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PALLADIUM-CATALYZED REACTIONS OF 2-ALKYNYL CARBONATES WITH TERMINAL ACETYLENES: A NEW SYNTHETIC METHOD FOR 1,2-DIEN-4-YNES

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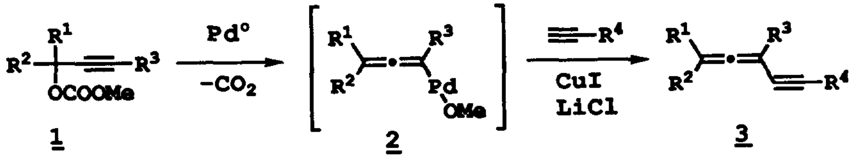
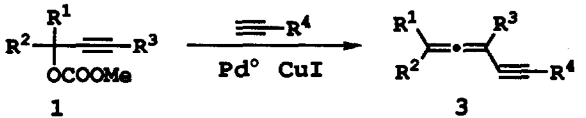
Summary; The reaction of substituted 2-alkynyl carbonates with terminal acetylenes in the presence of palladium-phosphine complex and copper(I) iodide proceeds to give 1,2-dien-4-ynes.

In our continuing studies on the palladium catalyzed transformations of 2-alkynyl carbonates **1**, which proceed by the formation of allenyl palladium complex **2** as an intermediate,[1] we have attempted their reaction with terminal acetylenes, expecting the formation of 1,2-dien-4-ynes **3** (allenyl acetylenes). Allenyl acetylenes are present in naturally occurring compounds produced by some microorganisms,[2] and their simple synthetic method is highly desirable. Also this study is a part of our synthetic studies toward cumulative ene-yne-allene systems which are attracting attention for their DNA cleavage action.[3] The known synthetic method is the palladium-catalyzed reaction of allenyl bromides with acetylenes or zinc acetylides.[4] As expected, we observed the formation of 1,2-dien-4-ynes **3** as shown below, and the results are presented in this paper.

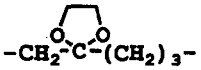
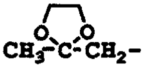
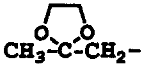
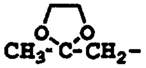
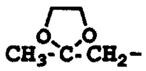


The reaction of alkenyl or aryl halides with terminal acetylenes catalyzed by palladium complex and CuI is known.[5] Thus we attempted reaction of 2-alkynyl carbonates with terminal acetylenes in the presence of a palladium phosphine complex and CuI without success. Then we tried the reaction in the presence of an excess of LiCl and observed a successful coupling reaction with acetylenes. A typical example is shown below.(Entry 9 in the Table) In THF (3 ml) were added CuI (20.2 mg, 0.106 mmol), LiCl (89.9 mg, 2.12 mmol), diethylamine (2.19 ml, 21.2 mmol), and $Pd(PPh_3)_4$ (62.0 mg, 0.053 mmol). Then a mixture of the carbonate (365.0 mg, 1.06 mmol) and tetrahydropyranyl ether of propargyl alcohol (148.4 mg, 1.06 mmol) in THF (2 ml) was added. After being stirred at a room temperature for 30 min, the reaction mixture was diluted with hexane (30 ml). After the usual work-up, the allenyl acetylene was isolated by column chromatography as a pale yellow oil (306 mg, 71%) as an unseparable mixture of four diastereomers. The structure was fully supported by its ^1H NMR(400 MHz) and ^{13}C NMR(100 MHz). Anal. Calcd. for $C_{23}H_{34}O_6$: C, 67.96; H, 8.43. Found: C, 67.75; H, 8.51.

Results of the reactions of several 2-alkynyl carbonates **1** with terminal acetylenes are shown in the table. The smooth reaction was observed with substituted 2-alkynyl carbonates. Although the reactants disappeared rapidly, no stable coupling product could be isolated when either R^1 or R^2 is hydrogen.



1 3

Entry	R^1	R^2	R^3	R^4	Yield(%)[a]
1	$-(CH_2)_5-$		n-Bu	CH_2OH	31
2			n-Bu	$CH_2OSiMe_2{}^tBu$	60
3	n-C_6H_{13}	CH_3	H	CH_2OTHP	65[b]
4	n-C_6H_{13}	CH_3	n-Bu	CH_2OTHP	69
5	n-C_6H_{13}	CH_3	CH_2OTHP	CH_2OTHP	60
6	n-C_6H_{13}	CH_3	CH_2OTHP	n-Bu	42
7		CH_3	n-Bu	CH_2OTHP	83
8		CH_3	n-Bu	CH_2OH	62
9		CH_3	CH_2OTHP	CH_2OTHP	71
10		CH_3	CH_2OTHP	CH_2OH	66

a) Carbonate 1(0.5 mmol), acetylene(0.5 mmol), CuI(0.05 mmol), Et_2NH (10.0 mmol), LiCl(1.0 mmol), $Pd(PPh_3)_4$(5 mol%) were used. The reaction was carried out at room temperature for 0.5 h.

b) Carbonate(1.0 mmol), acetylene(2.0 mmol), CuI(1.0 mmol), Et_3N (1.0 mmol), LiCl(10.0 mmol), $Pd(OAc)_2$(5 mol%), and tri-O-tolylphosphine(20 mol%) were used. The reaction was carried out at 0°C for 1h.

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