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A zerovalent nickel-2,2′-bipyridine complex: an efficient catalyst for electrochemical homocoupling of *ortho*-substituted halides and their heterocoupling with *meta*- and *para*-substituted halides

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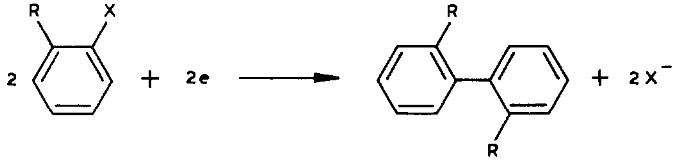
Abstract

Electroreduction of *ortho*-substituted halides ArX in a nickel-2,2′-bipyridyl system and *N*-methylpyrrolidone as solvent gave the homocoupling product ArAr. The nickel-2,2′-bipyridyl system is also a catalyst for the electrochemical heterocoupling of ArX with *meta*- or *para*-substituted halides Ar′X′.

Introduction

We recently reported a new method for the coupling of organic halides [1]. Electroreduction of the halides is performed in an undivided cell using a magnesium anode, a gold gauze cathode and a nickel complex of 2,2′-bipyridine (bipy) as catalyst. The electrolysis is conducted at a constant potential of -1.2 V/e.c.s. and corresponds to the redox transition Ni^{II}/Ni^0 in *N*-methylpyrrolidone (NMP) as solvent.

We applied this method to the homocoupling of *ortho*-substituted aromatic halides (reaction 1) and the heterocoupling of *ortho*- with *para*- or *meta*-substituted aromatic halides (reaction 2).



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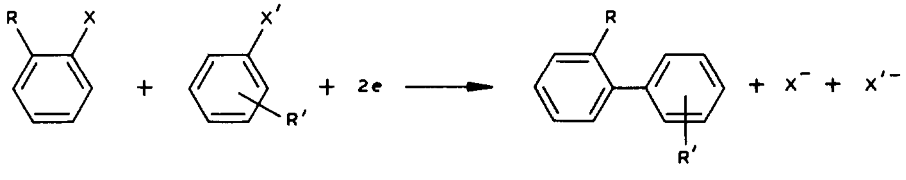

(2)

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Attempts to chemically couple *ortho*-substituted halides have often been unsuccessful [2] and yields are generally low.

Heterocoupled products can be synthesized by several electrochemical methods, viz.:

(a) electroreduction of a mixture of ArX and Ar′X′ in the presence of nickel complexes [1]

$$\mathrm{ArX + Ar'X' + 2e^- \xrightarrow{\text{“Ni”}} ArAr' + X^- + X'^-}$$

(b) electroreduction of ArPdX in the presence of Ar′X′ [3]

$$\mathrm{ArX \xrightarrow{Pd^0} ArPdX \xrightarrow[Ar'X']{2e^-} ArAr' + X^- + X'^- + Pd^0}$$

(c) reaction of an organolithium compound Ar′Li with ArNiX [4]

$$\mathrm{Ar'Li + ArNiX \rightarrow ArAr'Ni}$$

followed by the electrooxidation of the intermediate organonickel complex

$$\mathrm{ArAr'Ni \xrightarrow{-2e^-} ArAr' + Ni^{II}}$$

The first method is limited to halides having similar reactivities towards zerovalent nickel. The second requires a two-step procedure and use of expensive compounds (iodides and palladium). In the third method, the organolithium compound must be prepared before the electrochemical reaction can be performed.

In the present experiments, electrochemical coupling was achieved in one step. Good yields of coupling products such as ArAr or ArAr′, were obtained very easily.

Experimental

The electrochemical cell used has been described in detail previously [1]. A cylindrical magnesium rod (anode) which was surrounded by a stainless steel or gold gauze (cathode) was placed in a diaphragm-less cell. *N*-Methylpyrrolidone (NMP) (30 ml) was used as solvent and KI (15 mmol) was used as supporting electrolyte. $\mathrm{NiBr_2bipy}$ (0.6 mmol), bipy (1.2 mmol) and ArX (6 mmol) were added to this solution in the case of the homocoupling reaction and $\mathrm{NiBr_2bipy}$ (1.2 mmol) and bipy (2.4 mmol), ArX (6 mmol) and Ar′X′ (6 mmol) in the case of a heterocoupling reaction.

Electrolysis was carried out at room temperature under 1 atmosphere of argon. In earlier experiments, electrolysis was conducted at a controlled potential, i.e. the level at which $\mathrm{Ni^{II} \rightarrow Ni^0}$ [1], but we now operate essentially at constant current (5 $\mathrm{mA/cm^2}$). Compounds such as chloroacetophenone however, were too easily reduced, and in this case, the potential of the gold gauze cathode was maintained at -1.2 V/e.c.s. The solution was then added to aqueous 6 *N* HCl and the products extracted with ether. The ethereal solution was analysed by GLC and/or mass spectrophotometry.

Results and discussion

Homocoupling of ortho-substituted halides

When the electrolysis was performed with the potential of the cathode at the level of the redox transition $\mathrm{Ni^{II} \rightarrow Ni^0}$, and in the presence of ArX, the intensity fell

Table 1

Results of oxidation of $Ar_2Nibipy$ by O_2

Number of cycles	1	2	3	4
ArX consumed (%)	14	27	40	49
Yield (%) of dimer vs. ArX consumed	91	92	88	88

almost to zero when the quantity of electricity reached 4 moles of electron per mole of Ni^{II}. This is in agreement with the overall reaction:

$$2\ ArX + NiBr_2bipy + 4\ e^- \rightarrow Ar_2Nibipy + 2\ X^- + 2\ Br^-$$

In most cases this electrochemical reduction leads to a stable diarylnickel species $Ar_2Nibipy$. Voltammetric recordings showed that the $Ar_2Nibipy$ species is reversibly reducible at −1.5 V/e.s.c., which probably corresponds to the following process:

$$Ar_2Nibipy + e^- \rightarrow Ar_2Nibipy^{\cdot-}$$

This electroreduction of $Ar_2Nibipy$ does not give biaryl.

On the other hand, $Ar_2Nibipy$ can be oxidized at +0.2 V/e.c.s. to give almost quantitative yields of biaryl and Ni^{II}. Bubbling oxygen into the solution containing Ar_2Ni formed after passage of 4 moles of electron per mole of Ni^{II} provides a convenient method for ArAr recovery. Ar_2Ni decomposes to ArAr and the Ni^{II} is regenerated almost quantitatively as indicated by voltammetric data. Once the cell has been purged with argon a new cycle of Ni^{II} electroreduction can be commenced. This procedure was used to prepare biaryls, and the results of the homocoupling of *ortho*-chloroanisole after various numbers of cycles are as shown in Table 1.

The yield of dimer was nearly constant, as was the recovery of nickel(II). The quantity of dimer formed greatly exceeded the amount of catalyst. The same procedure was used with various halides ArX, and the results after one cycle are summarised in Table 2.

It is clear that the chlorides, known to be much less reactive to Ni^0 than bromides and particularly iodides, give better yields of dimers. In addition, the percentage of ArH obtained is lower for the chlorides (10%), than for the bromides (30%).

Table 2

Results of oxidation of $Ar_2Nibipy$ by O_2 with various halides ArX

ArX	Yield of dimer (%) vs. ArX consumed
2-Bromoanisole	45
2-Bromotoluene	67
2-Chloroanisole	91
2-Chloroacetophenone	94
1-Bromo-2-methyl-naphthalene	20
2-Chlorotoluene	90
2-Fluorobromobenzene	68
2-Chlorobenzenotrifluoride	100
2-Bromoaniline	71
2-Bromobenzonitrile	88

Table 3

Results for coupling between *ortho*-substituted aromatic halides ArX (0.2 M) and Ar′X′ (0.2 M)

ArX	Ar′X′	10^2ArAr ($M\ l^{-1}$)	10^2ArAr′ ($M\ l^{-1}$)	10^2Ar′Ar′ ($M\ l^{-1}$)	R (%) = $\frac{\text{ArAr}'}{\text{RX consumed}}$ [a]
2-Chloroanisole	Chlorobenzene *	3.4	8.2	3.4	42
2-Chloroanisole *	4-Chlorobenzonitrile	2.6	1.8	13	10
2-Chloroanisole	4-Chlorotoluene *	4.7	5.9	4	35
2-Chloroanisole *	3-Chloroanisole	0.75	1.3	6.9	50
2-Chloroanisole *	4-Chloroanisole	4.2	5.5	1.9	49
2-Chloroanisole *	Bromobenzene	3.5	1.2	8.2	11
2-Chlorotoluene *	Chlorobenzene	1.4	5.8	4.9	50
2-Bromoanisole	Chlorobenzene *	2.5	0.65	0.3	31
2-Bromoanisole	4-Chlorobenzonitrile	2.6	5.2	3.4	36
2-Chlorobenzeno-trifluoride	Chlorobenzene *	3.7	0	0	0
2-Chlorobenzeno-trifluoride	Bromobenzene *	1.4	1.7	0.6	15

[a] RX (i.e. ArX or Ar′X′) denotes the least reactive halide (indicated by *) and 80–90% of it was consumed. A quantity of electricity of ca. 1200 coulombs is required. If the reactivities of ArX and Ar′X′ are very different, e.g. 2-chloroanisole and 4-chlorobenzonitrile, only a small amount of ArAr′ is formed.

Heterocoupling of ortho-substituted aryl halides with meta- and para-substituted halides

When a mixture of $NiBr_2$bipy, ArX and Ar′X′ was electrolysed as for the homocoupling, no fall in intensity occurred after the passage of 4 moles of electron per mole of nickel(II). The reaction was stopped only when one reactant had been completely converted. Table 3 shows the results obtained for the coupling between *ortho*-substituted aromatic halides ArX (0.2 M) and different Ar′X′ (0.2 M). Electrolysis was performed at constant current.

Mechanism of the catalytic coupling process

The different mechanisms proposed for coupling of aryl halides [1,2b,5] all involve formation of ArNiX in an oxidative addition process:

$\mathrm{ArX + Ni^0 \rightarrow ArNiX}$

The homocoupling reaction then is possibly of the type:

$\mathrm{2\ ArNiX \rightarrow Ar_2Ni + NiX_2}$

The voltammetric curves show that the *ortho*-substituted diarylnickel compounds Ar_2Ni are stable under argon, unlike the *meta*- and *para*-substituted compounds. The following possibility for the mechanism for cross-coupling can be ruled out:

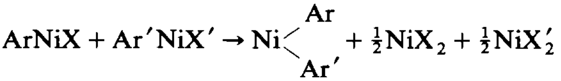
$\mathrm{Ar_2Ni + Ar'X' \not\rightarrow ArAr' + ArNiX'}$

In order to study this latter reaction we synthesized the stable Ar_2Ni compound (ArX = 2-chloroanisole) in situ and added chlorobenzene. No reaction occurred. Cross-coupling products would appear to be formed by the following scheme:

$\mathrm{Ni^{II} + 2e \rightarrow Ni^0}$

$\mathrm{Ni^0 + ArX \rightarrow ArNiX}$

$\mathrm{Ni^0 + Ar'X' \rightarrow Ar'NiX'}$



$$\mathrm{ArNiX + Ar'NiX' \rightarrow Ni\begin{smallmatrix}\diagup Ar \\ \diagdown Ar'\end{smallmatrix} + \tfrac{1}{2}NiX_2 + \tfrac{1}{2}NiX'_2}$$

The above reactions are limited by the formation of Ar_2Ni or Ar'_2Ni species. Good results, i.e. involving ca. 50% yields, were obtained only with ArX and Ar'X' having similar reactivities.

Conclusion

The described electrochemical preparation of *ortho*-substituted dimers by homo- or cross-coupling is particularly easy. Unlike the chemical method, it is catalytic with respect to a nickel precursor, and gives good yields of homo- and hetero-coupling products. Studies aimed at improving the heterocoupling between aromatic halides of different reactivities are now in progress.

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