraminopyridine with stannous chloride and hydrochloric acid.<sup>6</sup>

The possibility that 2-aminopyridine is formed by hydrolysis of the 2-nitraminopyridine can be ruled out, as Ia is stable under the conditions used and  $n$  would be about 3  $F/mol$ .

The evolution of about 1 mol of nitrogen per 2 mol of Ie formed makes it likely that the two products are formed in the same process. Scheme 1 could account for the available evidence.

The formation of Ic and Id requires 6 and 5  $F/mol$ , respectively, and a 50 % yield of both Ic and Id would thus require  $n = 5.5$ , in accordance with the experimental findings.

The first step is a reduction of the nitro group to a nitroso group; the reduction of *C*-nitro compounds at all pH and secondary *N*-nitramines in alkaline solution<sup>1</sup> have been shown to pass through nitroso compounds. Elimination of water from the nitroso compound would yield the diazonium ion VIII, which could be reduced to a hydrazine; the further reduction must

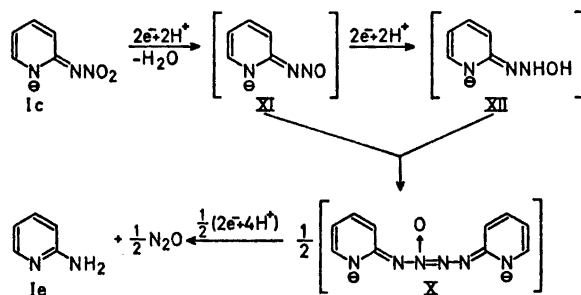


Scheme 1.

be very fast, otherwise some 2-chloropyridine would be formed. Although this reduction path cannot be excluded, there is no evidence to support it.

The suggested reduction path of the intermediate primary *N*-nitrosamine VII is the same as that for secondary *N*-nitrosamines in which no formation of a diazonium ion is possible. The *N*-hydroxyhydrazine IX may or may not be dehydrated before reduction.

No direct evidence for the condensation of VII and IX to the tetrazene-*N*-oxide X is available. In acid solution *N*-oxides generally are reducible, and as azoxybenzene in acid solution is reducible, through the easier reducible azobenzene, to hydrazobenzene, a reduction of X to a tetrazane would be expected. The tetrazane would then collapse to amine and nitrogen.

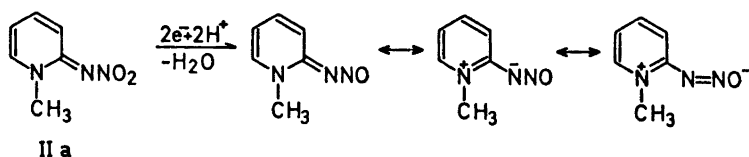


Scheme 2.

Another possibility could be a condensation between the hydrazine Ic and the *N*-nitrosamine VII to a tetraazene which through a tetrazane formed Id and N<sub>2</sub>.

At pH 13 Scheme 2 accounts for the experimental evidence, such as  $n = 4$  *F*/mol, and the isolation of Id as product.

The first step is similar to the first two-electron reduction of IIa in alkaline solution:

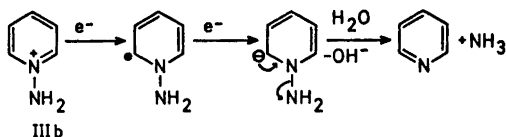


The reduction potential of secondary *N*-nitramines is generally less negative than that of the corresponding *N*-nitrosamines. The polarographic investigation of pyridine-2-diazotate (Ib = XI) shows, however, that Ib is reducible at the potential necessary for the reduction of Ia. The products obtained from the reduction of Ia and Ib are the same;  $n = 2$  *F*/mol for Ib and 4 *F*/mol for Ia.

The condensation reaction is similar to that occurring during the reduction of *C*-nitro compounds; the *N*-oxide group of the tetraazene-*N*-oxide would probably not be reducible in alkaline solution and the tetraazene-*N*-oxide formed on reduction would collapse into amine and N<sub>2</sub>O. In the intermediate pH-range both Scheme 1 and 2 may be followed.

In Scheme 2 is thus also suggested a reduction route for pyridine-2-diazotate (Ib = XI). Ib is the first example so far of a polarographically reducible diazotate, but diazotates of other  $\pi$ -electron deficient heteroaromatic amines might be expected to behave similarly. Monoprotonation of Ib to pyridine-2-diazotic acid is not possible to any appreciable extent as the compound rapidly is protonated and loses water to the diazonium ion which reacts with any nucleophile with loss of nitrogen.

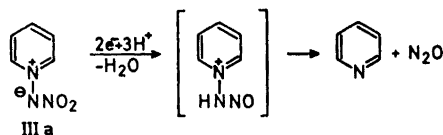
1-Aminopyridine (IIIb) is reducible at all pH-values; at pH > 6 the half-wave potentials are independent of pH. The reduction may be formulated as



The  $pK$  of pyridine-1-nitroimide IIIa is about 4,<sup>7</sup> so in acid solution the protonated molecule is reduced. In both acid and alkaline solution IIIa is reduced to pyridine with  $n = 2$  *F*/mol.

The two-electron reduction of IIIa could involve either a reductive cleavage of the nitrogen-nitrogen bond to pyridine and H<sub>2</sub>N<sub>2</sub>O<sub>2</sub> in a similar way as that found for IIIb, or a reduction to the nitroso derivative which could decompose

into pyridine and nitrous oxide; thermal decomposition of nitrosophenylhydrazine is known to produce aniline and nitrous oxide.<sup>9</sup>



A cleavage of the other nitrogen-nitrogen bond would produce 1-aminopyridine and nitrous acid, both of which are reducible, the latter only in acid solution.

### EXPERIMENTAL

The equipment used for polarography and electrolysis has been described previously. The IR-spectra were recorded on a Perkin-Elmer Infracord or a Beckman IR 18A spectrophotometer; for the UV-spectra a Bausch and Lomb Spectronic 505 was used.

**Materials.** 2-Nitraminopyridine,<sup>10</sup> 3-nitraminopyridine,<sup>11</sup> 4-nitraminopyridine,<sup>12</sup> 1,2-dihydro-1-methyl-2-nitroiminopyridine,<sup>13</sup> 1-aminopyridiniumiodide,<sup>14</sup> 2-hydrazinopyridine,<sup>15</sup> sodium pyridine-2-isodiazotate,<sup>16</sup> and pyridine-1-nitroimide<sup>7,8</sup> were prepared by known methods.

**Reduction of 2-nitraminopyridine (Ia).** Ia (1 g) was reduced in deaerated, prerduced N hydrochloric acid containing 40% ethanol at  $-0.45$  V (SCE),  $n=5.4-5.6$ . A yield of 420 mg of 2-hydrazinopyridinium chloride (Ic) and 405 mg of 2-aminopyridinium chloride (Id) was determined by anodic polarography (Ic) and UV-spectroscopy (Id). The UV-spectrum of the catholyte was inconsistent with an appreciable concentration of 2-chloropyridine (< 2%); the same result was obtained from GLC. During the electrolysis 65 ml of a gas evolved. The reduction completed, the catholyte was evaporated *in vacuo*. TLC on silica with ethanolic HCl as eluent showed only two products, Ic ( $R_F=0.25$ ) and Id ( $R_F=0.59$ ). The residue was dissolved in ethanol; on addition of ether Ic precipitated (360 mg), recrystallized from ethanol, m.p.  $181-183^\circ$  ( $183^\circ$ ),<sup>17</sup> picrate, m.p.  $160^\circ$  ( $161^\circ$ ).<sup>15</sup>

The absence of ammonium chloride in the residue was demonstrated by IR-spectroscopy and by dissolving the residue in aqueous base and distilling most of the aqueous phase into a flask containing 4 N HCl.

Similar reductions of Ia (2 g) in 2 N, resp. 6 N hydrochloric acid gave 1200 mg, resp. 1660 mg of 2-hydrazinopyridine hydrochloride, and 850 mg, resp. 540 mg of 2-aminopyridine hydrochloride. Reduction of Ia in N HCl at  $5^\circ\text{C}$  did not change the ratio of Ic to Id. In an acetate buffer ( $n=6.2$ ), pH 5, the polarographically determined yield of Ic was nearly quantitative; 840 mg Ic, HCl were isolated.

Reduction of Ia in 0.2 N potassium hydroxide ( $E=-1.70$  V (SCE),  $n=3.95$ ) yielded Id as main product, m.p. of picrate  $223-225^\circ$  ( $224-225^\circ$ );<sup>17</sup> during the reductions a small amount ( $\sim 5\%$ ) of Ic could be detected in the catholyte; in the final reduction mixture, the yield of Ic was about 2%. Ic is unstable at high pH and decomposes to pyridine and nitrogen.

**Reduction of 1,2-dihydro-1-methyl-2-nitroiminopyridine (II).** II (1 g) was reduced in N HCl containing 40% ethanol at  $-0.45$  V (SCE),  $n=5.6-5.7$ . 2-Hydrazino-1-methylpyridinium chloride (IIc) (700 mg) and 2-amino-1-methylpyridinium chloride (IIId) (365 mg) were determined by anodic polarography and UV-spectroscopy, respectively. TLC on silica with ethanolic HCl showed IIc ( $R_F=0.13$ ) and IIId ( $R_F=0.26$ ). The catholyte was evaporated *in vacuo*, dissolved in ethanol, filtered, and IIc precipitated on addition of ether, 680 mg, m.p.  $198-198.5^\circ$ . (Found: C 35.91; H 6.09; N 21.63; Cl 35.83. Calc. for  $C_6H_{11}Cl_2N_3$ : C 36.75; H 5.65; N 21.43; Cl 36.17), m.p. of picrate  $159-160^\circ$ . From the filtrate IIId was precipitated as the picrate, m.p.  $199-201^\circ$  ( $203^\circ$ ).<sup>19</sup>

Reduction of II in a phosphate buffer, pH 12.5, at  $-1.2$  V (SCE) gave IIId,  $n=3.9$ . IIId was isolated as the picrate.



*Reduction of 3-nitraminopyridine (IVa).* 3-Nitraminopyridine (1 g) was reduced in 6 N HCl containing 40 % ethanol at  $-0.45$  V (SCE),  $n=6.2$ . Isolated were 887 mg 3-hydrazinopyridine dihydrochloride (IVe), m.p.  $227-230^\circ$ . (Found: C 32.70; H 4.99; N 23.11; Cl 38.82. Calc. for  $C_5H_9Cl_2N_3$ : C 32.98; H 4.98; N 23.08; Cl 38.95), m.p. of picrate  $152-152.5^\circ$ . No 3-aminopyridine was detected.

Reduction in N HCl of IVa (1 g,  $n=5.8$ ) yielded 550 mg IVc and 340 mg 3-aminopyridine dihydrochloride (IVd); the latter was determined by UV-spectroscopy (at  $\lambda=257$  nm and  $332$  nm); TLC on silica with ethanolic hydrogen chloride separated IVc ( $R_F=0.42$ ) from IVd ( $R_F=0.54$ ).

Reduction of IVa in 0.2 N potassium hydroxide containing 40 % ethanol at  $-1.70$  V (SCE) gave IVd,  $n=4.5$ . The reduction completed, the catholyte was made acid with hydrogen chloride, evaporated *in vacuo*, and the residue treated with ethanol. The potassium chloride was removed by filtration and the filtrate evaporated; the residue was identified as 3-aminopyridine dihydrochloride (IVd) by the m.p.  $171-172^\circ$  ( $173.5-174.5^\circ$ ),<sup>20</sup> the IR-spectrum, and the  $R_F$ -value on silica with ethanolic HCl as eluent.

*Reduction of 4-nitraminopyridine (Va).* Va (1 g) was reduced in N hydrochloric acid containing 40 % ethanol at  $-0.65$  V (SCE),  $n=6.1-6.2$ . The yields of 4-hydrazinopyridine hydrochloride (Vc) (515 mg) and 4-aminopyridine hydrochloride (Vd) (260 mg) were determined by anodic polarography and UV-spectroscopy, respectively. TLC on silica with ethanolic HCl as eluent confirmed the presence of Vc ( $R_F=0.53$ ) and Vd ( $R_F=0.59$ ).

Reduction of Va in 6 N hydrochloric acid gave Vc as the only detectable product, decomp.  $240-243^\circ$  ( $242-244^\circ$ ).<sup>21</sup> (Found: C 32.92; H 4.49; N 23.23; Cl 39.61. Calc. for  $C_5H_9Cl_2N_3$ : C 32.98; H 4.98; N 23.08; Cl 38.95), m.p. of picrate  $210-212^\circ$ . Reduction of Va in 0.2 N potassium hydroxide containing 40 % ethanol gave Vd, isolated as described for IVd.

*Reduction of 1-aminopyridinium iodide (IIIb).* IIIb (1 g) was reduced in a deaerated and prerduced 0.5 N HCl at  $-0.90$  V (SCE),  $n=2$ . The reduction completed, the catholyte was evaporated *in vacuo*, the residue treated with absolute ethanol, and ammonium chloride filtered off. The presence of pyridine in the filtrate was shown by UV-spectroscopy and pyridine hydrochloride, isolated on evaporation, m.p.  $80-82^\circ$ ; m.p. of picrate  $163^\circ$  ( $165-166^\circ$ ).<sup>22</sup>

Reduction of IIIb in 0.2 N KOH ( $n=2$ ) at  $-1.35$  V (SCE) yielded pyridine, which was shown by UV-spectroscopy.

*Reduction of pyridine 1-nitroimide (IIIa).* Pyridine 1-nitroimide (IIIa) (100 mg) was reduced at  $-0.75$  V (SCE) in 0.2 N hydrochloric acid containing 30 % ethanol,  $n=2.2$ . The product was pyridine, identified by its smell, the UV-spectrum, and m.p. and IR-spectrum of the picrate. No nitrous acid was formed during electrolysis according to the polarograms.

Reduction of IIIa (100 mg) in 0.1 N potassium hydroxide at  $-1.10$  V (SCE) ( $n=1.7$ ) also yielded pyridine identified as above. No nitrite could be detected polarographically in the catholyte after lowering pH to 1.

*Reduction of 2-hydrazine-1-methylpyridinium chloride (IIc).* IIc (0.25 g) was reduced at  $-1.2$  V (SCE) in 0.16 N hydrochloric acid,  $n=1.7$ . The catholyte was evaporated *in vacuo*. TLC on silica with ethanolic HCl as eluent showed only one product ( $R_F=0.26$ ) identified as 2-amino-1-methylpyridinium chloride (IIc) from the IR-spectrum and m.p.  $198-199.5^\circ$  of the picrate.

*Oxidation of 2-hydrazinopyridine (Ic).* Ic (1 g) was oxidized in 0.5 N potassium hydroxide at  $-0.1$  V (SCE),  $n=1.8$ . A cathodic wave at  $-1.3$  V (SCE) appeared during the oxidation; attempts to isolate the reducible compound failed; only pyridine was obtained.

In another experiment, Ic (200 mg) was oxidized as above; after completion of the oxidation the reducible compound was reduced at  $-1.4$  V (SCE). Some Ic (50 mg) was formed, the yield estimated by UV-spectroscopy.

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