# Electroreductive Coupling of Organic Halides with Aldehydes Catalyzed by Nickel(0) Complex with 2,2'-Bipyridine

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#### Received July 13, 1999

Abstract—A method of electrosynthesis of secondary alcohols from aldehydes and organic halides under the action of nickel(0) complexes is proposed. The key stage is addition of  $\sigma$ -complex RNi(I)bipy (bipy is 2,2'-bipyridine) to the aldehyde group.

Present-day organic chemistry strives to combine the search for new reactions with the optimization of known and new methods of syntheses. Economic as well as environmental considerations make the investigators to raise the selectivity of reactions and use more simple experimental conditions. It is for these reasons that homogeneous catalysis is coming into ever increasing use, since it has marked advantages, especially from the viewpoint of selectivity and efficiency. As a matter of fact, transition metal complexes in lower oxidation states, such as electrochemically generated Ni(0, I), Pd(0), or Co(I), can react with various functional groups to catalyze the formation of the C-C bond [1]. The reactions of addition to the carbonyl bond is still studied to a lesser extent. Two main types of the reaction are known, namely, allylation of carbonyl compounds, and the Reformatsky reaction [2,3]. In the first case one must use the catalytic system PdCl<sub>2</sub>–ZnCl<sub>2</sub> [2], and in the latter case the reaction occcurs only with  $\alpha$ -chloroacetates [3].

The aim of the present study was to examine the possibility of using  $\sigma$ -organic complexes RNi(II)Xbipy (bipy is 2,2'-bipyridine) obtained by the reaction of Ni(0) complex Ni(bipy) with organic halides for the addition to the carbonyl group under the conditions of electrolysis with soluble anodes.

The character of the reaction of organometallic compounds with carbonyl derivatives depends on their nature. Grignard reagents are able to add to the carbonyl group to reduce it to hydroxy group. Transition metals, including Ni, Pt, and Mo in various oxidation states, can coordinate with the carbonyl group [4], two types,  $\pi$ - and  $\sigma$ -coordination being distinguished [5, 6]. In the majority of complexes the

carbonyl group is  $\sigma$ -coordinated, while  $\pi$ -coordination is less common [6].  $\sigma$ -Complexes are formed with aliphatic, and  $\pi$ -complexes with aromatic aldehydes and ketones. For some complexes, such as rhenium(0) ones with aromatic aldehydes, there is observed an equilibrium between the two types of complexes [7]. The predominance of  $\pi$ - or  $\sigma$ -character of coordination depends on the basisity of the carbonyl group [7]. As an example, donor groups in the aromatic ring enhance the basic character of the carbonyl group, while acceptor groups, on the contrary, cause a fall in the basicity thus promoting delocalization of the double bond in the molecule and favoring  $\pi$ -binding.

We suggested that in the presence of organic halides the electrochemically generated Ni(0)bipy complexes either  $\sigma$ -complexes RNi(II)Xbipy, or the products of oxidative addition RNi(I)bipy, would react with carbonyl group to give the products of reductive addition and, eventually, alcohols. Of particular interest was investigation of the possibility of synthesis of alcohols with electron-acceptor substituents in the aromatic ring which are impossible to prepare by common chemical methods in one stage. In addition, voltammetry and preparative electrolysis make it possible for the mechanism of the reaction to be studied by breaking the reaction up and simulating the separate parts. Up to now the reactions of organonickel compounds with carbonyl group were not studied.

The preliminary experiments on functionalization of carbonyl compounds were performed in an unseparated cell with a magnesium anode and  $NiBr_2bipy$  as a catalyst precursor. As an electrolyte we used a solution of  $Bu_4NBF_4$  in DMF with added benzaldehyde and 2-bromotoluene. It was found that under

Coupling of organic halides with aldehydes catalyzed by Ni(0)bipy (1 mmol NiBr<sub>2</sub>bipy, 15 mmol ArX, 7.5 mmol RCHO,  $Bu_4NBF_4$  as a background electrolyte,  $c \times 10^{-2}$  mol l<sup>-1</sup>, I 0.1 A, nickel gauze as a cathode, 20°)

ArX	RCHO	Product	Anode	Yield, % from C <sub>6</sub> H <sub>5</sub> CHO
2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	С <sub>6</sub> Н <sub>5</sub> СНО	C <sub>6</sub> H <sub>5</sub> CH(OH)C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -2	Mg Zn Ni Fe b	$ \begin{array}{r}     14 \ (75^{a}) \\     18 \\     61 \\     63 \\     80 \end{array} $
2-BrC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CHO	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH(OH)C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -2	Ni b	60 71
$\begin{array}{c} 2\text{-BrC}_{6}\text{H}_{4}\text{CH}_{3} \\ 2\text{-BrC}_{6}\text{H}_{4}\text{CH}_{3} \\ 2\text{-BrC}_{6}\text{H}_{4}\text{NH}_{2} \\ 2\text{-BrC}_{6}\text{H}_{4}\text{OCH}_{3} \\ 4\text{-CIC}_{6}\text{H}_{4}\text{CO}_{2}\text{CH}_{3}^{\text{c}} \\ \text{CH}_{3}\text{C}(\text{Br})\text{=CHCH}_{3} \end{array}$	$\begin{array}{c} {\rm Cyclohexanone} \\ {\rm C_8H_{17}CHO} \\ {\rm C_6H_5CHO} \end{array}$	$\begin{array}{c} 2\text{-}\mathrm{CH}_{3}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{C}_{6}\mathrm{H}_{10}(\mathrm{OH})\text{-}1\\ \mathrm{C}_{8}\mathrm{H}_{17}\mathrm{CH}(\mathrm{OH})\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{CH}_{3}\text{-}2\\ \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{CH}(\mathrm{OH})\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{NH}_{2}\text{-}2\\ 2\text{-}\mathrm{CH}_{3}\mathrm{OC}_{6}\mathrm{H}_{4}\mathrm{CH}(\mathrm{OH})\mathrm{C}_{6}\mathrm{H}_{5}\\ \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{CH}(\mathrm{OH})\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{CO}_{2}\mathrm{CH}_{3}\text{-}4\\ \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{CH}(\mathrm{OH})\mathrm{C}(\mathrm{CH}_{3})\text{=}\mathrm{CHCH}_{3}\\ \end{array}$	Ni b Ni b b	50 58 42 85 50 <sup>c</sup> 52

<sup>a</sup> 7 mmol NiBr<sub>2</sub>bipy. <sup>b</sup> Stainless steel. <sup>c</sup> Yield from ArCl, 7.5 mmol RCHO.

certain conditions a product of addition to the carbonyl group, (2-methylphenyl)phenylcarbinol was formed as a result of electrosynthesis, and the yield of the latter compound was proportional to the concentration of  $NiBr_2$ bipy in the solution (see table and Fig. 1). The above observation makes it possible to suggest that nickel(II) ions are fixed in nickel(II) alcoholate and moved out of the cycle. 2-Bromotoluene as a model compound was used because on reaction with Ni(0) it forms stable organonickel compounds which makes it possible for the reaction pathway to be followed.

The absence of the catalytically active form of nickel(II) after passing 2 F of electricity per mol Ni at -1.2 V is evidenced by the voltammograms of the solution: the reduction wave of NiBr<sub>2</sub>bipy disappears,



**Fig. 1.** Plot of the concentration of the reaction product, (2-methylphenyl)phenylcarbinol, in the electrolyte vs. the initial concentration of NiBr<sub>2</sub>bipy (Mg anode, -1.35 to -1.47 V).

and only waves at more negative potentials remain. Moreover, it was shown that at the potential of reduction Ni(II)/Ni(0) of -1.2 V relative to a saturated mercurous chloride electrode no alcohol is formed, and the target coupling process takes place only at more negative potentials corresponding to further reduction of the  $\sigma$ -complex TolNiBr (Tol is 2-tolyl), -1.35 V (Fig. 2). The following scheme of the reaction can be suggested.

$$\begin{split} \mathrm{Ni}^{+2}\mathrm{Br}_{2}\mathrm{bipy} &+ 2\bar{e} \longleftrightarrow \mathrm{Ni}^{0}\mathrm{bipy} &+ 2 \mathrm{Br}^{-} &-1.2 \mathrm{V}, \ (1) \\ \mathrm{Ni}^{0}\mathrm{bipy} &+ \mathrm{TolBr} \longrightarrow \mathrm{TolNi}^{+2}\mathrm{Brbipy} \quad (\mathrm{stable}), \ (2) \\ \mathrm{TolNi}^{+2}\mathrm{Brbipy} &+ \mathrm{PhCHO} \xrightarrow{} & (3) \\ \mathrm{TolNi}^{+2}\mathrm{Brbipy} &+ \bar{e} \longrightarrow \mathrm{TolNi}^{+1}\mathrm{bipy} &+ \mathrm{Br}^{-} &-1.35 \mathrm{V}, \ (4) \\ \mathrm{TolNi}^{+1}\mathrm{bipy} &+ \mathrm{PhCHO} \longrightarrow \mathrm{PhCH-Tol} &+ \mathrm{bipy}, \ \ (5) \\ & 0 \\ \mathrm{O-Ni} \end{split}$$

Anode-generated atoms of magnesium do not substitute for nickel(II) in the forming alcoholate, and the catalyst is thus consumed. We speculated that replacing the anode by a nickel or a one similar with it in properties would allow the catalyst to be consumed in significantly lower amounts because of regeneration. The results of electrosyntheses are given in the table. It is evident that the syntheses proceed at high yields of the alcohol with the use of nickel or iron, as well as stainless-steel anodes, and other aromatic aldehydes with donor groups in the ring (CH<sub>3</sub>O) and aliphatic aldehydes and cyclohexanone can be involved into the reaction. As arylating agents

1-amino-2-bromobenzene and 2-bromo-1-methoxybenzene can be used which, but only those with ortoposition of the donor substituent probably provide stability of the ArNi(I)bipy reagent. In the case of meta- and para-substituents biaryls Ar<sub>2</sub> are mainly formed, and no noticeable addition to the carbonyl bond is observed. At the same time, alcohol with an acceptor substituent CO<sub>2</sub>Me in the ring was obtained with reasonable yields when X = Br was changed by X = Cl. This allowed the homocoupling reaction of ArNi(I)bipy with ArX to be slowed down and to direct the process to the functionalization of the aldehyde, but in this case three- or four-fold excess of the aldehyde is needed. The fact that aromatic aldehydes with acceptor substituents in the ring which favor  $\pi$ -binding practically do not enter the reaction (only trace amounts of the corresponding alcohols were found), and that the reaction does take place with aliphatic aldehydes, is suggestive of the predominantly  $\sigma$ -character of binding between organonickel complex and the C=O group of the aldehyde.

$$\begin{array}{c} H & N \\ R - \underbrace{- O}_{Ni-Ar} \xrightarrow{K - C = O}_{Ni-Ar} \end{array}$$

It can be thus concluded that electroreductive coupling of organic halides and aldehydes catalyzed by nickel complex with 2,2'-bipyridine is an efficient process demonstrating the potentialities of homogeneous electroreductive reactions.

### **EXPERIMENTAL**

The reaction products were identified by means of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy on a Brucker (200 MHz) spectrometer, their concentrations in the course of electrolysis were monitored by GLC with the use of dodecane as an internal reference. For the electroanalytical experiments we used an EGG-PARC 273A potentiostat with the EGG-PARC M270 software.

The solvent DMF (Merck, main substance content over 99.5%) was dried over 4 Å molecular sieves and used without further purification. Tetrabutylammonium fluoborate (over 99%) was dried at 70°C in a vacuum for 24 h and then kept in a dry vessel. The complex NiBr<sub>2</sub>bipy was prepared from NiBr<sub>2</sub>. 3H<sub>2</sub>O and equivalent of 2,2'-bipyridine in ethanol; the solution was left for 12 h, the precipitate was filtered off, washed with ethanol, and dried at 70°C in a vacuum for 24 h. Aryl halides and carbonyl compounds were commercial products (Aldrich).

As an anode we used a magnesium rod (Johnson Mattey) which was polished prior to every experiment.



**Fig. 2.** Plot of the yield of (2-methylphenyl)phenylcarbinol vs. the quantity of electricity consumed in the process.

The reference electrode was saturated mercurous chloride electrode placed into DMF and  $Bu_4NBF_4$  and separated from the solution by a glass barrier. For the preparative syntheses we used a cylindrical cathode made of nickel gauze. The process was carried out under galvanostatic conditions at *I* 100–200 mA (20°). The experimental conditions: into 40 ml of the solvent (DMF) 15 mmol of an organic halide ArX and 7.5 mmol of a carbonyl compound RCHO (in the case of 4-ClC<sub>6</sub>H'<sub>4</sub>O<sub>2</sub>CH<sub>3</sub> 7.5 mmol of ArX and 30 mmol of RCHO, respectively), 1 mmol of NiBr<sub>2</sub>bipy was added; the background electrolyte was  $Bu_4NBF_4$  (*c*  $10^{-2}$  mol  $1^{-1}$ ).

(2-Methylphenyl)phenylcarbinol. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , pp: 2.09 s (3H), 2.43 s (1H), 5.79 s (1H), 6.98–7.20 m (1H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 142.89, 141.48, 135.37, 130.53, 128.46, 127.54, 127.16, 126.31, 126.13, 73.29, 19.40.

(2-Aminophenyl)phenylcarbinol. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 6.43–6.68 m (2H), 5.73 s (1H), 3.47 s (2H), 2.28 s (1H), 6.90–7.10 m (2H), 7.15–7.47 m (5H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 128.67, 128.52, 128.42, 128.23, 127.34, 126.31, 118.09, 116.72, 74.65.

**1-(2-Methylphenyl)cyclohexanol.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 7.18–6.95 m (4H), 2.21 s (3H), 2.19–1.09 m (10H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_C$ , ppm: 134.22, 130.17, 129.02, 128.40, 125.36, 40.62, 30.64, 28.85, 24.14, 23.77, 22.39, 20.02, 14.11.

**1-(2-Methylphenyl)-1-octanol.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 7.30–7.34 m (1H), 6.95–7.10 m (4H), 4.77–4.71 m (1H), 2.19 s (3H), 1.57–0.75 m (17H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 142.92, 134.14, 130.65, 130.04, 126.75, 126.54, 125.98, 125.00, 119.77, 114.68, 70.44, 37.95, 31.69, 29.17,

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29.37, 29.10, 29.05, 27.51, 26.17, 25.83, 22.46, 18.81, 13.87.

**2-Methoxyphenyl(2-methylphenyl)carbinol.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 2.43 s (3H), 3.98 s (3H), 6.48 s (1H), 7.04–7.44 m (8H), 7.48–7.73 m (1H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 156.81, 140.44, 135.40, 131.05, 130.63, 129.99, 128.57, 127.62, 127.00, 126.35, 125.73, 120.51, 119.74, 110.27, 67.92, 55.18, 18.98.

**2-Methoxyphenyl(phenyl)methanol.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 7.32–6.98 m (9H), 5.95 s (1H), 3.63 s (3H), 2.0 s (1H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 156.49, 143.40, 132.01, 131.35, 128.50, 128.01, 127.58, 126.96, 126.47, 120.65, 110.60, 71.66, 55.20.

**4-Methoxycarbonylphenyl(phenyl)carbinol.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 7.82–7.86 m (2H), 7.73–7.11 m (7H), 5.69 s (1H), 4.50 s (1H), 3.75 s (1H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 196.9, 167.12, 148.91, 143.26, 131.79, 129.73, 129.02, 128.61, 128.49, 127.84, 127.58, 126.99, 126.65, 126.35, 115.23, 75.77, 52.11.

**2-Butenyl-2-methyl-1-phenyl-1-ol.** <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 7.11–7.31 m (6H), 5.58–5.69 q (1H), 5.02 s (1H), 2.92 s (1H), 1.53–1.76 m (3H), 1.45 m (3H). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_{\rm C}$ , ppm: 142.64, 142.49, 137.53, 137.27, 130.26, 128.18, 127.94, 127.20, 127.05, 126.92, 126.65, 126.11, 125.39, 121.92, 120.88, 79.02, 13.02, 11.49.

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