

## A CONVENIENT SYNTHESIS OF ACETYLENES : CATALYTIC SUBSTITUTIONS OF ACETYLENIC HYDROGEN WITH BROMOALKENES, IODOARENES, AND BROMOPYRIDINES

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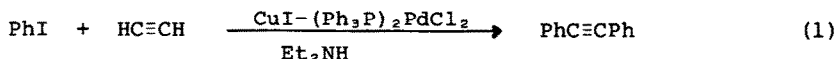
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Stephans-Castro coupling of copper (I) arylacetylenes with iodoarenes<sup>1)</sup> or iodoalkenes<sup>2)</sup> is a useful reaction for the synthesis of acetylenes in laboratories, its scope being sometimes limited by the violent reaction conditions and by the difficulties in preparations of cuprous acetylides.

We now report that an acetylenic hydrogen can be easily substituted by iodoarenes, bromoalkenes or bromopyridines in the presence of a catalytic amount of bis(triphenylphosphine)palladium dichloride - cuprous iodide in diethylamine under a very mild condition. Very recently, Cassar<sup>3)</sup> and Heck<sup>4)</sup> reported independently the same substitution reaction catalyzed by similar catalysts. In our method, the reaction proceeds under a milder condition in the presence of a co-catalyst, cuprous iodide, and gives more satisfactory results for the direct synthesis of symmetrically disubstituted acetylenes from acetylene gas.

The following is a typical example. Cuprous iodide (0.05 mmol) was added

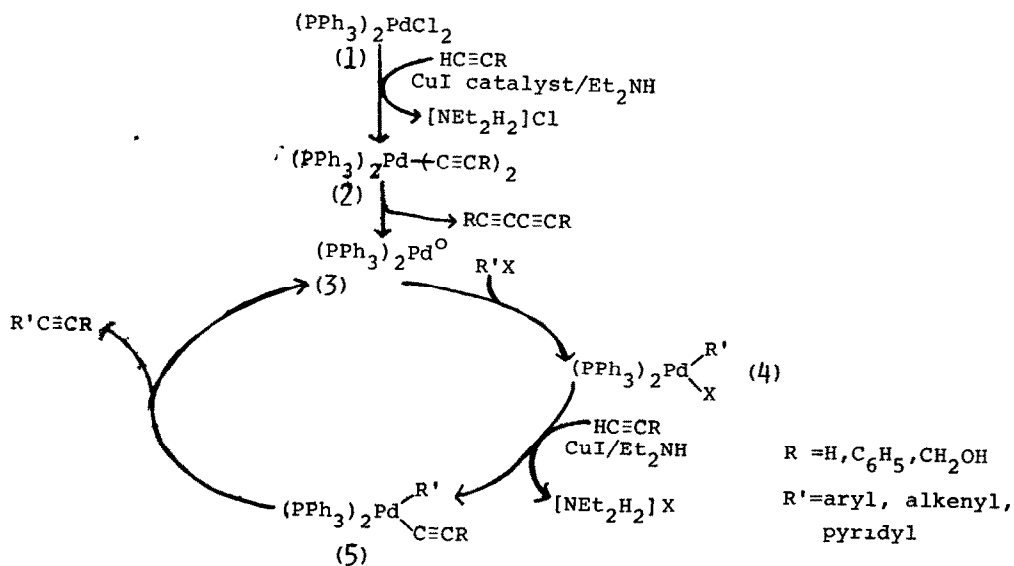


to a mixture of bis(triphenylphosphine)palladium dichloride (0.1 mmol) and diethylamine solution (60 ml) of iodobenzene (10 mmol) under a nitrogen atmosphere in a flask equipped with a gas inlet tube and a magnetic stirrer. A slow current of acetylene was passed through the reaction mixture for 6 hr. at room temperature. After removal of diethylamine under reduced pressure, water was added to the residue. The mixture was extracted with benzene. The concentrated

benzene-extract was passed over a short alumina column to remove the catalyst. The benzene-~~eluent~~ was evaporated to give crude diphenylacetylene, which was recrystallized from ethanol (85% yield). By the similar procedure, di(2-pyridyl)acetylene and 1,6-diphenylhexa-3-yn-1,5-diene were prepared in good yields from 2-bromopyridine and  $\beta$ -bromostyrene, respectively.

In general, the complete reactions can be achieved by stirring for 3~6 hr at room temperature after the addition of cuprous iodide to a mixture of terminal acetylenes and halides, such as bromopyridines or bromoolefins in the presence of a catalytic amount of bis(triphenylphosphine)palladium dichloride in diethylamine and the yields are generally very high. Representative results are summarized in Table 1. The ready availability of the catalyst and the reagents, the simplicity of the procedures, and the mildness of the reaction-conditions suggest that the reaction will be highly useful for the preparation of internal acetylenes from acetylene gas and terminal acetylenes in laboratories.

Although the detailed mechanism of the reaction is yet to be clarified, it seems likely that the substitution occurs through an initial formation of bis(triphenylphosphine)dialkynylpalladium(II) (2), which gives a catalytic species,



Scheme 1.

Table 1. Preparation of Acetylenes by  $(PPh_3)_2PdCl_2$ -CuI Catalyst in  $Et_2NH$  at Room Temperature

Halide (mmol)	Acetylene (mmol)	Reaction Time (hr)	Catalyst <sup>a)</sup> (mmol)	Product (% Yield <sup>b)</sup> )
iodobenzene (10)	acetylene	6	A (0.05) CuI (0.1)	diphenylacetylene (85)
iodobenzene (10)	phenylacetylene (10)	3	A (0.05) CuI (0.1)	diphenylacetylene (90)
iodobenzene (10)	propargyl-alcohol (10)	3	A (0.05) CuI (0.1)	3-phenylpropargyl-alcohol (80)
1,4-diodobenzene (5)	phenylacetylene (10)	3	A (0.05) CuI (0.1)	1,4-bis(phenylethynyl)-benzene (98)
vinylbromide (60)	phenylacetylene (40)	3	A (0.1) CuI (0.2)	4-phenylbut-1-en-3-yne (91)
vinylbromide (140)	propargyl-alcohol (100)	3	A (0.1) CuI (0.2)	penta-4-en-2-yn-1-ol (40)
E-2-bromostyrene (20)	acetylene	6	A (0.1) CuI (0.2)	1,6-diphenylhexa-3-yn-1,5-diene (95) *c)
E-2-bromostyrene (10)	phenylacetylene (10)	3	A (0.05) CuI (0.1)	E-1,4-diphenylbuta-1-en-3-yne (90)
E-2-bromostyrene (40)	propargyl-alcohol (40)	3	A (0.05) CuI (0.1)	5-phenylpenta-4-en-2-yn-1-ol (70)
1,1-diphenyl-2-bromoethylene (5)	phenylacetylene (5)	3	A (0.05) CuI (0.1)	1,1,4-triphenylbuta-1-en-3-yne (99) *d)
1-bromocyclopentene (30)	phenylacetylene (30)	3	A (0.05) CuI (0.1)	phenyl(1-cyclopentyl)-acetylene (95) *e)
1-bromocyclopentene (30)	propargyl-alcohol (30)	3	A (0.05) CuI (0.1)	3-(1-cyclopentyl)propargylalcohol (70) *f)
2-bromopyridine (20)	acetylene	6	A (0.1) CuI (0.2)	di(2-pyridyl)acetylene (60)
2-bromopyridine (40)	phenylacetylene	3	A (0.05) CuI (0.1)	phenylpyridylacetylene (99)
2-bromopyridine (30)	propargyl-alcohol (30)	3	A (0.1) CuI (0.2)	3-(2-pyridyl)propargylalcohol (27) *g)

\* All new compounds had correct chemical analyses and consistent spectral properties.

a) A :  $(PPh_3)_2PdCl_2$  b) Yields are isolated and purified products. c) m.p. 131-2°C

d) m.p. 106-7°C e) b.p. 90°C/1mmHg f) b.p. 83°C/3mmHg g) b.p. 125°C/3mmHg

bis(triphenylphosphine)palladium(0) (3), through a reductive elimination of 1,4-diphenylbutadiyne. Subsequent oxidative addition of aryl or vinyl halide to (3), followed by an alkynylation of the adduct (4), to give an aryl- or vinyl-alkynyl derivative of palladium (5), which easily regenerates the original bis(triphenylphosphine)palladium(0) (3) through the reductive elimination of the substitution products. The alkynylation of the starting catalyst (1) or an oxidative adduct (4) in the catalytic cycle in scheme 1 is catalyzed by cuprous iodide in the presence of diethylamine<sup>6</sup>).

A system of cuprous iodide and tetrakis(triphenylphosphine)palladium(0) or bis(diphenylphosphino)ethane-palladium dichloride can also catalyze the substitution in diethylamine. In either case, no catalytic substitution of acetylenes occurs at room temperature in the absence of cuprous iodide, indicating that the role of cuprous iodide is important to facilitate the substitution reaction.

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#### REFERENCES AND NOTES

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- 3) L. Cassar, *J. Organometal. Chem.* **93**, 253 (1975).
- 4) H. A. Dieck and F. R. Heck, *J. Organometal. Chem.* **93**, 259 (1975).
- 5) We wish to thank Dr. Y. Fujikura of Kao Soap Co., Ltd., Wakayama, Japan, for a gift of this compound.
- 6) A  $\sigma$ -alkynyl metal complex can be easily prepared by the reaction of an appropriate metal halide and a terminal acetylene in the presence of an equimolar amount of diethylamine and a catalytic amount of cuprous halide, e.g.  $(\text{PBu}_3)_2\text{PdCl}_2 + \text{HC}\equiv\text{CPh} \xrightarrow[\text{r.t. 30 min.}]{\text{CuI/Et}_2\text{NH}} \text{trans}-(\text{PBu}_3)_2\text{Pd}-(\text{C}\equiv\text{CPh})_2$ .