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ELECTROCHEMICAL ALKYLATION OF 2,2'-DIPYRIDYLAMINE

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A method was developed for preparation of alkyl-(2,2'-dipyridyl)amines, consisting of the reaction of alkyl halides with the N anion electrochemically generated from 2,2'-dipyridylamine. The alkylation occurs regiospecifically, and CH_2Cl_2 can also be used as the methylating agent. Complexes of alkyl-(2,2'-dipyridyl)amines with Pd(2+) and Cu(2+) salts were obtained.

2,2'-Dipyridylamine (I) is widely used as a chelating ligand in coordination chemistry. Many complexes of various metals containing (I) in deprotonated or neutral form are known [1-4]. Apparently, products of alkylation of (I) at an exocyclic nitrogen atom, alkyl-(2,2'dipyridyl)amines (ADPA), can also be used as chelate formers. With respect to their structure, complexes of metals with ADPA should apparently be analogous to chelates of un-deprotonated (I).

However, the literature contains almost no information on ADPA, probably because of certain difficulties in their synthesis. As is known, alkylation of 2-aminopyridine occurs at the nitrogen atom of the pyridine ring, and only in the presence of strong bases, such as NaNH₂, is it possible to carry out substitution at the amino group [5]. 2-(Alkylamino)-pyridines behave similarly, and, correspondingly, during heating with alkyl halides, (I) is alkylated exclusively at the ring nitrogen atoms [6, 7]. The reaction of (I) with CH_2I_2 results in formation of a six-membered ring involving both nitrogen atoms of pyridine rings. In a patent [8], Webb et al. attempted to obtain methyl-(2,2'dipyridyl)amine by the reaction of MeI with (I) in the presence of NaH, but the desired product was recovered only as a dihydrobromide and in low yield.

Recently it was shown that the electrochemical generation of N anions from nitrogenous bases containing the NH group open up interesting possibilities in carrying out N-alkylation processes [9, 10]. In the present paper, we consider the formation of ADPA from (I) and alkyl halides under conditions of cathodic electrolysis (see preliminary communication [11]).

According to data of voltammetric measurements, there was one wave (Fig. 1, curve 1) with $E_1^1 = -2.6$ V (with respect to Ag/0.1 N Ag⁺) on the polarization curves of reduction of (I) at a Pt rotating disk electrode in a 0.1 N solution of Bu_4NBF_4 in abs. MeCN. According to coulometric measurements, the height of this wave corresponded to transfer of one electron. On the polarization curves recorded during potentiostatic (E = -2.7 V) electrolysis of (I), an anodic wave with $E_{1/2} = -0.4$ V (curve 2) appeared and grew. It can be assumed that the species undergoing oxidation at $E_{1/2} = -0.4$ V was an anion that was generated as a result of cathodic cleavage of the N-H bond (cf. with [9] and [10]). A confirmation of this is the fact that the addition of MeI to the solution after electrolysis of (I) led to disappearance of the anodic wave with $E_{1/2} = -0.4$ V on the polarization curves. Apparently, anion (II), which was formed under conditions of cathodic electrolysis, was alkylated in the presence of MeI. This was indicated by the appearance (curve 3) of a wave of oxidation

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Fig. 1. Polarization curves of 2,2'-dipyridylamine (I) recorded with Pt rotating disk electrode in 0.1 N solution of Bu_4NBF_4 in abs. MeCN: 1) at (I) concentration 7.8·10⁻³ M; 2) during electrolysis (E = -2.7 V) on reduction wave of (I); 3) during electrolysis of (I) after addition of MeI; 4) curve of supporting electrolyte.

of I⁻ (addition of Bu₄NI to the catholyte caused an increase of the height of this wave without a change of its $E_{1/2}$). We should note that the current-dependent yield of anion (II) during the electrolysis of (I) was quantitative. This follows from the data obtained by using a rotating ring-disk electrode (see below) and also from the fact that an increase of the height of the anodic wave of anion (II) during electrolysis occurred in parallel to the decrease of the reduction wave of (I). By using the rotating ring-disk electrode, it was determined that electrolysis at a disk potential ($E_d = -2.7$ V) chosen at the plateau of the reduction wave of (I) led to the appearance of the above-mentioned anodic wave ($E_{1/2} = -0.4$ V) at the ring electrode. The current efficiency of this wave was close to quantitative (N = 0.42 at N_{theor} = 0.442) and was practically independent of the rate of rotation of the electrode, which indicates the formation of a stable species.

On the basis of these data, we developed an efficient method for alkylation of (I) consisting in the reaction of alkyl halides (MeI, AllBr, and PhCH₂Cl) with N anion (II), electrochemically generated from (I). The alkylation occurred regiospecifically at the exocyclic nitrogen atom, and ADPA (IIIa-c) were obtained in 60-73% yields in this way.



The structure of (IIIa-c) was confirmed by data of IR, PMR, and mass spectroscopy. Compounds (IIIa) and (IIIb) are viscous liquids, distilled under vacuum without decomposition, and (IIIc) was recovered in the form of colorless crystals, freely soluble in organic solvents.

In previous papers [10, 12], we showed that methylene chloride can be used as a methylating agent under conditions of cathodic electrolysis. Developing these investigations, we determined that during the electrochemical generation of anion (II) from (I) in CH_2Cl_2 the formation of (IIIa), recovered in 50% yield, also occurs. Apparently, the reaction of (II) with CH_2Cl_2 affords chloromethyl-(2,2'-dipyridyl)amine (IV), which is reduced at the cathode faster than it reacts with another anion with conversion to aminal (V)



In complexation reactions with salts of bivalent metals, ADPA behave like bidentate ligands and form complexes of composition $[M(ADPA)]X_2$. Thus, from (IIIa) and $PdCl_2(PhCN)_2$ in benzene we obtained yellow crystalline chelate (VI), whose structure was confirmed by data of IR and PMR spectroscopy. Similarly, the reaction of a solution of (IIIb) in methanol with an aqueous solution of CuCl₂ gave green crystalline chelate complex (VII)



The electrochemical method of alkylation of (I) opens up possibilities for preparation of more complex ligands containing functional groups in the N-alkyl substituent.

EXPERIMENTAL

Current-voltage and coulometric measurements were carried out in an argon atmosphere in a controlled-temperature (25 ± 0.1°C) cell with cathodic and anodic spaces separated by a glass filter. The polarization curves were recorded with a Pt rotating disk electrode (S = 7.61 · 10⁻³ cm²). In investigations using a rotating ring-disk electrode, we used an electrode with the following characteristics: $S_d = 0.239 \text{ cm}^2$, $S_c = 0.261 \text{ cm}^2$, and N = 0.442. The potential was fed to disk and ring electrodes by two self-reacting P-5827M potentiostats. The supporting electrolyte was 0.1 N Bu₄NBF₄ in abs. MeCN.

Preparative electrolysis was carried out in a glass cell equipped with a ceramic diaphragm in an Ar atmosphere at 20°C. The cathode was a Pt foil (S = 35 cm²), the anode was a Pt foil (S = 21 cm²), and stirring was carried out with a magnetic stirring device. The effective volumes of the catholyte and anolyte were 80 and 40 ml, respectively. Cyclohexene was added for binding of Br_2 into the anolyte. Electrolysis was carried out under galvanostatic conditions.

The PMR spectra were recorded on a Bruker WM-250 instrument, the IR spectra were recorded on a UR-20 spectrometer, and the mass spectra were recorded on a Varian MAT CH-6 instrument.

<u>Methyl-(2,2'-dipyridyl)amine (IIIa).</u> a. The catholyte was 0.1 M Bu₄NBr and 2 g (0.0117 mole) of (I) in MeCN, and the anolyte was 0.1 M Bu₄NBr and 3 ml (0.03 mole) of cyclohexene in MeCN. We passed 1.1 F of electricity per mole (I \approx 0.08 A), and 1.7 g (0.012 mole) of MeI was added to the catholyte in one portion. The reaction mixture was left overnight under argon, the MeCN was driven off, and the residue was extracted with hexane (20 ml \times 6). After the hexane had been driven off, distillation yielded 1.59 g (73%) of (IIIa) with bp 110-112°C (1 mm) and nD^{2°} 1.6247. Found: C 70.86; H 6.20; N 22.90%. C₁₁H₁₁N₃. Calculated: C 71.33; H 5.99; N 22.68%. Mass spectrum, m/z: 185 [M]⁺; 169 [M-Me]⁺. IR spectrum (CHCl₃, ν , cm⁻¹): 1590, 1565 (C=N, C=C). PMR spectrum (CDCl₃, δ , ppm): 3.60 singlet (N-Me), 6.82 triplet (2 β -H_{Py}), 7.14 doublet (2 β '-H_{Py}), 7.48 triplet (2 γ -H_{Py}), 8.31 doublet (2 α -H_{Py}).

b. The catholyte was 0.25 M Bu₄NBr and 1 g (0.0058 mole) of (I) in CH_2Cl_2 , and the anolyte was 0.25 M Bu₄NBr and 3 ml (0.03 mole) of cyclohexene in CH_2Cl_2 . We passed 3.2 F of electricity per mole (I \approx 0.12 A). The CH_2Cl_2 was driven off from the catholyte, the residue was extracted with hexane (20 ml \times 6), and, after removal of hexane, 0.86 g of crude (IIIa) was recovered; for separation from (I), the crude (IIIa) was passed through a column (the sorbent was Silpearl, and the eluent was $CHCl_3$ -EtOH, 4:1). We obtained 0.54 g (50%) of (IIIa).

<u>Allyl-(2,2'-dipyridyl)amine (IIIb).</u> The catholyte was 0.1 M Bu₄NBr and 1 g (0.0058 mole) of (I) in MeCN, and the anolyte was 0.1 M Bu₄NBr and 3 ml (0.03 mole) of cyclohexene in MeCN. We passed 1.1 F of electricity per mole (I \approx 0.08 A), after which we added 0.7 g (0.006 mole) of allyl bromide. We recovered (IIIb) as in the preceding run. We obtained

1.48 g (60%) of (IIIB) with bp 123-125°C (1 mm) and n_D^{20} 1.6240. Mass spectrum, m/z: 211. Found 73.81; H 6.43; N 20.22%. $C_{13}H_{13}N_3$. Calculated: C 73.90; H 6.21; N 19.89%. PMR spectrum (CDC1₃, δ , ppm): 4.77-4.88 multiplet (CH₂=), 5.02-5.20 multiplet (NCH₂), 5.90-6.08 multiplet (CH=), 6.80 triplet (2 β -H_{Py}), 7.13 doublet (2 β '-H_{Py}), 7.50 triplet (2 γ -Hy), 8.30 doublet (2 α -H_{Py}).

Benzyl-(2,2'-dipyridyl)amine (IIIc). The catholyte was 0.1 M Bu₄NBr and 1.2 g (0.007 mole) of (I) in MeCN, and the anolyte was 0.1 M Bu₄NBr and 3 ml (0.03 mole) of cyclohexene in MeCN. We passed 1.1 F of electricity per mole (I \approx 0.09 A) and added 0.89 g (0.007 mole) of benzyl chloride. The catholyte was held for 8 h, the MeCN was driven off, and the residue was extracted with hexane. After the hexane had been driven off and the residue recrystal-lized from ether, we obtained 1.25 g (68%) of colorless crystals of (IIIc) with mp 83-84°C. Found: C 78.34; H 5.93; N 16.32%. C₁₇H₁₅N₃. Calculated: C 78.13; H 5.79; N 16.08%. Mass spectrum, m/z: 261 [M]⁺. PMR spectrum (CDCl₃, δ, ppm): 5.53 singlet (NCH₂), 6.87 triplet (2β-H_{Py}), 7.05-7.65 multiplet (Ph + 2β'-H_{Py} + 2γ-H_{Py}), 8.35 doublet (2α-H_{Py}).

 $\frac{\text{Complex of (IIIa) with PdCl_2 (VI)}{1000029}$ To a solution of 0.11 g (0.00029 mole) of PdCl_2-(PhCN)_2 in 10 ml of benzene was added with stirring a solution of 0.05 g (0.00027 mole) of (IIIa) in 2 ml of benzene. The whole was stirred for 10 h at 20°C, and the resulting yellow precipitate was filtered. We obtained 0.07 g (72%) of (VI) with decomposition temp. >220°C (DMF). Found: C 36.43; H 3.04; N 12.03; Pd 29.55; Cl 19.75%. C₁₁H₁₁N₃PdCl₂. Calculated: C 36.44; H 3.06; N 11.59; Pd 29.35; Cl 19.56%. IR spectrum (KBr, v, cm⁻¹): 1582, 1601 (C=C, C=N). PMR spectrum (DMSO-d₆, δ , ppm): 3.70 singlet (Me), 7.32 triplet (2 β , H_{Py}), 7.51 doublet (2 β '-H_{Py}), 8.10 triplet (2 γ -H_{Py}); 8.65 (2 α -H_{Py}).

<u>Complex of (IIIb) with $CuCl_2$ (VII)</u>. To a solution of 0.092 g (0.00054 mole) of $CuCl_2 \cdot 2H_2O$ in 0.35 ml of water was added 0.114 g (0.00054 mole) of (IIIb) in 0.35 ml of methanol. The mixture was left at 20°C for 24 h, the resulting dark-green crystals were filtered, and 0.14 g (75%) of (VII) with mp 119-120°C was obtained. Found: C 44.94; H 3.60; N 12.03%. $C_{13}H_{13}N_3CuCl_2$. Calculated: C 45.16; H 3.79; N 12.16%. IR spectrum (KBr, v, cm^{-1}): 1578, 1600 (C=C, C=N), 1640 (C=C).

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