



Cobalt-catalyzed electrochemical vinylation of aryl halides using vinylic acetates

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Abstract—The electroreduction of aryl halides (bromides or chlorides) allows the coupling reaction with vinylic acetates, in the presence of 2,2'-bipyridine and catalytic amounts of cobalt bromide, leading to styrene derivatives in good yields. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Styrene derivatives are very useful chemical intermediates. For preparing both β -substituted or unsubstituted styrene, the Heck reaction is a powerful method.¹ However, the palladium-catalyzed arylation of enol esters provides substituted 2-arylaldehydes and ketones as major products.² These styrene derivatives can also be prepared from organometallic reagents such as vinylic stannanes³ or silanes,⁴ which are synthesized via an intermediate vinyl-palladium species.⁵ Direct Pd catalyzed routes have been described starting from 5-iodopyrimidine,⁶ however, the same reaction applied to iodobenzene⁷ leads to a complex mixture with less than 20% of styrene. More recently, various unsymmetrical *trans*-stilbenes have been synthesized by cross-coupling from reactive phenylvinylacetate and various substituted iodobenzenes using montmorillonite supported palladium catalyst in a single step.⁸ In both cases, cross-coupling reactions are restricted to aryl iodides substituted by an electron-donating group and require palladium complexes catalysis.

In the course of our recent works⁹ on electrochemical cobalt-catalyzed reactions, we described the electrochemical allylation of aryl halides with allylic acetates.¹⁰ This work deals with the cobalt catalyzed coupling of various aryl bromides or chlorides with vinylic acetates. If the reaction is carried out in the presence of stoichiometric amount 2,2'-bipyridine, this new efficient carbon–carbon bond synthesis successfully leads to styrene derivatives. This new method allows the preparation of α -substituted styrenes which are hardly accessible by current methods.

This process has also been extended to the coupling of heteroaromatic halides (X=Cl or Br) with various vinylic acetates.

2. Results and discussion

All reactions are conducted in a one-compartment cell already described,¹¹ using a sacrificial iron anode and a stainless steel grid as the cathode. The ionic conductivity of the medium is ensured by addition of NBu_4BF_4 as supporting electrolyte. Electrolyses are run at constant current intensity of 0.2 A (0.01 A/cm²), at room temperature and under inert atmosphere of argon. During the electrolysis, the cathodic potential during the electrolysis remain at ca. -1.6 V/SCE. The consumption of ArX is monitored by GC analysis. Electrolyses are stopped after total consumption of ArX. In a typical experiment, 50 mL of a mixture of solvent (45 mL of acetonitrile and 5 mL of pyridine) containing 10 mmol of ArX (0.2 M), 25 mmol of vinyl acetate (0.5 M), 1 or 2 mmol of CoBr_2 (0.02 or 0.04 M) depending on the nature of X and 0.5 mmol of NBu_4BF_4 (0.01 M) were introduced in the cell. Careful investigations of the nature of the catalyst provided a clear-cut evidence for the key role of the ligand (2,2'-bipyridine). Indeed, no more than 15% of coupling product was detected when the reaction was performed with only 0.5 equiv. or without 2,2'-bipyridine. The use of 2,2'-bipyridine in stoichiometric amount (1 equiv. vs ArX) was necessary to avoid the formation of the reduced product and the yield of the coupling product increased to 62% in the case of the reaction with *p*-bromoanisole. The 2,2'-bipyridine is used to complex cobalt but that 1 equiv. vs ArX is required because electrogenerated Fe(II) ions undergo competitive complexation of 2,2'-bipyridine. These new results prompted us to extend the coupling reaction to various aryl bromides using

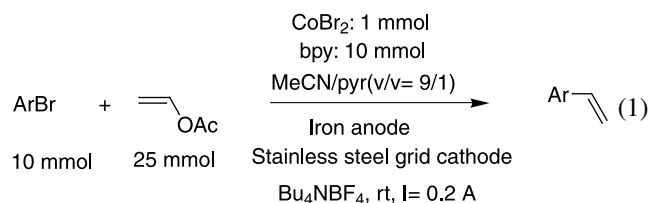
Keywords: electrochemical vinylation; vinylic acetates; aryl halides.

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the conditions described in Eq. (1) and results are reported in Table 1

Table 1. Coupling reaction between aryl bromides and vinyl acetate

Entry	ArBr	Isolated yield (%) / ArBr
1	C ₆ H ₅ Br	52 [1]
2	<i>p</i> -MeOC ₆ H ₄ Br	62 [2]
3	<i>p</i> -PhOC ₆ H ₄ Br	44 [3]
4	<i>p</i> -MeC ₆ H ₄ Br	53 [4]
5	<i>p</i> -iPrC ₆ H ₄ Br	40 [5]
6	<i>m</i> -MeOC ₆ H ₄ Br	54 [6]
7	<i>o</i> -MeOC ₆ H ₄ Br	<5
8	<i>p</i> -EtOCOC ₆ H ₄ Br	<5
9	<i>p</i> -NCC ₆ H ₄ Br	<5



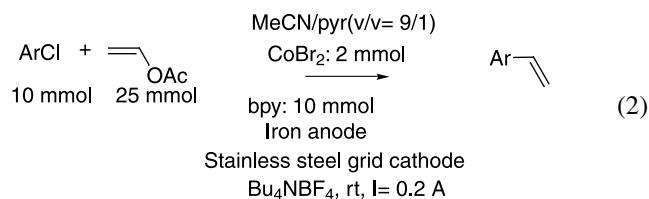
It is worth noting that good yields are obtained with bromobenzene (Table 1, entry 1) and aryl bromides substituted by an electron-donating group such as OMe, Me, *i*-Pr (Table 1, entries 2–6). However, when the substituent is in *ortho* position, only traces of the corresponding methoxystyrene are observed (Table 1, entry 7). Moreover, the presence of an *ortho* substituent strongly affects the coupling reaction with this catalytic system. Indeed, aryl bromides substituted by an electron-withdrawing group like ethyl 4-bromobenzoate (Table 1, entries 8, 9), which are more reactive, lead to a small amount of coupling product (less than 5%/ArBr), the major product being the reduced one.

As already mentioned for the electrochemical addition or vinylation of aryl halides onto olefins^{9b} or with acrylic esters,¹² respectively, the use of a consumable iron anode is essential for the reaction to remain catalytic in cobalt. With other metal, e.g. Al, Zn or Mg, only the reduced product (ArH) was obtained.

In these reactions, electrolyses are run with a cathodic potential of -1.6 V/SCE which corresponds to the reduction of bipyridine stabilized 'ArylCo' species.

We have thus extended the vinyl acetate coupling process to aryl chlorides (Eq. (2)). These halides must be activated by the presence of an electron-withdrawing group on the aromatic nucleus to react with electrogenerated cobalt species as already mentioned in our electrochemical process. Results are reported in Table 2.

In the reaction involving aryl chlorides, 0.2 equiv. of cobalt catalyst (0.04 M) per ArCl are introduced in the medium to increase the yield, all other parameters being identical to the reaction carried out from aryl bromides coupling (Eq. (2))

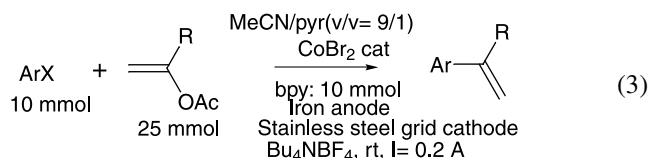


Satisfactory yields are obtained with methyl 4-chlorobenzoate (Table 2, entry 10) and *p*-chloroacetophenone (Table 2, entry 11). In the case of the reaction with *p*-chlorobenzonitrile (Table 2, entry 12), a low yield was obtained.

Table 2. Coupling reaction between aryl chlorides and vinyl acetate

Entry	ArCl	Isolated yield (%) / ArCl
10	<i>p</i> -MeOCOC ₆ H ₄ Cl	57 [7]
11	<i>p</i> -MeCOC ₆ H ₄ Cl	60 [8]
12	<i>p</i> -NCC ₆ H ₄ Cl	15 [9]

We have also extended the process to other vinylic acetates with various aromatic halides (bromides and chlorides) as described in Eq. (3)



X=Br: CoBr₂: 1 mmol; X=Cl: CoBr₂: 2 mmol

Results are reported in Table 3.

The reaction with commercially available isoprenyl acetate was first investigated. Good yields are obtained for the coupling reaction with aryl bromides (Table 3, entries 13, 14). Starting from various aromatic chlorides, coupling products were obtained in good yields (Table 3, entries 15–21).

We have also investigated the reaction of methyl 4-chlorobenzoate with other more substituted vinylic acetates. Satisfyingly, the coupling reaction takes place with excellent yields in the case of cyclopentenyl and 3,4-dihydronaphthyl acetates (Table 3, entries 22, 23) easily obtained using known procedures.¹³ Better yields are obtained using substituted vinylic acetate considering the fact that vinyl acetate is poorly soluble in this medium.

The process was finally extended to heteroaromatic chlorides (Scheme 1).

Good yields were obtained in the reaction of isopropenyl acetate with 4-chloroquinoline (65%) and 3-chloropyridine (73%) as described in Scheme 1.

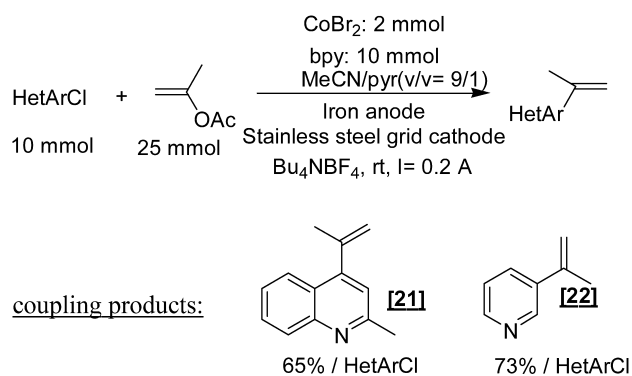
3. Conclusion

We have achieved a new coupling reaction¹⁴ of various functionalized aromatic and heteroaromatic halides (X=Br or Cl) with various vinylic acetates using a cobalt catalyst. This catalytic process is a convenient route for the

Table 3. Coupling reaction between aromatic halides and vinylic acetates

Entry	ArX		Isolated yield (%) / ArX
13	<i>p</i> -MeOC ₆ H ₄ Br		61 [10]
14	<i>p</i> -MeC ₆ H ₄ Br		47 [11]
15	<i>p</i> -MeOCOC ₆ H ₄ Cl		92 [12]
16	<i>p</i> -MeCOC ₆ H ₄ Cl		76 [13]
17	<i>p</i> -F ₃ CC ₆ H ₄ Cl		81 [14]
18	<i>p</i> -NCC ₆ H ₄ Cl		20 (56 CC) [15]
19	<i>p</i> -FC ₆ H ₄ Cl		67 [16]
20	<i>m</i> -F ₃ CC ₆ H ₄ Cl		74 [17]
21			70 [18]
22	<i>p</i> -MeOCOC ₆ H ₄ Cl		70 [19]
23	<i>p</i> -MeOCOC ₆ H ₄ Cl		57 [20]

preparation of α -substituted styrene derivatives in good yields. The reaction has been extended to several aryl bromides and chlorides, compounds which have never been used before for the direct vinylation using vinylic acetates.

**Scheme 1.**

This simple experimental procedure appears to be a mild and useful method for the synthesis of various vinyl-aryl compounds and cobalt associated to bipyridine appears more efficient for this reaction than palladium complexes. From a mechanistic point of view, Co(II) associated to bipyridine is reduced either in Co(I) or Co(0). The resulting low valent cobalt complex most likely reacts with ArX by oxidative addition to form an ArCo species. This last species could undergo a substitution reaction with the carbon attached to the ester group. Studies are now in progress to try to get insights about the mechanism of this electrochemical reaction.

4. Experimental

GC analysis was carried out using a 25-m DB1 capillary column. Mass spectra were recorded with an ITD spectrometer coupled to a gas chromatograph (DB1, 30 m). Column chromatography was performed on silica gel 60, 70–230 mesh. ¹H, ¹³C and ¹⁹F spectra were recorded in CDCl₃ at 200 MHz with TMS as an internal standard.

The electrochemical cell was similar to that described previously.¹² All solvents and reagents were purchased and used without further purification. Acetonitrile and pyridine were stored under argon.

4.1. General procedure for the coupling of aryl bromides with vinylic acetates

In an undivided cell using a consumable iron anode and a stainless steel grid as the cathode, CoBr₂ (0.219 g, 1 mmol), 2,2'-bipyridine (1.56 g, 10 mmol), ArBr (10 mmol) and vinylic acetate (25 mmol) were placed in a mixture solvent of acetonitrile/pyridine (45 mL/5 mL). The ionic conductivity of the medium is ensured by addition of NBu₄BF₄ (0.165 g, 0.5 mmol) as supporting electrolyte. The solution was electrolyzed under argon at room temperature at constant current intensity of 0.2 A (0.01 A/cm²) until the aryl bromide is totally consumed. The solution was hydrolyzed with HCl (2N) and extracted with diethyl ether, the organic layer washed with brine, dried and the solvent evaporated under vacuum. Coupling products were isolated by column chromatography on silica gel with pentane/ether as eluent.

4.2. General procedure for the coupling of aryl chlorides with vinylic acetates

The procedure used for aryl chlorides is the same that aryl bromides excepted for amount of CoBr₂ (0.438 g, 2 mmol).

4.3. Registry numbers (provided by the authors)

Styrene (**1**), 100-42-5; 4-methoxy-styrene (**2**), 637-69-4; 4-phenoxy-styrene (**3**), 4973-29-9; 4-methyl-styrene (**4**), 622-97-9; 4-isopropyl-styrene (**5**), 2055-40-5; 3-methoxy-styrene (**6**), 626-20-0; 4-ethenyl-benzoic acid methyl ester (**7**), 1076-96-6; 1-(4-ethenyl-phenyl)ethanone (**8**), 10537-63-0; 4-ethenyl-benzonitrile (**9**), 3435-51-6; 4-isopropenyl-1-methoxy-benzene (**10**), 1712-69-2; 4-isopropenyl-1-methyl-benzene (**11**), 1195-32-0; 4-isopropenyl-benzoic

acid methyl ester (**12**), 26581-23-7; 1-(4-isopropenylphenyl)ethanone (**13**), 5359-04-6; 1-isopropenyl-4-trifluoromethyl-benzene (**14**), 55186-75-9; 4-isopropenyl-benzonitrile (**15**), 19956-03-7; 4-fluoro-1-isopropenyl-benzene (**16**), 350-40-3; 1-isopropenyl-3-trifluoromethyl-benzene (**17**), 368-79-6; 1-isopropenyl-naphthalene (**18**), 1855-47-6; 3-isopropenyl-pyridine (**22**), 15825-89-5.

4.4. Product analysis

4.4.1. 4-(Cyclopent-1-enyl)-benzoic acid methyl ester (19). Yield: 70%; ^1H NMR (200 MHz) δ (ppm): 8.12 (d, 2H, $J=8.4$ Hz), 7.60 (d, 2H, $J=8.4$ Hz), 6.45 (t, 1H, $J=2.0$ Hz), 4.05 (s, 3H), 2.76 (m, 4H), 2.19 (m, 2H); ^{13}C NMR (50 MHz) δ (ppm): 166.7, 141.5, 140.9, 129.4, 129.0, 128.0, 125.1, 51.7, 33.3, 32.8, 23.0; EI/MS, m/z (%): 202 (71) [M], 171 (20), 170 (17), 169 (11), 144 (11), 143 (100), 142 (17), 141 (18), 128 (43), 115 (23). Anal. calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.20; H, 6.98; O, 15.82. Found: C, 77.08; H, 6.91; O, 15.43.

4.4.2. 4-(3,4-Dihydro-1-naphthyl)-benzoic acid methyl ester (20). Yield: 57%; ^1H NMR (200 MHz) δ (ppm): 8.24 (d, 2H, $J=8.3$ Hz), 7.59 (d, 2H, $J=8.3$ Hz), 7.25 (m, 4H), 6.30 (t, 1H, $J=4.7$ Hz), 4.09 (s, 3H), 3.01 (t, 2H, $J=7.9$ Hz), 2.58 (td, 2H, $J=7.9, 4.7$ Hz); ^{13}C NMR (50 MHz) δ (ppm): 166.9, 145.7, 139.4, 136.8, 134.5, 129.7, 129.0, 128.9, 128.8, 127.8, 127.4, 126.4, 125.4, 52.0, 28.3, 23.6; EI/MS, m/z (%): 265 (22) [M+1], 264 (100) [M], 249 (26), 233 (14), 231 (10), 206 (14), 205 (80), 204 (22), 203 (38), 202 (36), 190 (16), 189 (14), 149 (10). Anal. calcd for $\text{C}_{18}\text{H}_{16}\text{O}_2$: C, 81.79; H, 6.10; O, 12.11. Found: C, 82.19; H, 6.02; O, 11.84.

4.4.3. 4-Isopropenyl-2-methyl-quinoleine (21). Yield: 65%; ^1H NMR (200 MHz) δ (ppm): 7.75 (d, 1H, $J=8.4$ Hz), 7.62 (dd, 1H, $J=8.4, 0.9$ Hz), 7.27 (m, 1H), 7.05 (m, 1H), 6.71 (s, 1H), 5.05 (t, 1H, $J=1.6$ Hz), 4.72 (s, 1H), 2.36 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (50 MHz) δ (ppm): 158.2, 150.2, 148.1, 141.9, 128.9, 125.3, 125.0, 124.1, 119.7, 117.0, 25.0, 24.2; EI/MS, m/z (%): 184 (12) [M+1], 183 (89) [M], 182 (33), 181 (19), 169 (14), 168

(100), 167 (31), 166 (11). Anal. calcd for $\text{C}_{13}\text{H}_{13}\text{N}$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.23; H, 7.35; N, 7.42.

Acknowledgements

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