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A Facile Synthesis of Diynes

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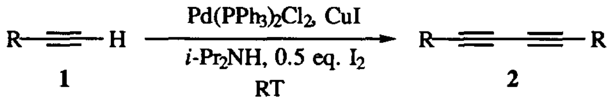
Abstract: *Terminal alkynes undergo self-coupling reactions in the presence of palladium bis(triphenyl phosphine) dichloride, copper(I) iodide, iodine and diisopropyl amine to give the corresponding diynes in good yields.* © 1997 Elsevier Science Ltd.

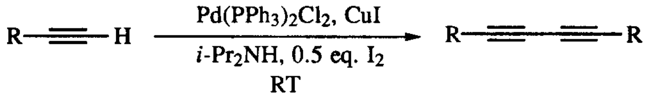
Diynes are important compounds in terms of the solid state properties of their homopolymers.[1] This series of compounds can be synthesized by (1) oxidative dimerization of terminal acetylenes,[2] (2) Pd(0)-Cu(I) catalyzed self-coupling of terminal alkynes in the presence of chloroacetone and benzene,[3] (3) Pd(0)-Cu(I) catalyzed cross-coupling reaction of terminal alkynyl halides with terminal alkynes,[4] (4) reaction of 1-alkynyl ethers with lithium reagents,[5] (5) reaction of aluminium acetylide complexes with cuprous bromide,[6] (6) reaction of lithium dialkyl diaryl borates with iodine,[7] and more recently (7) *via* dimerization of terminal acetylene and allyl bromide with Pd(0) catalysis under phase transfer conditions (only GC yields reported).[8]

Scheme 1



This communication describes a facile method for the synthesis of symmetrical conjugated diynes by the reaction of 1-alkynes with iodine in diisopropyl amine in the presence of catalytic amounts of $Pd(PPh_3)_2Cl_2$ and CuI, as described in **Scheme 1**. Our method has similarities to a related process reported by Rossi and coworkers. These workers reacted 1-alkynes with $Pd(PPh_3)_4$, CuI, Et_3N in benzene in the presence of chloroacetone. It is not clear what is the role of the haloacetone. However, under these conditions, arylacetylenes gave good to excellent yields of diaryldiynes, while aliphatic-1-alkynes afforded mixtures of 1,4-dialkyl-1,3-butadiynes (30 - 50%) and 3-alkyl-4-(1-alkynyl)-hexa-1,5-diyn-3-enes (28 - 50%). Our procedure gives excellent yields with both arylacetylenes and aliphatic-1-alkynes and no separation problem is encountered with the aliphatic acetylenes. We used $Pd(PPh_3)_2Cl_2$ instead of the more expensive and air sensitive $Pd(PPh_3)_4$ and diisopropyl amine instead of the more expensive triethyl amine.

Table 1. Pd(0)-Catalyzed Self-coupling Reaction of 1-Alkynes



Entry	R	reaction time (hr)	isolated yield [a]
1	Ph	2	88%[b]
2	n-C_4H_9	2	86%[c]
3	n-C_6H_{13}	2	84%[c]
4	n-C_7H_{15}	2	84%[c]
5	n-C_8H_{17}	2	88%
6	n-C_9H_{19}	2	64%[d]
7	n-C_9H_{19}	8	71%[d]
8	n-$C_{10}H_{21}$	2	65%[d]
9	n-$C_{10}H_{21}$	12	77%[d]

[a] All products gave satisfactory ^1H, $\{^1H\}^{13}C$ NMR and GC-MS data.

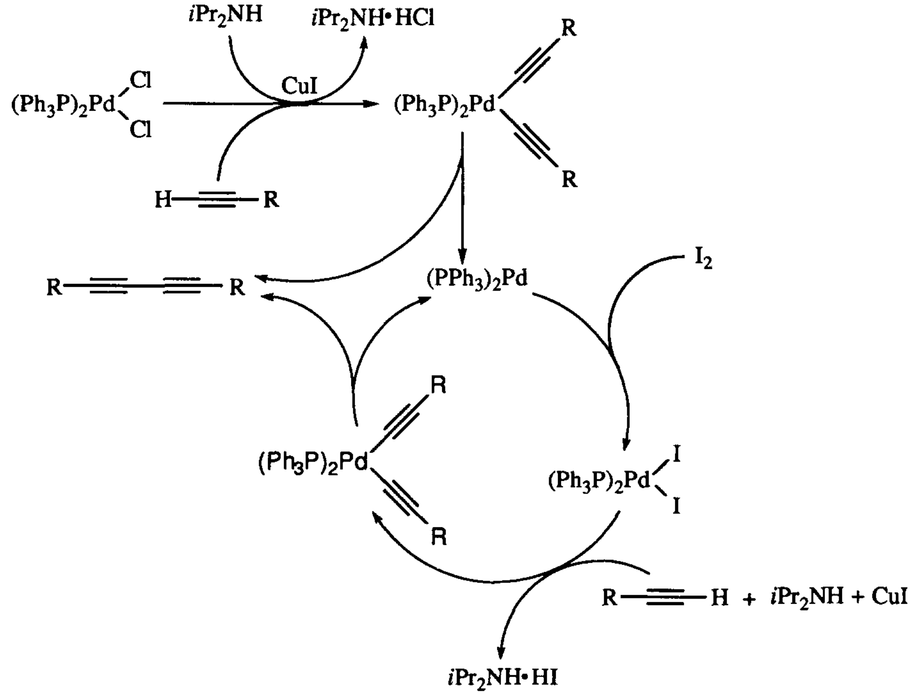
[b] mp: 85 - 6 °C (literature mp: 87 - 88 °C)[9].

[c] GLPC purity > 98%.

[d] Starting material was not completely consumed. Unreacted 1-alkyne was removed by distillation at *ca.* 80 °C / 0.1 mm Hg.

As illustrated in **Table 1**, good to excellent isolated yields of conjugated diynes could be obtained by treatment of 1-alkyne **1** with one half equivalent of iodine, $Pd(PPh_3)_2Cl_2$ and CuI in diisopropyl amine at room temperature. We have also found that in the absence of $Pd(PPh_3)_2Cl_2$ the reaction yielded a mixture containing 1,2-diiodostyrene (major), iodophenylacetylene and phenylacetylene. Without CuI, a similar mixture was obtained. However, without I_2 only 27% (RT / 2 hours) to 30% (RT / 12 hours) of **2** was isolated, although no by-product was detected. A typical reaction procedure is as follows: to a mixture of phenylacetylene (0.42 g, 98%, 4.00 mmol), $Pd(PPh_3)_2Cl_2$ (0.04 g, 0.05 mmol, 1.3 mol%), CuI (0.04 g, 0.21 mmol, 5 mol%), I_2 (0.51 g, 2.00 mmol, 0.5 eq.), diisopropyl amine (6 ml) was added. The mixture was stirred at room temperature for two hours. The reaction mixture was poured onto a silica gel column and washed with pentane. Removal of the solvent yielded 0.36 g (88%) white crystals, mp: 85 - 6^0C (literature mp: 87 - 88^0C)[9]. ^{1}H NMR ($CDCl_3$): 7.34 (m, 6 H), 7.52 (m, 4 H); {^{1}H}^{13}C NMR ($CDCl_3$): 132.49 (s), 129.19 (s), 128.43 (s), 121.79 (s), 81.55 (s), 73.93 (s); GC-MS (EI): 202 ($M^{+\cdot}$, 100), 174 (4.5), 150 (7.9), 101 (13.9).

Scheme 2



Coupling of vinyl iodides with terminal alkynes, CuI, amines and Pd(0) catalysis has been well documented.[10] It has been found that in many cases small amount of symmetrical diyene was always observed as the by-product. By scrutinizing the mechanism, we rationalized that the diynes were produced *via* a reductive-elimination from the *bis*(triphenylphosphine) dialkynylpalladium, which was derived from 1-alkyne and $Pd(PPh_3)_2Cl_2$ in the presence of CuI and amine. This reductive-elimination also generates the active palladium(0) species, $Pd(PPh_3)_2$. We chose the conditions described in **Table 1** and used I_2 to regenerate the Pd(II) catalyst from the Pd(0) formed in the catalytic cycle. Recurrent formation of *bis*(triphenylphosphine) dialkynylpalladium and subsequent reductive-elimination eventually convert all the 1-alkyne to the corresponding diyne. Consequently, we suggest that the formation of diynes in this work occurs *via* the mechanistic route described in **Scheme 2**.

Thus, we have described a simple, facile method for the high yield synthesis of symmetrical conjugated diynes *via* a one-pot reaction. The costs of the catalysts and reagents are moderate and the reactions can be carried out rapidly under mild conditions.

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