

Water as Solvent for Nickel-2,2'-Bipyridine-Catalysed Electrosynthesis of Biaryls from Haloaryls

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Abstract: Reductive homocoupling of aryl halides into biaryls was achieved by electrolysis of aqueous emulsions, either in an undivided cell fitted with a sacrificial anode, or in a divided diaphragm cell, and in the presence of nickel-2,2'-bipyridine as catalyst. Reactions were also run in a filter-press cell.

Keywords: biaryl electrosynthesis; nickel-bipyridine catalysis; water as solvent.

Introduction

Environmental considerations now constrain chemists to integrate the control of risks (and costs) into their procedures, and the recent literature includes various approaches which have been developed with the aim of achieving a “green chemistry”.^[1]

In this context, synthetic electrochemical processes belong to the environmentally friendly methods since the use of electricity as a reagent does not involve the formation of any side-product. However, the range of carbon-carbon bond forming reactions by direct electroreduction is not very large, and the reactions are mostly conducted in polar aprotic solvents (DMF, NMP, etc.).^[2,3] Several groups, including our laboratory, have found interest in combining electrochemistry and homogeneous catalysis in view of developing new organic synthetic processes.^[4] In this field, a large part of our work focuses on the formation of C–C bonds by electroreductive coupling of organic halides with electrophiles in the presence of catalytic systems involving low-valent transition metal complexes generated electrochemically.^[4]

We have shown recently that the low-valent nickel-mediated electroreductive coupling of aryl halides can be efficiently achieved in methanol/ethanol mixtures^[5] or in pure ethanol^[6] instead of the usual aprotic solvents.^[7] This infers that the required electroreduction of the Ni(II) catalyst precursor arises in the usable cathodic potential range of alcohols, and also that the intermediate organonickel species are compatible with the proton activity of an alcoholic medium. Then, a new challenge was to attempt similar coupling reactions in water, the safest solvent, which also would allow the use of common and cheap salts as supporting electrolytes.

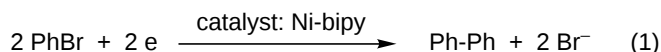
Two groups have already reported the chemical conversion of aryl halides into biaryls with moderate to good yields, by using zerovalent palladium complexes as catalysts and formate ions,^[8] or pressurised molecular hydrogen,^[9] or zinc powder^[10] as reducing agents in hot organic/water (o/w) emulsions.

Association of zinc powder and palladium catalysis is also efficient to convert aryl iodides into biaryls in water/acetone mixtures.^[11] To our knowledge, similar reactions have not been attempted in water by use of both electrochemistry and catalysis by transition metal complexes. The sole related examples are the work by Rusling et al. who reported that electrolysis of heterogeneous aqueous solutions containing an organic halide (RX) and a complex of cobalt leads to the coupling product R–R. Thus 1,5 hexadiene^[12] or bibenzyl^[13] were obtained in low yields from the respective allyl chloride or benzyl halide.

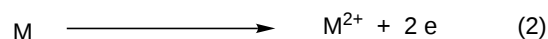
We chose the homocoupling of haloaryls into biaryls as a model reaction to show that association of electrochemistry and homogeneous catalysis can offer an efficient and clean method to achieve reductive syntheses of C–C bonds from organic halides in water. Synthesis of biaryls is of interest since the biaryl moiety is a building block of many pharmaceutical or agrochemical products.^[14]

Two electrochemical devices were employed to perform the reaction. In order to demonstrate the ability of the coupling, the electrolyses were first conducted in an undivided cell fitted with a sacrificial metallic anode (M) as previously used with aprotic or alcoholic solvents,^[3,5–7] and the model reagent was

At the cathode:



At the anode:



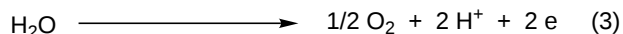
bromobenzene. In these experimental conditions the electrochemical reactions are as shown in Equations (1) and (2).

The metal M is sufficiently electropositive to be easily oxidised, e.g., M = Mg, Zn, Fe, Ni, etc. The use of the consumable anode technique in aprotic solvents offers the

advantage of not requiring a separator between catholyte and anolyte.^[3] Actually, the ion-exchanger membranes commonly used as separators have low performances (high resistivity, lifetime, etc.) in organic solvents.

Although this electrochemical device is simple and easy to scale-up,^[15] it does not offer an environmentally friendly method since metallic salts are produced in stoichiometric amounts. This is the reason why we later used the two-compartment cell described in the experimental section.

The cathodic reaction is the same as the one in the undivided cell (Equation 1). However, in the anolyte a “green process” is



now involved since it consists in electrooxidation of water into dioxygen, Equation (3).

The use of an anion-exchanger diaphragm between the two compartments avoids migration of protons toward the cathodic compartment. The electric neutrality of the anolyte is kept by the transfer of anions from the catholyte to the anolyte.

Results and Discussion

Electrosynthesis of Biphenyl from Bromobenzene in an Undivided Cell

The solutions consisted of a PhBr/H₂O emulsion with added NaCl as supporting electrolyte and stabilised by a surfactant. The catalyst was an equimolar mixture of divalent nickel bromide and 2,2'-bipyridine (bipy) as ligand. The electrolyses were carried out under galvanostatic conditions between two nickel electrodes.

As shown in Table 1, the yields in biphenyl are strongly dependent on the nature of the surfactant. In the absence of surfactant, or when the solution contained an anionic surfactant, PhBr was reduced mainly to benzene. The yields in biphenyl were only slightly higher in the presence of a zwitterionic or a cationic surfactant. Actually the best yield was obtained from solutions supplemented with a neutral surfactant. Therefore, further experiments were conducted only by using either Igepal CO-720 or Brij 35. This work is not

however advanced enough to fully explain the positive effect of the surfactants. In addition to their properties both as stabilising agent of the o/w emulsion and catalyst of phase transfer, several other features can be envisaged. An adsorption of the surfactant at the surface of the cathode may induce the presence of an hydrophobic layer which allows a limitation of protonation reactions of organometallic intermediates, so favouring the transformation of PhBr into Ph-Ph rather than into PhH. We do not either exclude that some of the surfactant used can act as ancillary ligand of the intermediary Ni-bipy species. Also, most of the studied surfactants give micelles in water, which could possibly act as hydrophobic micro-reactors. Nevertheless, the presence of micelles does not seem crucial since the results are not very different with DDAB, which is not a micellar agent in water.

A catalytic pathway involving nickel species is undoubtedly involved since, in the absence of nickel salt, the direct electroreduction of PhBr is not possible; only water is reduced. With regard to the ligand of nickel, we have electrolysed solutions of NiBr₂ either free of ligand, or supplemented with pyridine or 2,2'-dipyridylamine. Compared to solutions supplemented with bipy, the rate of conversion of PhBr was very weak in the absence of ligand and only traces of Ph-Ph were obtained.

However, even with NiBr₂ + bipy, the faradaic yield of conversion of PhBr was low (25 – 30%). This can be due to a side-reaction involving a direct or a nickel-mediated electroreduction of protons. Indeed, when an acid, e.g., acetic acid, was added to the initial solution, PhBr was scarcely consumed. We have then investigated if the reaction could be improved by increasing the pH of the solution. The data presented in Table 2 show the relevant results.

We can see that the addition of NaOH (0.1 mol L⁻¹) to the initial solution increased the yield in biphenyl, but such a high value of pH induced the formation of an abundant precipitate, presumably nickel hydroxide arising from Ni²⁺ anions released by the electrooxidation of the nickel rod used as anode. A better solution was the use of a buffering system involving a weak base like ammonia or an amine. In these conditions, the formation of biphenyl became the major reaction and simultaneously the electric charge required to consume the bromobenzene did not exceed 1.6 – 2 F/mol of PhBr, corresponding

Table 1. Influence of a surfactant on the Ni-catalysed electrosynthesis of Ph-Ph from PhBr in an undivided cell.^[a]

surfactant				current density (mA/cm ²)	Ph-Ph Yield (%)
formula	name	class	amount (mmol)		
none				1.2	10
Me-(CH ₂) ₁₁ OSO ₃ ⁻ , Na ⁺	SDS	anionic	3	1.2	19
(Me) ₃ N ⁺ CH ₂ -CO ₂ ⁻	Betaïne	zwitterionic	3	1.2	27
Me-(CH ₂) ₁₅ N ⁺ (Me) ₃ , Br ⁻	CTAB	cationic	3	1.2	34
(Me-(CH ₂) ₁₁) ₂ N ⁺ (Me) ₂ , Br ⁻	DDAB	cationic	0.15 ^[b]	1.2	27
Me-(CH ₂) ₈ -C ₆ H ₄ -(OCH ₂ -CH ₂) ₁₂ OH	Igepal CO-720	neutral	3	2.5	34
Me-(CH ₂) ₈ -C ₆ H ₄ -(OCH ₂ -CH ₂) ₁₂ OH	Igepal CO-720	neutral	0.3	2.5	23
Me-(CH ₂) ₈ -C ₆ H ₄ -(OCH ₂ -CH ₂) ₁₂ OH	Igepal CO-720	neutral	3	1.2	44
Me-(CH ₂) ₁₁ -(OCH ₂ -CH ₂) ₂₃ OH	Brij 35	neutral	0.3	1.2	45

^[a] General conditions : water (50 cm³) + NaCl (0.1 mol L⁻¹) + PhBr (10 mmol) + NiBr₂ · 5 H₂O (1.5 mmol) + bipy (1.5 mmol) + surfactant, θ = 40 °C, electric charge = 4000 C (4 F/mol of PhBr) allowing a full consumption of PhBr.

^[b] DDAB is weakly soluble.

Table 2. Influence of pH on the Ni-bipy-catalysed electrosynthesis of Ph-Ph from PhBr in an undivided cell.^[a]

buffering system	measured pH	surfactant	current density (mA/cm ²)	Ph-Ph Yield (%)
NaOH, 0.1 mol L ⁻¹	12.4	Brij 35	8	55
NH ₃ , 0.1 mol L ⁻¹	11	Brij 35	1.2	63
NH ₃ , 0.1 mol L ⁻¹	11	Brij 35	2.5	68
NH ₃ , 0.1 mol L ⁻¹	11	Brij 35	8	76
NH ₃ , 0.1 mol L ⁻¹	11	Brij 35	13.5	70
NH ₃ , 0.1 mol L ⁻¹	11	Igepal CO-720	1.2	67
NH ₃ , 0.1 mol L ⁻¹	11	Igepal CO-720	2.5	58
NH ₃ , 0.1 mol L ⁻¹	11	Igepal CO-720	8	38
Pyridine, 0.1 mol L ⁻¹	9.4	Brij 35	8	20
MeNH ₂ , 0.1 mol L ⁻¹	11.7	Brij 35	8	49
NH ₃ , 0.1 mol L ⁻¹				
+ NH ₄ Cl, 0.01 mol L ⁻¹	10.1	Brij 35	8	73
MeNH ₂ , 0.1 mol L ⁻¹				
+ HCl, 0.05 mol L ⁻¹	10.4	Brij 35	8	72

^[a] General conditions: water (50 cm³) + NaCl (0.1 mol L⁻¹) + PhBr (10 mmol) + surfactant (0.3 mmol for Brij 35 or 3 mmol for Igepal CO-720) + NiBr₂ · 5 H₂O (1.5 mmol) + bipy (1.5 mmol), $\theta = 40^\circ\text{C}$, electric charge = 2000 C (2 F/mol of PhBr) allowing a full consumption of PhBr.

to a 50–65% faradaic yield. Undoubtedly, both the protonation reaction leading to benzene and the direct or mediated side-electroreduction of water decreased when the value of pH was increased. Besides the effect of the pH, we do not exclude that ammonia or an amine can also be involved as ligand of Ni²⁺ ions or some other nickel intermediates. Actually, during the progress of electrolyses we could observe a lowering of the pH, probably due to the complexation between the base and the Ni²⁺ ions released by the electrooxidation of the sacrificial anode. In this series of experiments we have also noted that the neutral surfactant Brij 35 gave higher yields than Igepal CO-720, especially when the current density was increased.

The method has been successfully extended to other liquid aryl bromides, e.g., 4-FC₆H₄Br and 4-CF₃-C₆H₄Br. When starting from a solid compound, e.g., 4-BrC₆H₄-COCH₃, the o/w emulsion was obtained by the previous dissolution of the substrate in a minimum amount of toluene or *o*-xylene. If the aryl bromide, ArBr, bears an acidic function, e.g., 4-BrC₆H₄-CO₂H, addition of one equivalent of NaOH induces its dissolution in the solution buffered with ammonia or methylamine so giving a homogeneous solution. In all these cases, after addition of the surfactant Brij 35 and NiBr₂ + bipy, ArBr was converted into Ar-Ar with moderate to good yields (50–70%), ArH being the sole side-product detected.

Electrosynthesis of Biaryls from Haloarenes in a Divided Cell

As mentioned above, the sacrificial anode technique was later replaced by a “less polluting” one using a cell divided in two compartments separated by an anion-exchanger membrane. The cell design is described in the experimental part.

The anodic compartment was filled with aqueous potassium hydroxide and the anode was a Ti-Pt plate allowing the oxidation of water into oxygen, and of transferred Cl⁻ into ClO⁻. The cathodic compartment was fitted with a nickel foam cathode and contained the ArX/H₂O emulsion, the surfactant Brij 35, the supporting electrolyte NaCl, a pH buffering system,

and the nickel catalyst. Electrolyses were run by applying a constant current intensity and the rate of conversion of ArX during the electrolysis was measured by GC analysis of samples. Figure 1 presents the results of a typical experiment with PhBr. The GC analysis of samples was not convenient to monitor the formation of biphenyl since it precipitates in part, especially when PhBr is almost fully consumed. The evolution of the selectivity in Ph-Ph was then obtained from several experiments involving various electric charges, followed by the analysis of the mixture.

The rates of conversion of PhBr both in the undivided or in the divided cell are close to the theoretical value, up to half consumption of PhBr (cf. Figure 1). During the first part of electrolysis, Ph-Ph is obtained with quite similar selectivity (60–70%) in both devices. However, discrepancies appear in

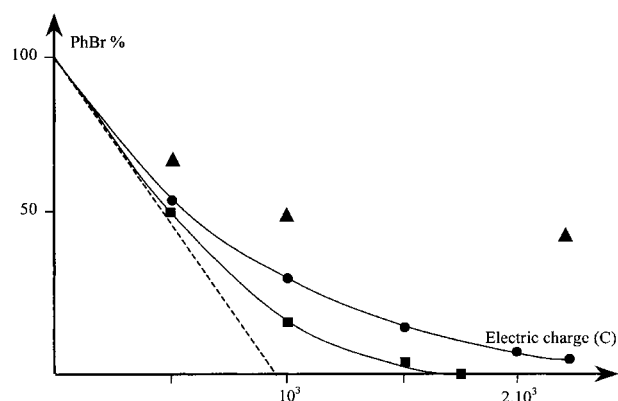


Figure 1. Ni-bipy-catalysed electrolytic conversion of PhBr in a PhBr/H₂O emulsion: —■— in the undivided cell; —●— in the two-compartment cell; ---- theoretical curve for a 100% faradaic yield; —▲— selectivity in Ph-Ph (%) for electrolyses, in the divided cell, stopped respectively at 5 · 10², 10³ and 2.2 · 10³ C. General conditions: water (50 cm³) + NaCl (0.1 mol L⁻¹) + Brij 35 (0.3 mmol) + NH₃ (0.1 mol L⁻¹) + PhBr (10 mmol) + NiBr₂ · 5 H₂O (1.5 mmol) + bipy (1.5 mmol), $\theta = 40^\circ\text{C}$, current density = 8 mA/cm².

prolonged electrolyses. As shown by Figure 1, the reaction requires a larger electric charge in the divided cell than in the undivided one. Also, the selectivity in Ph-Ph becomes lower during the progress of the electrolyses in the two-compartment cell and reaches only 40–45% for a full consumption of PhBr, while this selectivity was almost constant (60–70%) in the undivided cell. These differences in behaviour do not seem to arise from a deactivation of the catalyst since extra addition of $\text{NiBr}_2 \cdot 5 \text{H}_2\text{O}$ or $\text{NiBr}_2 \cdot 5 \text{H}_2\text{O} + \text{bipy}$ does not modify appreciably the results.

Another difference we have remarked between the two methods is the evolution of the pH. Contrary to what was observed in the undivided cell, we have noted, in the diaphragm cell, an increase of the pH, due to the side reduction reaction of water which releases hydroxide anions. However, we cannot confirm at the present time that this explains the lowering of the faradaic yield and the selectivity.

Exhaustive electrolyses of some aryl bromides have been performed in the diaphragm cell. In each experiment 20 mmol. of ArBr were involved and a constant current intensity of 0.1 A was supplied during 14 hours what corresponds to an electric charge of 2.5 F/mol of ArBr. Results are presented in Table 3. In these experiments, ArBr was almost fully consumed and the yields in biaryl were moderate.

According to preceding remarks about the progress of the electrolyses, a better selectivity is expected if the electrolysis is stopped when only a part of ArBr is converted. Then we carried out electrolyses involving a lower electric charge in order to transform only about 60–85% of the starting molecule. In this series of experiments aryl bromides and aryl chlorides were tested. Results in Table 4 show that the selectivity in biaryl from ArBr is good in this case. It appears also that the reaction is moderately effective when starting with aryl chlorides.

Syntheses with a Filter-Press Cell

All these results concerning partial or exhaustive electrolyses in the diaphragm cell show that our initial goal has been obtained. However, the laboratory electrochemical device used until now does not allow a scale-up of the process. The most common type of design for large-scale electroorganic preparation is the commercially available filter-press type, where pumps ensure the flow through the cell of solutions contained in tanks.

Table 3. Ni-bipy-catalysed electrosynthesis of biaryls from aryl bromides in a divided cell.^[a]

ArBr	rate conversion of ArBr (%)	Ar-Ar isolated yield (%)
PhBr	100	38
4- $\text{CF}_3\text{C}_6\text{H}_4\text{Br}$	90	57
3- $\text{CF}_3\text{C}_6\text{H}_4\text{Br}$	100	62
4- $\text{CH}_3\text{C}_6\text{H}_4\text{Br}$	88	16
4- $\text{FC}_6\text{H}_4\text{Br}$	100	33
3- $\text{CH}_3\text{OC}_6\text{H}_4\text{Br}$	96	21

^[a] General catholyte conditions: water (50 cm³) + NaCl (0.3 mol L⁻¹) + NH_3 (0.1 mol L⁻¹) + ArBr (20 mmol) + Brij 35 (0.3 mmol) + $\text{NiBr}_2 \cdot 5 \text{H}_2\text{O}$ (1.5 mmol) + bipy (1.5 mmol), $\theta = 40^\circ\text{C}$, current density = 10 mA/cm², electric charge = 5000 C (2.5 F/mol of ArBr).

Table 4. Ni-bipy-catalysed electrosynthesis of biaryls from aryl halides in a divided cell.^[a]

ArX	rate conversion of ArX (%)	Ar-Ar selectivity (% CPG)
PhCl	86	59
4- $\text{CF}_3\text{C}_6\text{H}_4\text{Cl}$	60	29
3- $\text{CF}_3\text{C}_6\text{H}_4\text{Cl}$	81	28
4- $\text{CH}_3\text{C}_6\text{H}_4\text{Cl}$	67	32
4- $\text{FC}_6\text{H}_4\text{Cl}$	92	40
3- $\text{CH}_3\text{OC}_6\text{H}_4\text{Cl}$	75	38
PhBr	86	54
4- $\text{CF}_3\text{C}_6\text{H}_4\text{Br}$	70	72

^[a] General catholyte conditions: water (50 cm³) + NaCl (0.3 mol L⁻¹) + MeNH_2 (0.5 mol L⁻¹) + HCl (0.25 mol L⁻¹) + ArX (10 mmol) + Brij 35 (0.1 mmol) + $\text{NiBr}_2 \cdot 5 \text{H}_2\text{O}$ (1.5 mmol) + bipy (1.5 mmol), $\theta = 40^\circ\text{C}$, current density = 30 mA/cm², electric charge = 1700 C (1.7 F/mol of ArX).

We are currently attempting the transposition of reactions described in this paper in a filter-press cell. The experimental conditions are not yet optimised but the preliminary results, presented in Table 5, are encouraging since three aryl bromides have been converted into the corresponding biaryls with a moderate to good selectivity.

Table 5. Ni-bipy-catalysed electrosynthesis of biaryls from aryl bromides in a filter-press cell.^[a]

ArBr	rate conversion of ArBr (%)	Ar-Ar selectivity (% CPG)
PhBr	43	56
4- $\text{CF}_3\text{C}_6\text{H}_4\text{Br}$	40	69
3- $\text{CF}_3\text{C}_6\text{H}_4\text{Br}$	39	58

^[a] General catholyte conditions: NaCl (0.5 mol L⁻¹) + MeNH_2 (0.5 mol L⁻¹) + HCl (0.25 mol L⁻¹) + ArBr (0.4 mol L⁻¹) + Brij 35 ($6 \cdot 10^{-3}$ mol L⁻¹) + $\text{NiBr}_2 \cdot 5 \text{H}_2\text{O}$ ($6 \cdot 10^{-2}$ mol L⁻¹) + bipy ($6 \cdot 10^{-2}$ mol L⁻¹), $\theta = 40^\circ\text{C}$, current density = 40 mA/cm², electric charge = 1 F/mol of ArBr.

Conclusion

In conclusion, we have shown that the electroreductive coupling of aryl halides mediated by a catalytic system based on nickel-2,2'-bipyridine complexes can be achieved in water, which avoids the use of polar aprotic solvents. Moreover, the electrolyses can then be conducted in a divided cell equipped with a usual ion-exchanger which allows us to choose at will a simple and clean anodic reaction. At present the performance of this work is devoted, on the one hand to the scale-up of this homocoupling reaction by using classical electrolytic flow cells, on the other hand to an extension to cross-coupling reactions of aryl halides with electrophiles. We have also initiated an electroanalytical study of the Ni-bipy complexes in water with a view to determine the behaviour and properties of the catalytic system in this solvent.

Experimental Section

Syntheses with an Undivided Cell

The solution: The solvent (50 cm³) was distilled water without further purification and all products were used as received. The supporting electrolyte was NaCl (0.1 mol L⁻¹). The solution was buffered by addition of a base (aqueous NH₃ or MeNH₂, etc.) and aqueous HCl in a suitable amount and the pH was then measured (see Table 2). For the catalyst, no preliminary preparation of an NiBr₂-bipy complex was required: NiBr₂·5 H₂O (1.5 mmol) and 2,2'-bipyridine (1.5 mmol) were added to the solution. The surfactant (for nature and amount see Tables 1 and 2) and the aryl bromide was finally added. The ArBr/H₂O emulsion was then obtained by stirring with a magnet then warmed at 40 °C.

The electrochemical cell: The electrochemical undivided cell used for the consumable anode technique has been already described elsewhere.^[3,15] This "beaker-cell" had a volume of 50 cm³ and was fitted with a cylindrical nickel foam cathode (40 cm²) which surrounded a sacrificial nickel rod (diameter 1 cm) anode. Before each experiment the cell and electrodes were rinsed with dichloromethane then with water.

The electrolysis: Galvanostatic electrolyses were carried out with a power source (TTI, PL 310, 32V-1A) by applying a current intensity (for values see Table 2) between the two electrodes. The progress of the aryl bromide consumption vs. the electric charge was checked by GC analysis of samples. Assuming a 100% faradaic yield, the theoretical electric charge required to a full conversion of ArBr into Ar-Ar is 96500 C mol⁻¹.

Syntheses with a Two-Compartment Cell

The used divided cell is presented in Figure 2. Each compartment had a volume of 50 cm³. The cathode was a circular (10 cm²) nickel foam. The anode was a circular (10 cm²) Ti-Pt plate. The diaphragm was a circular piece of an anionic membrane (neosepta AHA-1). The catholyte was prepared in the same manner as the solution used with the undivided cell (see above). The anolyte was an aqueous solution (50 cm³) of KOH (0.5 mol L⁻¹). Electrolyses were also carried out under galvanostatic conditions (0.1 – 0.3 A) and checked by GC analysis of samples.

Syntheses with a Filter-Press Cell

The filter-press device was a commercially available cell (Microflow, Electrocell AB, Sweden). This design consisted of rectangular plate electrodes (16 cm² for each) separated by insulating frames, which formed compartments for the electrolyte. The anion-exchanger membrane was maintained between a pair of gaskets. Each solution was passed from a tank through the cell by a peristaltic pump. The aqueous catholyte (0.1 – 1 L) contained NaCl (0.5 mol L⁻¹), MeNH₂ (0.5 mol L⁻¹) and aqueous HCl (0.25 mol L⁻¹), NiBr₂·5 H₂O and 2,2'-bipyridine (6·10⁻² mol L⁻¹ for each), the surfactant Brij 35 (6·10⁻³ mol L⁻¹) and ArBr (0.4 mol L⁻¹). The anolyte contained KOH (0.3 mol L⁻¹). Electrolyses were also carried out under galvanostatic conditions (0.3 A – 1.8 A) and checked by GC analysis of samples.

Purification and Analysis of the Products

When the aryl halide was almost fully consumed, the catholyte (or the global solution in the case of the undivided cell) was extracted twice with dichloromethane (2 × 50 cm³) and the cathodic compartment was rinsed with dichloromethane (20 cm³). The organic layer was dried over magnesium sulphate and evaporated. The crude products were purified by chromatography on a silica gel column (elution by pentane). The biaryls were characterised by ¹H NMR (δ ppm vs. TMS) and ¹³C NMR (δ ppm vs. CDCl₃) plus ¹⁹F NMR (δ ppm vs. CFCl₃) for fluorinated products, with a

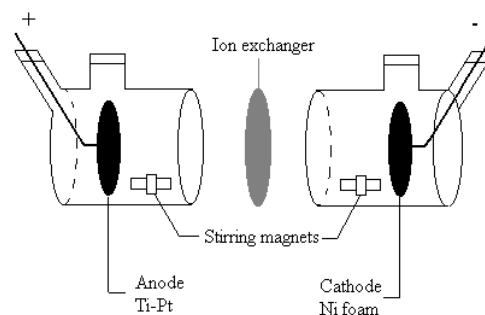


Figure 2. Diagram of the two-compartment cell used for the electroconversion of aryl halides into biaryls.

Brüker 200 MHz instrument, and by mass spectrometry (GCQ Thermofinnigan). All the biaryls obtained are known products and gave satisfactory spectroscopic values.

Acknowledgements

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