Electrochemical Conversion of Functionalised Aryl Chlorides and Bromides to Arylzinc Species

Soline Sibille, Victorin Ratovelomanana and Jacques Périchon

Laboratoire d'Electrochimie, Catalyse et Synthèse Organique, L.E.C.S.O., 2 Rue Henri Dunant, 94320 Thiais, France

Electroreduction of aromatic chlorides or bromides in a cell fitted with a sacrificial zinc anode, in the presence of a nickel 2,2′-bipyridine complex affords the corresponding organozinc species in good yield.

Recent work[1,2] has dealt with the direct synthesis of functionalised arylzinc halides from zinc metal and aryl halides. Owing to the low reactivity of zinc in oxidative addition, only activated aryl iodides or bromides could be involved in such reactions. Metathesis with copper cyanide in stoichiometric amounts enabled coupling with α,β-enones, acid chlorides or allylic halides.

We report herein a simple electrolysis procedure, using a nickel catalyst and a sacrificial zinc anode in an undivided cell, allowing the preparation of arylzinc species from aryl chlorides and bromides, in dimethylformamide (DMF) as solvent. The aromatic ring can bear various functional groups such as ester, nitrile or ketone.

These arylzinc species can be reacted under copper iodide catalysis with various electrophiles such as cyclohex-2-en-1-one, allyl chloride or trifluoroacetic anhydride.[3]

A typical procedure for the electrosynthesis was as follows. Freshly distilled DMF (35 ml), ArX (15 mmol), Ni (2,2′-bipyridine)$_3$(BF$_4$)$_2$ (1 mmol), $\mathrm{ZnBr_2}$ (5 mmol) and $\mathrm{NBu_4Br}$ (1 mmol) as supporting electrolyte were introduced into the electrolysis cell, fitted with a zinc rod (1 cm diameter) as the anode and a carbon fibre cathode (20 cm^2 area). A constant intensity of 0.15 A was applied, under argon, until 2 F mol^{-1} of halide have been passed (3000 C, around 5 h). Iodine titration of the resulting solution indicated a 60–70% conversion of ArX to ArZnX; less than 10% of ArX was recovered as biaryl, and around 30% as ArH.

As already reported in the case of the electrosynthesis of the Reformatsky reagent from α-chloroesters,[4] the mechanism for the arylzinc electrosynthesis involves (*i*) reduction of $\mathrm{Ni^{II}}$ to $\mathrm{Ni^0}$, (*ii*) oxidative addition of ArX to $\mathrm{Ni^0}$ and (*iii*) metal exchange between ArNiX and the $\mathrm{Zn^{II}}$ species arising from the anodic reaction, eqn. (1). Electroanalytical experiments performed on the $\mathrm{Ni^{II}/Ni^0}$ couple[4] gave clear evidence for the three reactions.

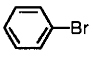
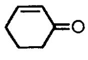
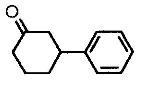
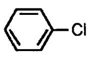
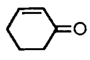
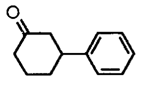
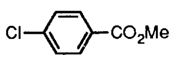
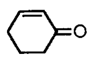
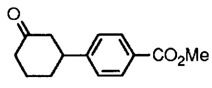
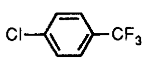
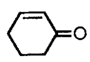
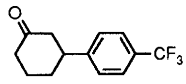
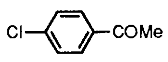
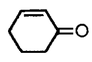
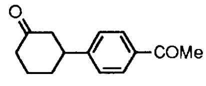
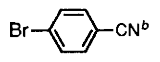
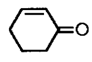
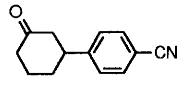
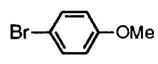
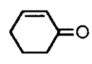
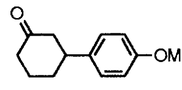
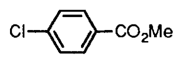
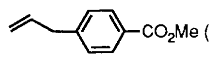
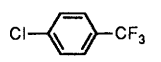
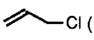
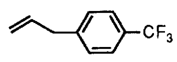
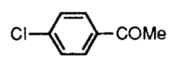
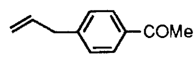
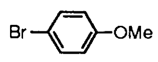
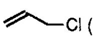
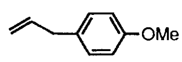
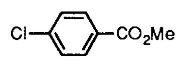
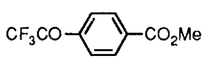
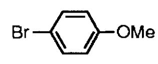
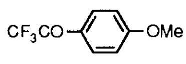
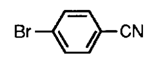
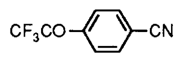
$$\mathrm{ArNiX + ZnX_2 \rightarrow ArZnX + NiX_2} \qquad (1)$$

Except for hydrolysis and iodonolysis, these organozinc reagents were found to be totally unreactive towards common electrophiles such as aldehydes, anhydrides or organic halides. Knochel's publication[1] on the ArZnX–CuCN metal exchange prompted us to investigate the properties of our electrogenerated arylzinc reagent in the presence of copper(I) species. We found that addition of a catalytic amount (1 mmol) of copper(I) iodide together with tetramethylethylenediamine (TMEDA, 10 mmol) to the electrolysed solution enabled coupling with various electrophiles. All the reactions could be performed at room temperature or with slight heating (30–40 °C).

Conjugate addition to cyclohex-2-en-1-one (10 mmol) was readily achieved in the presence of chlorotrimethylsilane (20 mmol, added dropwise). Whereas allyl bromide reacted instantaneously, coupling with allyl chloride required slight heating over a period of two hours. Finally, trifluoromethylketones were obtained from reaction with trifluoroacetic anhydride;[4] in this case, the CuBr–$\mathrm{Me_2S}$ complex (1 mmol) was preferable to the TMEDA complex. Typical results are given in Table 1.

We are now investigating the palladium-catalysed reactions of the organozinc reagent; whereas the nickel–2,2′-bipyridine complex does not promote the biaryl formation, as indicated

Table 1 Copper halide-catalysed coupling of electrogenerated arylzinc species with various electrophiles

ArX/15 mmol	Electrophile/mmol	Coupling product (%)[a]
	 (10)	 (52)
	 (10)	 (40)
	 (10)	 (44)
	 (10)	 (52)
	 (10)	 (54)
	 (10)	 (35)
	 (10)	 (54)
	 (18)	 (41)
	 (18)	 (48)
	 (18)	 (63)
	 (18)	 (56)
	$\mathrm{(CF_3CO)_2O}$ (14)	 (52)
	$\mathrm{(CF_3CO)_2O}$ (14)	 (32)
	$\mathrm{(CF_3CO)_2O}$ (14)	 (50)

[a] Isolated yield, based on initial ArX. All products gave satisfactory ^{1}H, ^{19}F NMR and mass spectra. [b] When 4-chlorobenzonitrile was used as starting material, decyanation was found to compete with dechlorination, and the nickel catalytic activity was rapidly lost.

$$\mathrm{ArZnX} + \mathrm{ArX} \overset{\mathrm{Ni}^0}{\not\longrightarrow} \mathrm{ArAr} \qquad (2)$$

$$\mathrm{ArZnX} + \mathrm{Ar'X} \xrightarrow{\mathrm{Pd}^0} \mathrm{ArAr'} \qquad (3)$$

by the low yield of biaryl formed during the arylzinc electrosynthesis [eqn. (2)], the palladium complex $\mathrm{PdCl_2(PPh_3)_2}$ (0.1 mmol) was able to catalyse the cross-coupling reactions [eqn. (3)], 4-trifluoromethyl-4′-cyanobiphenyl was thus obtained in a 65% yield from 4-trifluoromethylchlorobenzene as the source for the organozinc reagent, and 4-bromobenzonitrile.

In conclusion, the use of a sacrificial zinc anode associated with nickel catalysis offers a unique access to functionalised arylzinc compounds, from aryl chlorides or bromides. Work is in progress to optimize the electrosynthetic process, especially to lower the amount of hydrogenation product formed, and to develop the synthetic applications.

We thank the SNPE (Société Nationale des Poudres et Explosifs) and EDF (Electricité de France) for financial support of the work.

Received, 12th November 1991; Com. 1/05748K

References

1 T. N. Majiid and P. Knochel, *Tetrahedron Lett.*, 1990, **31**, 4413.
2 L. Zhu, R. M. Wehmeyer and R. D. Rieke, *J. Org. Chem.*, 1991, **56**, 1445.
3 F. A. J. Kerdesky and A. Basha, *Tetrahedron Lett.*, 1991, **32**, 2003.
4 A. Conan, S. Sibille and J. Périchon, *J. Org. Chem.*, 1991, **56**, 2018.