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Electrochemical vinylation of aryl and vinyl halides with acrylate esters catalyzed by cobalt bromide

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Abstract—A consumable anode process permits the electrochemical Heck reaction between aromatic or vinylic halides and acrylate esters using cobalt bromide as catalyst associated with bipyridine as ligand in a mixture of acetonitrile/triethylamine/pyridine as solvent. © 2002 Elsevier Science Ltd. All rights reserved.

Vinylation is a versatile process for the carbon–carbon bond formation and for the functionalization of a variety of organic halides. Vinylation of aryl and vinyl halides, the Heck reaction,[1] is generally performed by the catalytic action of a zero-valent palladium complex formed in situ by the reduction of a palladium salt.[2] Several natural products or biologically active compounds have been synthesized during the last two decades using this process as a key stage.[3] Indeed, this reaction has the advantage of tolerating various functional groups.

Though none of them could rival palladium in synthetic versatility, a number of other metals can catalyze Heck-type reactions,[4] but in most cases only aryl iodides lead to good yields. Nickel is a most appealing candidate for possible replacement of Pd catalysts. Nevertheless, the arylation of acrylate esters in the presence of nickel catalysts does not give cinnamates but β-arylpropionates as major products.[5] Recently, we have shown that $Co^{(I)}$ species generated in situ in acetonitrile/pyridine by electroreduction of $Co^{(II)}$ salts react quickly with aryl halides in an oxidative addition reaction.[6] This property associated with the use of the consumable anode process has been applied to the electrochemical preparation of arylzinc compounds,[7] as well as the electrochemical addition of aryl halides onto activated olefins.[8]

In this paper, we explore the scope of the use of cobalt bromide associated to 2,2′-bipyridine to promote the electrochemical vinylation of aryl and vinyl halides with acrylate esters as substrate in the solvent mixture acetonitrile/triethylamine/pyridine.

Results and discussion

All reactions were conducted in a one-compartment cell already described.[9] Solvents were used as received, and the reactions were conducted in a ternary solvent mixture of acetonitrile/triethylamine/pyridine (V/V/V = 7/2/1), under an inert atmosphere of argon at 70°C. The ionic conductivity was ensured by NBu_4BF_4 (0.01 M) added to the reaction mixture. Electrolyses were conducted at constant current intensity of 0.2 A (0.01 A/cm^2), with an iron consumable anode, associated to a stainless steel grid as the cathode. In a typical experiment, 35 ml of acetonitrile, 10 ml of triethylamine, 5 ml of pyridine containing 7.5 mmol of RX (0.15 M), 0.75 mmol of $CoBr_2$ (0.015 M), 10 mmol of 2,2′-bipyridine (0.2 M) and 20 mmol of ethyl acrylate (0.4 M) were introduced into the cell.

In these reaction conditions, the expected substitution product is often obtained predominantly, along with the conjugated addition as in the case of the nickel catalysis reported by Boldrini.[10] In all cases, traces of dimer (RR) are also observed. The product resulting of the hydrogenation of the organic halide is the third main compound. The presence of 2,2′-bipyridine in excess, i.e. 1.3 equiv. for 1 equiv. of RX, is of a crucial importance. Indeed, the amount of addition product increases when this proportion is lowered, and becomes the major product with only twice the amount of

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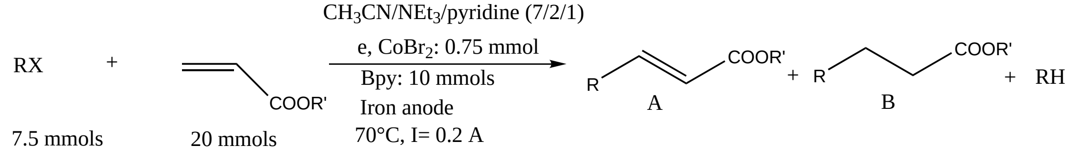
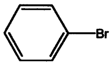
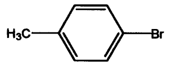
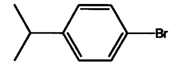
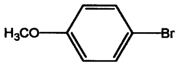
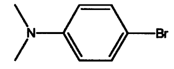
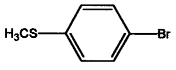
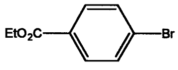
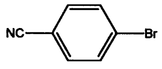
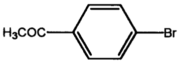
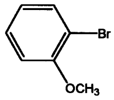
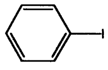
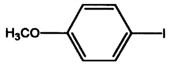
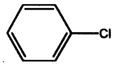
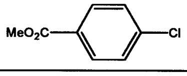
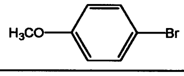
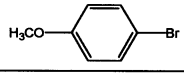
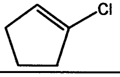
2,2′-bipyridine. Triethylamine and pyridine as bases are not strictly necessary, but enables a higher substitution versus addition product ratio.

As already mentioned for the electrochemical addition of aryl halides onto olefins,[8] the use of a consumable iron anode is necessary for the reaction to be catalytic

Table 1. Coupling of aryl and vinyl halides with acrylate esters catalyzed by $CoBr_2$



(1)

Entry	RX	R'	Heck product A yield[a] % vs initial RX	Addition product B Yield[b] % vs initial RX
1		Et	56	22
2		"	54	25
3		"	61	29
4		"	57	24
5		"	58	18
6		"	47	35
7		"	45	31
8		"	10	43
9		"	18	45
10		"	18 (b)	11
11		"	18	26
12		"	25	35
13		"	< 5	< 5
14		"	< 5	< 5
15		Bu	55	21
16		Me	36	40
17		Et	47	23

a. isolated yield ; all compounds were characterized by 1H and 13C NMR, IR and GC/MS analysis

b. compound characterized and yield estimated by GC/MS analysis in cobalt. Similar results were obtained with a consumable cobalt anode. With other metals, e.g. Al, Zn or Mg, only the reduction product (RH) was obtained.

Results are reported in Table 1 according to Eq. (1).

The reaction is stereoselective thus giving only *E*-olefins in all the studied cases. Bromobenzene (entry 1) and aryl bromides substituted by an electron-donating group in *para* position (entries 2–6) give the best results. With these reagents, the amount of addition product is about half that of the substitution product. This selectivity is reversed with aryl bromides substituted by electron-withdrawing groups: the addition product is generally obtained predominantly (entries 8–9), except with ethyl bromobenzoate (entry 7). In all cases, if the electrolysis is continued after total consumption of the organic halide, the substitution product is reduced into the corresponding β-arylpropionate ester.

It also comes out that the presence of an *ortho* substituent makes the coupling reaction very difficult (entry 10) with this catalytic system.

Aryl iodides which are very reactive towards electrogenerated $Co^{(I)}$ gave mainly the reduction product, along with the addition product (entries 11–12). With aryl chlorides (entries 13–14), which are less reactive than corresponding bromides, the chloride is not consumed and only traces of the Heck and the conjugated addition products are formed.

We have also studied the nature of the substituent on the ester group in the acrylate. With a butyl group (entry 15), yield was similar to that obtained with an ethyl group. On the other hand, with the methyl (entry 16), the Heck reaction product was formed in a minor way. No explanation was found until now.

We have extended the reaction to a vinyl chloride (entry 17) and found that in the conditions described before, the Heck product is the major one.

The results reported here illustrate that cobalt bromide is an efficient catalyst for the electrochemical vinylation of aromatic bromides (especially substituted by an electron-donating group) and vinyl chlorides with acrylate esters. This reaction must now be extended to other types of olefins (acrylonitrile, methylvinylketone, styrene…), and the role of iron as anode which has already been noticed previously will have to be studied more deeply.

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