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A new pathway for the preparation of diaryl acetylenes

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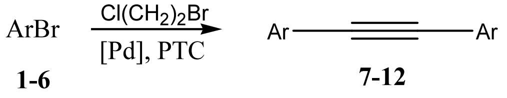
Abstract—A simple method for the preparation of diaryl acetylenes in yields up to 61% from aryl bromides and 1-bromo-2-chloroethane using the palladium catalyst (dppb)Pd(OAc)$_2$ under PTC conditions (solid KOH/18-crown-6) has been developed.

Conjugated systems have been a highly prominent research subject for over two decades because of their unique optical and electronic properties, and environmental stability.[1] Alkynes are important and in many cases convenient intermediates for the preparation of various synthetic precursors for the construction of valuable materials.[2] Diaryl acetylenes can be seen as components in mixed triple bond–arene conjugated oligomers, polymers, and dendrimers.[3] A number of methods have been used for the preparation of substituted alkynes.[4] One of the most common methods for bond formation between an acetylene and an arene is the Sonogashira coupling of aryl halide with a terminal acetylene catalyzed by palladium complexes and copper iodide. Silylated acetylenes and acetylene gas have served as a source of acetylenes in the Sonogashira reaction terminal acetylenes.[4,5] The acetylene–arene coupling can also be realized by reaction of aryl bromide with stannyl acetylenes in the presence of a palladium catalyst.[6]

As part of our ongoing research to create new materials,[7] we now report on a new pathway for the preparation of diaryl acetylenes. 1-Bromo-2-chloroethane was used as a source of 'acetylene' in the Sonogashira coupling. The diaryl acetylenes **7**–**12** were formed in the presence of one equivalent of 1-bromo-2-chloroethane but in a mixture of other products in low yields. To increase the selectivity of this reaction we optimized the aryl bromide **1**–**6**:1-bromo-2-chloroethane ratio. It was found that a twofold excess of 1-bromo-2-chloroethane to aromatic bromide is the optimal amount (Scheme 1). The high activity of a Pd catalyst with 1,4-bis(diphenylphosphino)butane (dppb) as ligand was demonstrated in Ref. 8. The presence of solid KOH/18-crown-6 is necessary for the successful dehydrohalogenation of 1-bromo-2-chloroethane.[9] The best results were obtained using the following catalytic system solid KOH/18-crown-6/Pd(OAc)$_2$/dppb in toluene in a molar ratio of 5.0:0.1:0.05:0.125.[10] We propose that initially the aryl bromide forms an adduct with palladium catalyst (dppb)Pd(ArBr)$_2$ (Scheme 2). In a second step, the subsequent Heck reaction[11] of vinyl chloride formed from 1-bromo-2-chloroethane under PTC conditions with the aryl bromides **1**–**6** gives the intermediate ArCH=CHCl, which undergoes elimination of HCl in the presence of base and leads to arylacetylenes. Then the arylacetylenes reacted with the second equivalent of aryl bromide in the presence of palladium catalyst to afford the desired diarylacetylenes **7**–**12** in yields up to 61% (Table 1). This step was proved experimentally. The reaction of phenylacetylene with bromobenzene in system Pd(OAc)$_2$/dppb/solid KOH/18-crown-6/PhMe at 100°C led to diphenylacetylene as a main product in 40% yield. The formation of aryl bromides homocoupling products (Ar–Ar) (5–20%) was also detected. In this way 1,2-diphenyl acetylene **7** was obtained in 47% yield from bromobenzene. Lower yields were obtained



Ar = Ph, 2-thienyl, 3-thienyl, 3-methyl-2-thienyl,
2-pyridyl, 3-pyridyl

Scheme 1. Palladium catalyzed synthesis of diarylethynes in the system BrCH$_2$CH$_2$Cl/solid KOH/Pd(OAc)$_2$/dppb/18-crown-6/toluene at 100°C.

Keywords: acetylene; aryl bromides; palladium catalysis; phase transfer catalysis.

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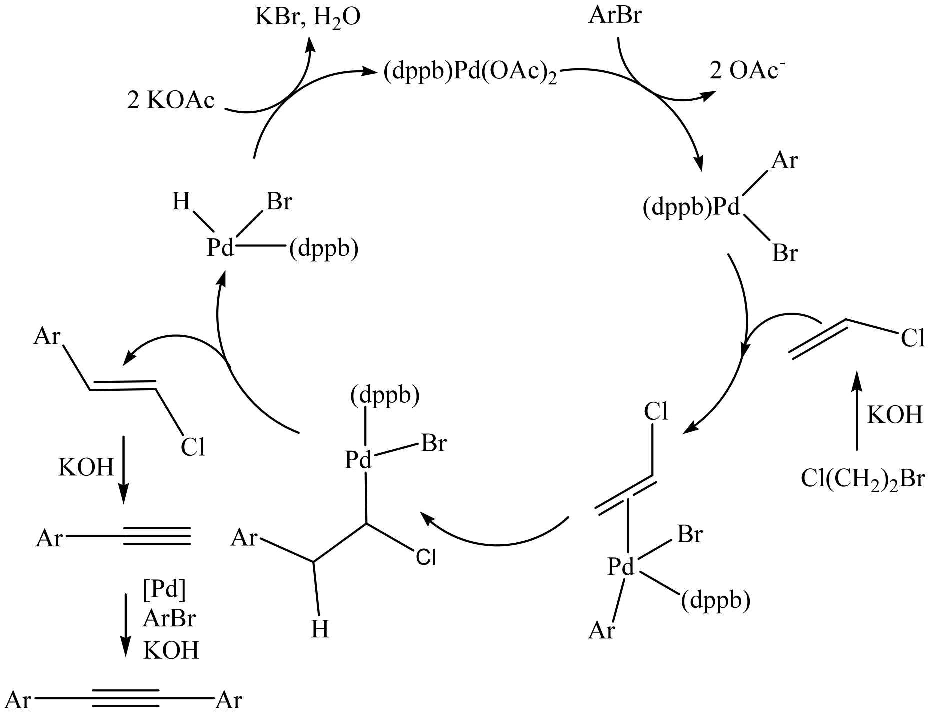

Scheme 2. Mechanism of palladium catalyzed synthesis of diarylethynes under PTC conditions.

Table 1. Palladium catalyzed synthesis of diarylethynes **7**–**12** from aryl bromides **1**–**6** in the system $BrCH_2CH_2Cl$/ solid KOH/$Pd(OAc)_2$/dppb/18-crown-6/toluene at 100°C

ArBr	Ar	Reaction time (h)	Products (yield, %)[a]
1	Ph	42	**7** (47)[5a,c–e]
2	2-Thienyl	48	**8** (26)[5a,b]
3	3-Thienyl	48	**9** (37)[5e,12]
4	3-Methyl-2-thienyl	72	**10** (30)[13]
5	2-Pyridyl	48	**11** (29)[14,15]
6	3-Pyridyl	42	**12** (61)[15]

[a] Isolated yields.

for dithienyl acetylenes **8**–**10**. It should be noted that 3-bromothiophene (37%) is more active in coupling than its 2-substituted analogue (26%). For full conversion of 3-methyl-2-bromothiophene the reaction required more time (72 h) probably due to steric effects caused by methyl group. Di(3-pyridyl)acetylene was prepared in the best yield (61%). All products were easily purified by chromatography on silica using hexane:ethyl acetate as eluent.

In summary, we have developed a simple method for the preparation of diaryl acetylenes from aryl bromides and 1-bromo-2-chloroethane using a palladium catalyst and PTC conditions, in one pot.

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10. Aryl(hetaryl) bromide **1**–**6** (1 mmol) was added to the mixture of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and 1,4-bis-(diphenylphosphino)butane (dppb) (53.3 mg, 0.125 mmol) dissolved in toluene (3 ml) in a *Pierce* reacti-vial (5 ml) under argon. After 5 min stirring, solid KOH (0.28 g, 5 mmol), 18-crown-6 (26 mg, 0.1 mmol) and 1-bromo-2-choroethane (0.165 ml, 2 mmol) were added. The reaction mixture was stirred for 4 h at 50°C and then at 100°C with all the substrate have been utilized (GC, see Table 1). Then the reaction mixture was filtered from precipitates and the solvent was removed under reduced pressure. The crude residue was chromatographed on silica using hexane:ethyl acetate as eluent.
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13. 1,2-Bis(3-methyl-2-thienyl)ethyne (**10**). Oil, yield 30%; MS, *m*/*e* 218 [$M^{•+}$]; ^1H NMR (200 MHz, $CHCl_3$) δ (ppm): 2.36 (s, 6H, CH_3), 6.83 (m, 2H, C-4), 7.25 (m, 2H, C-5); ^{13}C NMR (50.31 MHz, $CHCl_3$) δ (ppm): 14.05, 89.14 (C≡C), 115.01, 128.30, 131.10, 143.00.
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