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Pd(0)-CATALYZED ELECTROREDUCTIVE CARBOXYLATION OF ARYL HALIDES, β-BROMOSTYRENE, AND ALLYL ACETATES WITH CO_2

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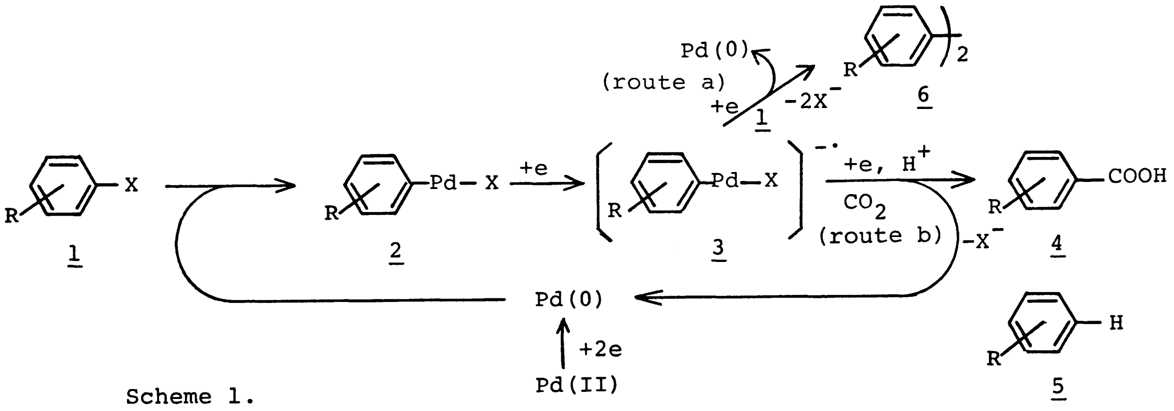
Electroreductive carboxylation of aryl halides, β-bromostyrene, and allyl acetates has been performed in an aprotic solvent saturated with carbon dioxide in the presence of a catalytic amount of $PdCl_2(Ph_3P)_2$ and/or $Pd(Ph_3P)_4$.

In the previous paper, we disclosed an efficient Pd-catalyzed electroreductive coupling of aryl halides **1**.[1] In this connection, we proposed a two-electron reduction mechanism which involved dipole inversion of σ-aryl Pd complex **2** and subsequent coupling with aryl halides **1** leading to biaryls **6** with liberating Pd(0) complex and halide ions (route a in Scheme 1). These considerations, in turn, prompted us to investigate a possibility of carboxylation of aryl halides **1** with CO_2 in a similar electroreductive Pd(0)-recycling system (route b).

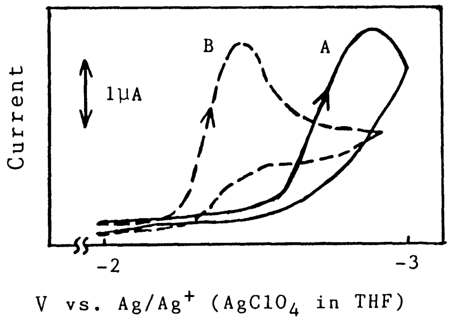
The electroreductive carboxylation of aryl halides **1** with CO_2 has received much attention as a promising tool for preparation of arene carboxylic acids **4**.[2,3] However, most attempts to the direct electroreductive carboxylation of **1** in an aprotic solvent saturated with CO_2 has proved to be unsuccessful due to the competitive formation of arenes 5 and/or biaryls **6** together with carboxylic acid **4** (10-38%).[2] Recently, Perichon, Fauvarque, and their coworkers have developed an efficient Ni(0)-catalyzed electroreductive carboxylation of **1** with CO_2 in a THF-HMPA-(Hg pool cathode) system, affording **4** in 40-87% yield.[3]



Scheme 1.

We now found that the Pd(0)-catalyzed electroreduction system was applied successfully to the carboxylation of aryl halides **1** and the carboxylation of vinyl bromide **7** and allyl acetates **10** and **13** was also performed in the analogous electroreductive media.

As a preliminary experiment, we carried out cyclic voltammetry on $PhPd(II)Br(Ph_3P)_2$ and $PhPd(II)Br(Ph_2PCH_2CH_2PPh_2)$ **2** (R = H; X = Br) in THF , showing the characteristic reduction peaks (Fig. 1). When the Pd(II)-complexes **2** in THF containing Bu_4NBF_4 (0.1 M) were electrolyzed at -2.4 — -2.9 V vs. Ag/Ag^+ with Hg-pool cathode under bubbling CO_2, carboxylic acid **4b** (R = H; 74-80%) was obtained. These results spurred us to investigate Pd-catalyzed carboxylation system (route b in Scheme 1).



100 mV/s with Au electrode (3.14 mm^2)
A: $PhPdBr(Ph_3P)_4$, 4 x 10^{-3}M
B: $PhPdBr(Ph_3PCH_2)^2$, 4 x 10^{-3}M

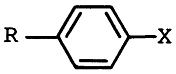
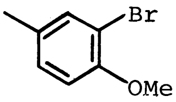
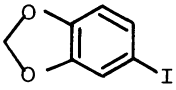
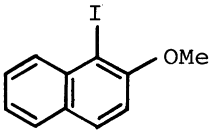
Fig. 1.

The Pd(0)-catalyzed electroreductive carboxylation was carried out in a divided cell fitted with Pt anode and Pb or Pt cathode (3 cm^2 each). A typical procedure (entry 1 in Table 1) is as follows. A DMF solution of Et_4NOTs (400 mg/7 ml) was charged into both the anode and cathode chambers. After bubbling of CO_2 gas into the catholytes for 30 min, 4-t-butyliodobenzene **1a** (R = Bu^t; X = I, 0.3 mmol), $Pd(II)Cl_2(Ph_3P)_2$ (14 mg, 0.02 mmol), and Ph_3P (14 mg, 0.04 mmol) were added to the cathode chamber. Under continuous bubbling of CO_2 gas, regulated dc power at 2.5 mA/cm^2 was supplied until most of the starting material **1a** was consummed (5.3 F/mol). Usual workup of the catholytes afforded desired carboxylic acid **4a** (85%) along with a small amount of t-butylbenzene **5a** (5%), while no detectable amount of 4,4'-di-t-butylbiphenyl **6a** (R = p-Bu^t) was isolated.

In place of the Pd(II) catalyst and Ph_3P, $Pd(0)(Ph_3P)_4$ was used successfully (entry 3).[4)] The presence of Pd(II) or Pd(0)-catalyst was indispensable for the preferential formation of **4a**, otherwise substantial quantity of **5a** (45%) was formed together with **4a** (38%). The proper choice of the cathode material is also significant for the carboxylation of **1a**, since the yield of **4a** decreased, depending on the employed cathode materials in the following order: Pb (85%) > Pt (78%) > Cu (76%) > Stainless (56%) > Ni (46%) > C (38%).

The results and conditions of the electroreductive carboxylation of aryl halides **1a-1i** are summarized in Table 1. The carboxylation of aryl iodides **1** (X = I) and aryl bromides **1** (X = Br) proceeded smoothly to give the corresponding carboxylic acids **4** in good yields, whereas aryl chloride **1e** gave no appreciable amount of **4e** (R = Bu^t) (entry 7). This fact would be ascribed to the difficulty in accumulation of enough σ-aryl Pd complex **2** (X = Cl) in the electrolysis media.[5)] Notably, biaryls **6** were not isolated in any entries in Table 1. Therefore, in the electrolysis media saturated with CO_2, σ-aryl Pd complex **3** seems to react with CO_2 (route b in Scheme 1) in preference to aryl halide **1** (route a).

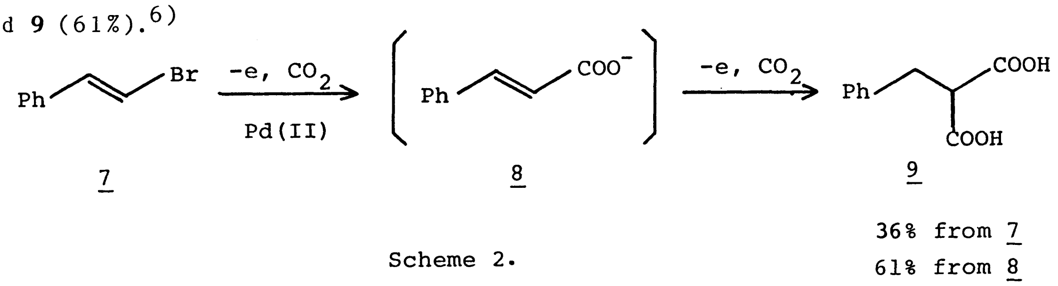
Table 1. Electroreductive Carboxylation of Aryl Halides

Entry	Aryl halides	Catalyst[a)]	Cathode	Electricity[b)]	Product yield/%[c)]	
				F/mol	4	5
						
1	1a (R = $\mathrm{Bu^t}$; X = I)	Pd(II)	Pb	5.3	85	5
2	1a (R = $\mathrm{Bu^t}$; X = I)	Pd(II)	Pt	3.0	77	12
3	1a (R = $\mathrm{Bu^t}$; X = I)	Pd(0)	Pb	4.3	76	15
4	1b (R = H; X = I)	Pd(0)	Pt	3.0	92	
5	1c (R = OMe; X = I)	Pd(0)	Pt	3.5	82	
6	1d (R = OMe; X = Br)	Pd(0)	Pt	4.5	47[d)]	
7	1e (R = OMe; X = Cl)	Pd(0)	Pt	4.5	--[e)]	
8	1f (R = Cl; X = I)	Pd(0)	Pt	4.5	66	
9	 1g	Pd(II)	Pt	5.2	80	
10	 1h	Pd(0)	Pt	3.0	76	13
11	 1i	Pd(II)	Pt	4.5	63	20

a) Pd(II): $Pd(II)Cl_2(Ph_3P)_2$ (0.07 equiv.)-Ph_3P(0.14 equiv.); Pd(0): $Pd(0)(Ph_3P)_4$ (0.07 equiv.). b) Unless otherwise noted, regulated dc power (2.5 mA/cm^2) was supplied until most of **1** was consumed. c) Isolated yields after column chromatography on SiO_2 (hexane/EtOAc: 10/1).

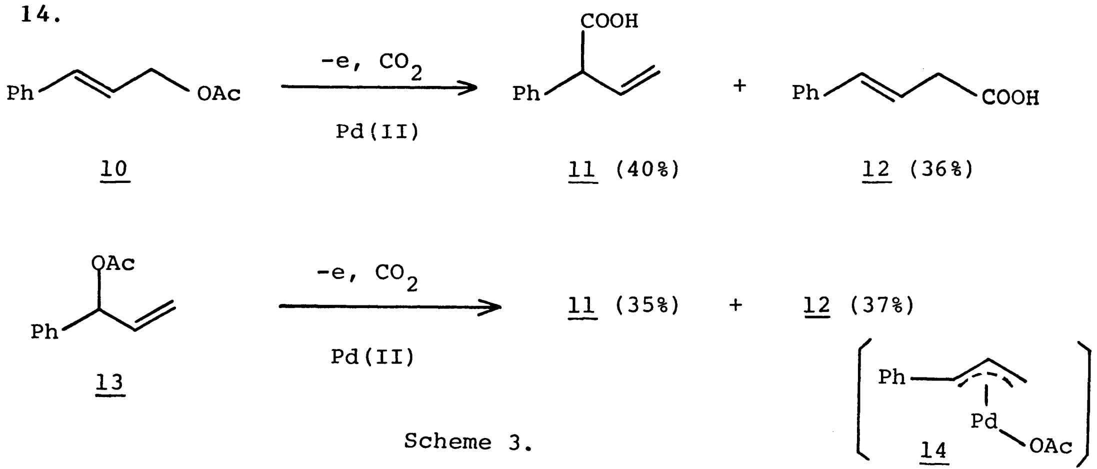
d) Bromide **1d** (33%) was recovered. e) Chloride **1e** (66%) was recovered.

As a further extention of this idea, we investigated a similar electroreductive carboxylation mediated with σ-vinyl or π-allyl Pd complex. Thus, electroreductive carboxylation of vinyl bromide **7** was carried out in a Pd(II) catalyst-DMF-Et_4NOTs-(Pb cathode) system under bubbling CO_2 gas. Passage of 4.5 F/mol of electricity afforded dicarboxylic acid **9** (36%), which would be formed via the primary product **8** (Scheme 2). Actually, electrolysis of the α,β-unsaturated carboxylic acid **8** (tetrabutylammonium salt) in a DMF-Et_4NOTs-(Pb electrode) afforded **9** (61%).$^{6)}$



Scheme 2.

Next, the Pd(0)-catalyzed electroreductive carboxylation was applied to the carboxylation of allyl acetates **10** and **13** in a Pd(II) catalyst-CH_3CN-Et_4NOTs-(Pb cathode) system (Scheme 3). Passage of 3 F/mol of electricity afforded a mixture of carboxylic acids **11** and **12** (Scheme 3) presumably arising from the same intermediate **14**.



Scheme 3.

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