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Cobalt bromide as catalyst in electrochemical addition of aryl halides onto activated olefins

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Abstract

The consumable anode process permits the electrochemical arylation of activated olefins from functionalized aryl halides when cobalt halide is used as catalyst, either associated with bipyridine and pyridine as ligands in DMF as solvent, or with only pyridine in acetonitrile as solvent.

Conjugate additions onto activated olefins are of great utility in organic synthesis for carbon–carbon bond formation.[1] Most applications involve the reaction of either organometallic reagents in the presence of cuprous salt and, in some cases, chlorotrimethylsilane, or cuprate reagents.[2] Thus, these methods require the preliminary preparation of air and/or moisture-sensitive organometallic magnesium,[3] lithium,[4] zinc,[5] or manganese[6] species. Moreover, the preparation of these organometallics from organic halides bearing a functional group like CO, COOR, or CN turns out to be quite difficult, or even impossible. Consequently, other chemical or electrochemical processes have been conceived to avoid such a difficult step. These processes involve a transition metal complex as catalyst, and are carried out in mild reaction conditions. The transition metal can be, for instance, nickel associated with various ligands such as cyclam[7] or salen[8] and an excess of zinc as reductant.[9] The cathodic reduction of a catalyst precursor can be alternatively used, as shown by our previous work on the arylation and alkenylation of activated olefins based on the combined use of a nickel salt as catalyst and a sacrificial iron anode and in the presence of common ligands like acetonitrile or pyridine.[10] We, and others, have also reported that the electrochemical conjugate addition of alkyl halides can be realized with cobalt complexes as catalysts.[11] But Co(I) species were said to be unreactive toward aromatic halides until we found, quite recently, that they can be activated by electroreduced Co(II) and we took advantage of this property to devise a new method of preparation of arylzinc compounds[12] in a very simple electrochemical process.

In this paper we explore the scope of the use of cobalt bromide, associated or not to bipyridine, as catalyst in the electrochemical coupling between aryl halides and activated olefins in solvent mixtures like DMF/pyridine or acetonitrile/pyridine.

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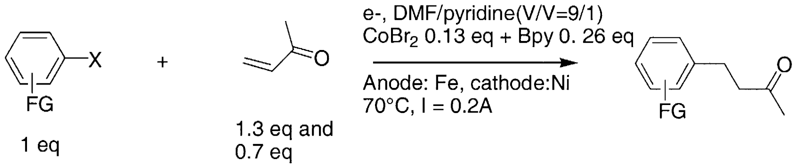
1. Results and discussion

1.1. Electroreductive coupling between aryl halides and methyl vinyl ketone

In DMF/pyridine with $CoBr_2$ in the presence of 2,2′-bipyridine (Bpy): All reactions are conducted under an inert atmosphere of argon at 70°C in commercial solvents without further purification. The ionic conductivity is ensured by NBu_4BF_4 (0.01 M) added to the reaction mixture.

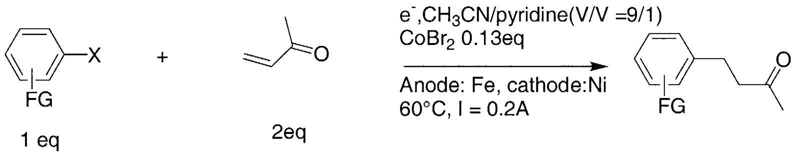
Electrolyses are conducted at constant current intensity of 0.2 A (0.01 A/cm^2) in an undivided cell already described,[13] with an iron consumable anode associated to a nickel foam as the cathode. Electrolyses are stopped after consumption of 2.2 F per mol of ArX. The cathodic potential during the electrolysis is constant between −1.2 V and −1.4 V versus SCE, i.e. close to the potential of the formation of the Co(I) complex from $CoBr_2Bpy_2$.[14] In a typical experiment, 45 ml of DMF, 5 ml of pyridine containing 7.5 mmols ArX (0.15 M), 1 mmol $CoBr_2$, 2 mmols 2,2′-bipyridine and 10 mmols methyl vinyl ketone (MVK) are introduced into the cell. When half of ArX is consumed, 5 mmols MVK are added to the solution. This overall excess of MVK is necessary to avoid the formation of biaryl. MVK is, however, preferably added in two portions to avoid the formation of a double adduct. Also, 2,2′-bipyridine as ligand of cobalt is of crucial importance since no addition product is observed when it is omitted. This contrasts with the formation of arylzinc species via cobalt catalysis where the presence of 2,2′-bipyridine is not necessary.[12] Finally, we have noticed that the presence of pyridine as co-solvent allows a slightly higher yield to be obtained. The results are reported in Table 1 according to Eq. (1).



(1)

Aryl bromides substituted by an electron-withdrawing group (entries 1–5 and 8) give better results than bromobenzene (entry 6). The adduct is also formed from *p*-bromobenzaldehyde, although in moderate yield. Aryl chlorides did not react at all. With an electron-donating group on the ring, only the iodo compounds are, but slightly, reactive (entry 7). With *o*-bromoacetophenone (entry 8), a Robinson annelation reaction leads to the cyclic product (H).

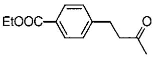
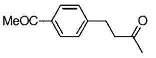
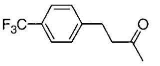
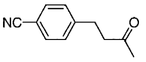
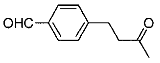
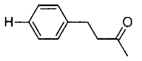
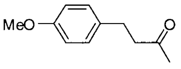
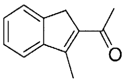
In CH_3CN/pyridine with $CoBr_2$: We also carried out the reaction in acetonitrile/pyridine. In this solvent mixture, 2,2′-bipyridine is not necessary. The experimental conditions are similar to those used above except that all MVK (i.e. 2 equiv. versus ArX) is now present at the beginning of the electrolysis, and the reactions are conducted at 60°C instead of 70°C in DMF. The results are reported in Table 2 according to Eq. (2).



(2)

The results are better than in DMF/pyridine (entries 9 and11). No Ar–Ar is formed, ArH being the only by-product. The yields can even be improved if ArX is added with a syringe pump. Thus, with *p*-bromobenzoate we obtain 78% instead of 70%. With *p*-chloroacetophenone the addition product is formed contrary to DMF/pyridine, but in low yield.

Table 1
Cobalt-catalyzed electrochemical addition of substituted aryl halides on MVK in DMF/pyridine

entry	FG	X	Coupling product	Yields/ArX (a)
1	p-COOEt	Br	 **A**	64
2	p-COMe	Br	 **B**	56
3	p-CF3	Br	 **C**	45
4	p-CN	Br	 **D**	55
5	p-CHO	Br	 **E**	30
6	H	Br	 **F**	33
7	p-OMe	I	 **G**	22
8	o-COMe	Br	 **H**	45

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

Table 2
Cobalt-catalyzed electrochemical addition of substituted aryl halides on MVK in CH_3CN/pyridine

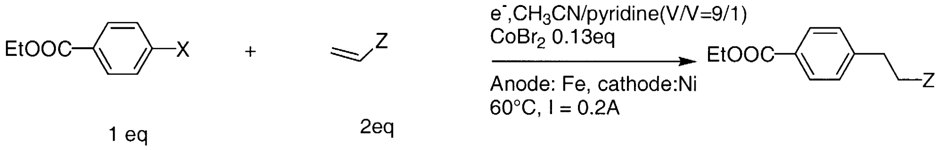
entry	FG	X	Coupling product	Yields/ArX (a)
9	p-COOEt	Br	**A**	70
10	p-COMe	Br	**B**	55
11	p-CN	Br	**D**	70
12	p-COMe	Cl	**B**	20

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

So, the solvent CH_3CN/pyridine offers advantages over DMF/pyridine of affording slightly better results and avoiding the use of 2,2′-bipyridine as ligand.

1.2. Electroreductive coupling between para*-bromobenzoate and other activated olefins in CH_3CN/pyridine*

The reaction conditions optimized with MVK are then applied to the arylation of other activated olefins according to Eq. (3).

 (3)

In the case of ethyl acrylate (Z=COOEt), the addition product is obtained in 35% yield along with the reduction product ArH and the dimer Ar–Ar. With acrylonitrile (Z=CN) the major product is ArH; the electrolysis also leads to the polymerization of acrylonitrile, and only traces of the addition product are found (<10%).

The results reported here illustrate that cobalt bromide is an efficient catalyst for the electrochemical addition of aryl bromides, substituted by electron-withdrawing groups, on activated olefins in a mixture of either DMF or acetonitrile and pyridine. It is worth mentioning that the use of iron as anode is also necessary. Indeed, with other metals, e.g. Al, Zn or Mg, no addition product is obtained. The possible role of the iron ions, already noticed in other reactions,[11b] remains to be elucidated. Work is also in progress to generalize and optimize these reactions which use a very simple electrochemical process, commercial solvents and reagents in very mild conditions.

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