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Pd(0)-CATALYZED ELECTRO-REDUCTIVE HYDROCOUPLING OF ARYL HALIDES WITH OLEFINS AND ACETYLENES

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Electro-reductive hydrocoupling of aryl halides with olefins and acetylenes has been performed in an $Et_4NOTs-DMF-(Pb\ cathode)$ system in the presence of catalytic amounts of $PdCl_2(Ph_3P)_2$.

Pd(0)-catalyzed cross coupling of aryl halides with olefins and acetylenes has been extensively investigated and proved to be an efficient procedure for obtaining aryl substituted olefins and acetylenes, respectively.¹⁾ In the previous paper,²⁾ we have disclosed a Pd(0)-catalyzed electroreductive dimerization of aryl halides. In consequence of the extension works, we found that an unique cross coupling of aryl halides 1 with olefins and acetylenes 2 into the corresponding hydrocoupling products 3 took place in a similar electrolysis system, in which the Pd(0)-catalysts were presumably recycled through a two electron reduction sequence (Scheme 1) in contrast to the conventional Pd-catalyzed reaction (route a).

Electrolysis was carried out in a divided cell fitted with Pt anode and Pb cathode (3 cm² each). A typical electrolysis procedure is as follows. A DMF solution of Et_4NOTs (500 mg/10 ml) was charged into both anode and cathode chambers and the cell was purged with argon gas. Into the cathode chamber were



successively added <u>t</u>-butylphenyl iodide (1a) (0.5 mmol), styrene 2a (4.5 mmol, 9 equiv.), $Pd(II)Cl_2(PPh_3)_2$ (0.034 mmol, 0.07 equiv.), and PPh_3 (0.1 mmol) and regulated dc power (2.5 mA/cm²) was supplied at ambient temperature until most of 1a was consumed (3-6 F/mol). The usual workup of the catholytes gave 1,2-diphenyl-ethane 3a in 85% yield (entry 1 in Table 1). Under similar electrolysis conditions, iodides 1b and 1c reacted with 2a to give 3b and 3c in 66-78% yields (entries 4 and 5), while bromides 1d and 1e were less effective for this purpose (entries 6 and 7). Cross coupling of 1a and/or 1b with isoprene 2b, phenyl-acetylene 2c, and bromostyrene 2d proceeded in the analogous way, affording the corresponding coupling products 3e-g, respectively (entries 8-11).³⁾

Although the mechanisms have not been clarified yet, it is very likely that the Pd-catalysts play a significant role in the hydrocoupling of 1 with 2, since the electrolysis in the absence of the Pd-catalysts afforded no appreciable amount of the hydrocoupling product (entry 3).

Table 1. Hydrocoupling of Aryl Halides with Olefins and Acetylenes							
Entry	Aryl	Olefin,	Product	Entry	Aryl	Olefin,	Product
	halide	acetylene	(yield/%) ^{a)}		halide	acetylene	(yield/%) ^{a)}
R ¹	$- \sum_{(R^1; X)} x$	Ph Ph	Ph	7	<u>le</u>	<u>2a</u>	$\underbrace{3d}_{32}^{Ph}$
1	<u>la</u> (Bu ^t ;I)	<u>2a</u>	$\frac{3a}{2a}$ (85)	8	<u>la</u>	2b Bu	3e (78)
2	la	<u>2a</u>	3a(52)				Ph
3	<u>la</u>	<u>2a</u>	3a () ^{C)}	9	la	Ph	t
4	<u>1b</u> (H;I)	<u>2a</u>	<u>3b</u> (78)			2c Bu	<u>3f</u> (74)
5	<u>lc</u> (MeO;I)	<u>2a</u>	<u>3c</u> (66)	10	la	Ph Br 2d	<u>3f</u> (45)
6	<u>ld</u> (Bu ^t ;Bı	c) <u>2a</u>	<u>3a</u> (17)	11	<u>1b</u>	<u>2c</u>	<u>3g</u> (72)

a) Isolated yield after column chromatography (SiO₂; hexane/EtOAc (5/1)).

b) With Pt cathode. c) Carried out in the absence of Pd-catalyst.

d) Naphthalene was recovered (67%).

References

 J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer-Verlag, Berlin, New York (1980), p. 137; R. F. Heck, Organic Reaction, <u>27</u>, 345 (1982); L. S. Hegedus; Tetrahedron, <u>40</u>, 2415 (1984); T.-A. Mitsudo, V. Fischettii, and R. F.Heck, J. Org. Chem., <u>49</u>, 1640 (1984); and references cited therein.

2) S. Torii, H. Tanaka, and K. Morisaki, Tetrahedron Lett., <u>41</u>, 1655 (1985).

3) Attempts to the cross coupling of **la** with non-conjugated olefins, e.g., ethyl vinyl ether, allyl alcohol, and allyl bromide, failed.

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