# SELECTIVE ELECTROCHEMICAL ALKYLATION OF 2,2'-DIPYRIDYLAMINE

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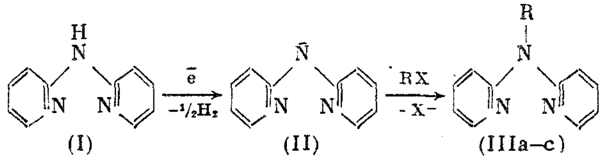
In recent studies on electrochemical synthesis using organic NH-acids [1, 2], it has been established that the action of alkyl halides on the N-anion (II) generated upon the cathodic electrolysis of 2,2'-dipyridylamine (I) leads to the formation of alkyl(2,2'-dipyridyl)amines (IIIa)-(IIIc), i.e., the alkylation occurs at the exocyclic nitrogen atom.



R = Me, X = I (a); R = All, X = Br (b); R = $PhCH_2$, X = Cl (c).

Anion (II) was detected by its oxidation wave ($E_{1/2}$ = −0.4 V relative to Ag/Ag$^+$) arising in the polarization curve during the hydrolysis of (I) on a platinum cathode (E = −2.7 V). The addition of RX to the solution leads to the disappearance of this wave. Thus, in the case of (I), feasibility has been demonstrated for the selective electrochemical alkylation of ambident nucleophiles with an amidine system.

The reaction of (I) with RX in the absence of base exclusively gives products of alkylation at the ring nitrogen atoms [3]. On the other hand, the action of MeI on (I) in the presence of NaH led to the formation of (IIIa) but this product could be isolated only as the dihydrobromide in low yield [4].

The electrolyses were carried out in a diaphragm cell in a galvanostatic mode (current 1-3 mA/cm$^2$, 1.1 F/mole, $V_{catholyte}$ = 80 ml, $V_{anolyte}$ = 40 ml) in 0.25 $NBu_4NBr$ in abs. acetonitrile containing 0.01 mole (I) and 0.01 mole RX. Products (IIIa)-(IIIc) were separated from the reaction mixture after removal of acetonitrile by extraction with hexane. Products (IIIa) and (IIIb) were purified by distillation, while (IIIc) was recrystallized from ether. The yield of (IIIa) was 73%, bp 110-111°C (1 torr), $n_D^{20}$ 1.6247. The yield of (IIIb) was 60%, bp 123-124°C (1 torr), $n_D^{20}$ 1.6240. The yield of (IIIc) was 68%, mp 83-84°C. The structures of (IIIa)-(IIIc) were supported by their IR, PMR, and mass spectra. The elemental analysis results were satisfactory.

We have used (IIIa)-(IIIc) as ligands for the preparation of $LMCl_2$ chelates, where L = (IIIa)-(IIIc) and M = Pd or Cu.

## LITERATURE CITED

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