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Electrosynthesis of functionalized organodizinc compounds from aromatic dihalides via a cobalt catalysis in acetonitrile/pyridine as solvent

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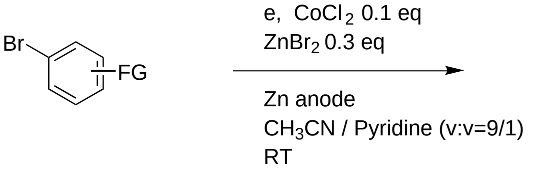
Abstract—Electroreduction of aryl-dichlorides or -dibromides in an electrochemical cell fitted with a sacrificial zinc anode and in the presence of cobalt halides as catalyst in acetonitrile/pyridine as solvent affords the corresponding organodizinc species in moderate to excellent yields with high selectivity. © 2001 Elsevier Science Ltd. All rights reserved.

Recent work in this laboratory has shown that Co^I formed by electroreduction of CoX_2 (X = Br or Cl) in dimethylformamide or acetonitrile as solvent containing pyridine as ligand for cobalt reacts rapidly with aryl bromides.[1] This explains the success in the electrosynthesis of arylzinc halides catalyzed by CoX_2 if the electroreduction is conducted in the presence of $ZnBr_2$ in a one-compartment cell fitted with a zinc sacrificial anode[2] (Scheme 1).

Aryldizinc compounds XZn-Ar-ZnX are also interesting synthetic intermediates. For example dibromobenzene appears to be an ideal starting material for the preparation of symmetrical and/or unsymmetrical disubstituted benzene derivatives by cross coupling of its dizinc derivative with aromatic halides in the presence of Pd(0).[3] If Rieke magnesium in excess (4 equiv. of Mg*) is sufficiently reactive to form the di-Grignard reagent by reaction with dibromobenzene at room temperature,[4] the corresponding dizinc reagent can only be prepared from diiodobenzene,[5] using the same procedure. This seriously limits the process owing to the difficulties in obtaining the aromatic diiodo compounds. To our knowledge, no method of synthesis of organodizinc compounds from aromatic dibromides or dichlorides has been reported. Therefore, we tried to extend our electrochemical process to the preparation of organodizinc compounds from aryl dibromides or dichlorides bearing functional groups. The combination of consumable zinc anode and nickel–bipyridine catalysis that we have already reported[6] was found unsuitable for the synthesis of the compounds it was aimed at. In all cases monozinc derivatives were the main products. Thus, for example, from 2,5-dibromothiophene 5-bromo-2-thienylzinc bromide was the only product.[7]

Results and discussion

Diorganozinc compounds were synthesized by the same method as described before for monoaryl halides using a cobalt catalysis. All reactions were conducted in a one-compartment cell already described,[8] using a consumable zinc anode and a nickel foam cathode, under an inert atmosphere of argon, at room temperature in



Scheme 1.

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commercial solvents used without purification. The presence of a supporting electrolyte is not necessary, the ionic conductivity of the medium being ensured by zinc bromide added in the medium as source of zinc(II) species.

Electrolyses were conducted at a constant current intensity of 0.2 A (0.01 A/cm^2), and stopped after consumption of 4 F per mole of ArX_2. The cathodic potential during the electrolysis was between −1.1 V and −1.3 V/SCE, which is the potential of the formation of a Co(I) complex from CoX_2–pyridine.

In a typical experiment, 50 ml of mixture of solvent (45 ml acetonitrile and 5 ml of pyridine) containing 10 mmols of ArX_2 (0.2 M), 2 mmols of $CoCl_2$ (0.04 M) and 2 mmols (0.04 M) of $ZnBr_2$ (formed by electroreduction of 1,2-dibromoethane in the presence of a zinc anode) were introduced into the cell.

The obtained organozinc species were reacted with iodine, for GC measurement of the resulting aryl diiodide, and using an internal standard (alcane). In some case, the aromatic organozinc species were coupled with phenyl iodide using $PdCl_2(PPh_3)_2$ as catalyst. The resulting products were isolated.

In Table 1, we have reported the results obtained with various aryl dibromides.

In all cases, only the diorganozinc compound is obtained at 4 F/mol. Analysis of the solution after consumption of 2 F/mol of ArX_2, showed in all cases, the formation of a mixture of the mono (Br-ArZnBr) and dizinc (BrZn-Ar-ZnBr) compounds.

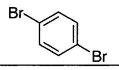
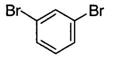
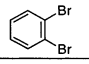
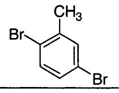
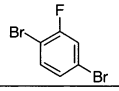
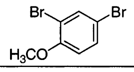
At 4 F/mol, all the starting compound ArX_2 is consumed and the mono zinc compound formed at 2 F/mol is transformed into the diorgano zinc species, BrZnArZnBr, which is the only organometallic present in the medium.

In all cases, good yields are obtained except in the case of *ortho*-dibromobenzene (entry 3). In this case, at 2 F/mol, only 16% of mono and dizinc compound are formed, at 4 F/mol, only the monozinc species formed is further transformed in dizinc compound. The reaction proceeds efficiently with aryl dibromides substituted by methyl, fluorine, or methoxy group (entries 4, 5, 6). An important point is the absence of biaryl compounds. The only by-product of the electrolysis (4 F/mol) is the reduced product ArH_2, likely formed by decomposition of the arylcobalt intermediate.[1]

We have also studied the formation of dizinc compounds from dichlorobenzenes and bromochlorobenzene. Results are reported in Table 2

In all cases, the monozinc compound is the major product at 2 F/mol. At more than 2 F/mol, the reaction does not proceed further, even when all the starting reagent is not consumed (entry 7). However, all the starting reagent is consumed at 2 F/mol when *p*-dichlorobenzene is activated with an electron-withdrawing group (entry 8). On the other hand, with *p*-bromochlorobenzene, only the monozinc compound

Table 1. Formation of dizinc species from dibromobenzene

entry	reagent	2F/mol BrArZnBr	 BrZnArZnBr %	4F/mol BrArZnBr	 BrZnArZnBr %
1		13	22	0	86(a)
2		7	11	0	51
3		6	10	0	16
4		12	18	0	66
5		22	15	0	73(b)
6		8	20	0	44

(a): the coupling with PhI using $PdCl_2(PPh_3)_2$ as catalyst gave 45% of Ph-Ph-Ph and 27% of Ph-Ph

(b): the coupling with PhI using $PdCl_2(PPh_3)_2$ as catalyst gave 45% of Ph-Ph(F)-Ph and 17% of Ph(F)-Ph.

Table 2. Formation of dizinc species from dichlorobenzene and bromochlorobenzene

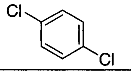
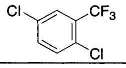
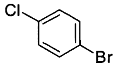
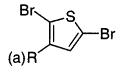
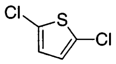
entry	reagent	2F/mol			4F/mol		
		XArZnX	XZnArZnX	ArX_2	XArZnX	XZnArZnX	ArX_2
		%			%		
7		27	8	54	28	10	51
8		69	14	17	73	19	0
9		63 (Cl-Ph-ZnBr)	0	0	38	30	0

Table 3. Formation of dizinc species from 2,5-dibromo or 2,5-dichlorothiophene

entry	reagent	2F/mol		4F/mol		
		XArZnX	XZnArZnX	XArZnX	XZnArZnX	ArX_2
		%		%		
10		11	11	0	28	0
11		23	2	26	2	60

a: R= H or Me

BrZnPhCl shows up at 2 F/mol and a part of this is transformed in dizinc species at 4 F/mol (entry 9). Contrary to aryl dibromides, the monozinc intermediate is always major from dichloro compounds.

We have also tried to form organozinc compounds from dibromo- or dichlorothiophene but yields are not satisfactory, as shown in Table 3.

2,5-Dibromothiophene and the 2,5-dichlorothiophene behave basically like the corresponding benzene reagents. At 2 F/mol, 2,5-dibromothiophene (entry 10) gives a mixture of mono and dizinc compounds, and at 4 F/mol only the dizinc compound is obtained. All the starting compound disappears at 2 F/mol. Reduction products are probably formed, thiophene and/or polythiophene. We have already reported the formation of thienyl zinc species from 3-substituted-2,5-dihalothiophene catalyzed by $NiBr_2Bpy$, where only the monozinc compound was obtained.[7] With a cobalt catalysis, we obtained a mixture of the mono and the dizinc compounds which give only the dizinc compound with an extra charge. On the contrary, dichlorothiophene (entry 11) gives mostly the mono zinc species at 2 F/mol (mono/di = 10) and all the starting reagent is not consumed. With an extra charge, there is no evolution, as with dichlorobenzene.

We can suppose that in the case of dichloro reagents (benzene and thiophene), the major electrochemical reaction is the reduction of Zn^{2+} formed by anode oxidation. This is accompanied by disappearance of the Co^I by disproportionation which occurs here more rapidly than the oxidative addition into an Ar–Cl bond.[1]

Conclusion

The electrosynthesis of diarylzinc species can be achieved using dibromobenzenes or activated dichlorobenzenes with moderate to excellent yields. In the case of *o*-dibromobenzene, the yield is poor. The mono and dizinc compounds are obtained simultaneously for these compounds at 2 F/mol except for bromochlorobenzene where only the monozinc species is detected. At 4 F/mol, only the dizinc species is obtained from dibromobenzenes. Contrary, dichlorobenzene reagents give a mixture of mono and dizinc compounds. This behavior is not surprising considering the most important reactivity of C–Br versus C–Cl bond. This is the reason why non-activated dichloro derivatives are not consumed and the monozinc species is the major organometallic product at the end of the reaction.

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