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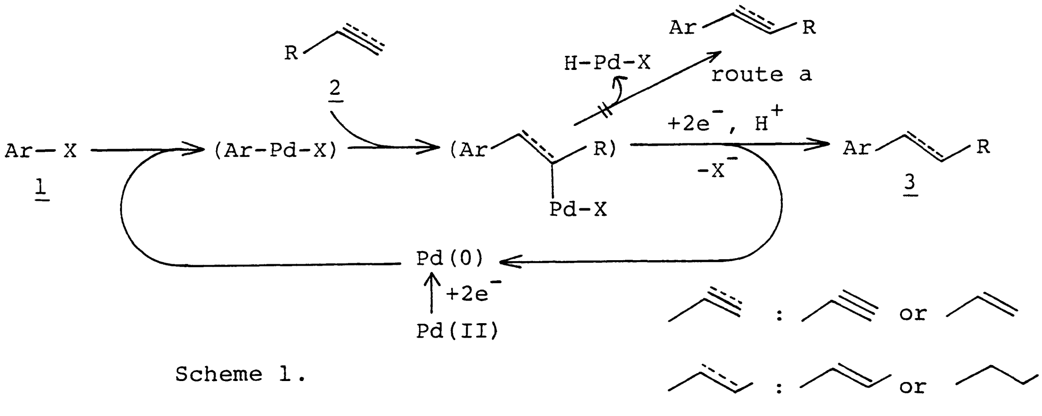
Pd(0)-CATALYZED ELECTRO-REDUCTIVE HYDROCOUPLING OF ARYL HALIDES WITH OLEFINS AND ACETYLENES

Sigeru TORII,* Hideo TANAKA, and Kazuo MORISAKI
Department of Industrial Chemistry, School of Engineering,
Okayama University, Okayama 700

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 cm^2 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

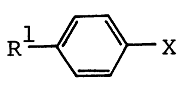
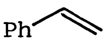
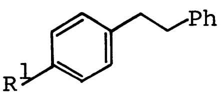
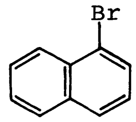
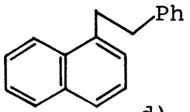
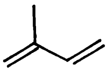
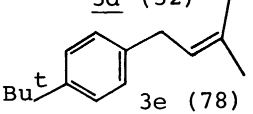
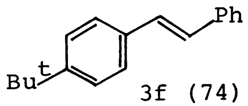
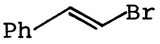
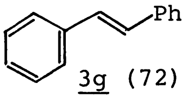


Scheme 1.

successively added t-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/cm^2) was supplied at ambient temperature until most of **1a** was consumed (3-6 F/mol). The usual workup of the catholytes gave 1,2-diphenylethane **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**, phenylacetylene **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 halide	Olefin, acetylene	Product (yield/%)$^{a)}$
	 (R^1; X)		
1	1a (Bu^t;I)	2a	3a (85)
2	1a	2a	3a (52)$^{b)}$
3	1a	2a	3a (--)$^{c)}$
4	1b (H;I)	2a	3b (78)
5	1c (MeO;I)	2a	3c (66)
6	1d (Bu^t;Br)	2a	3a (17)
7	 1e	2a	 3d (32)$^{d)}$
8	1a	 2b	 3e (78)
9	1a	 2c	 3f (74)
10	1a	 2d	3f (45)
11	1b	2c	 3g (72)

a) Isolated yield after column chromatography (SiO_2; hexane/EtOAc (5/1)).
b) With Pt cathode. c) Carried out in the absence of Pd-catalyst.
d) Naphthalene was recovered (67%).

References

1) J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer-Verlag, Berlin, New York (1980), p. 137; R. F. Heck, Organic Reaction, 27, 345 (1982); L. S. Hegedus; Tetrahedron, 40, 2415 (1984); T.-A. Mitsudo, V. Fischettii, and R. F.Heck, J. Org. Chem., 49, 1640 (1984); and references cited therein.
2) S. Torii, H. Tanaka, and K. Morisaki, Tetrahedron Lett., 41, 1655 (1985).
3) Attempts to the cross coupling of **1a** with non-conjugated olefins, e.g., ethyl vinyl ether, allyl alcohol, and allyl bromide, failed.

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