A Novel Diarylation Reaction of Alkynes by Using Aryltributylstannane in the Presence of Palladium Catalyst

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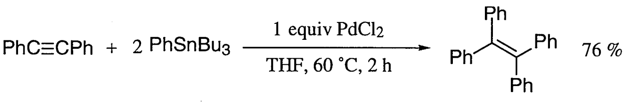
Some alkynes were diarylated by aryltributylstannane **2** in the presence of palladium salt in moderate to good yield with high stereoselectivity. The reaction was catalytic in palladium using copper(II) chloride dihydrate as a reoxidant.

Stereoselective synthesis of tetrasubstituted alkenes by dialkylation of alkynes has great difficulty in overcoming their steric restrictions. Using alkynes as a starting material, tetrasubstituted alkene was synthesized so far by the palladium or nickel-catalyzed ternary coupling reaction composed of ethynyltin compound, organic halide and alkyne[1] or by the palladium-catalyzed double silylation reaction using disilanes.[2] We have recently reported the palladium-catalyzed ternary coupling reaction of organotin compounds with organic halide involving insertion of alkene,[3] however, the use of alkyne instead of alkene significantly decreased the yield of ternary coupling product. During our study on the ternary coupling reaction composed of phenyltributyltin, *p*-bromotoluene and diphenylacetylene, we found that tetraphenylethylene was formed along with the desired *p*-tolyltriphenylethylene. The yield of tetraphenylethylene was greatly improved when the reaction of phenyltributyltin and diphenylacetylene was mediated by a stoichiometric amount of palladium(II) chloride in the absence of halide. Furthermore the reaction could be done catalytically with copper(II) chloride as a reoxidant.



To our knowledge, there is only one report which is concerned with palladium(II) mediated diphenylation of an alkyne with organometallic reagent.[4] The reaction, that used Grignard reagent as an organometallic, was stoichiometric in palladium(II) and the addition was not stereoselective. Therefore we now wish to disclose our results on this newly found catalytic and stereoselective diarylation reaction. We report herein that tetraphenylethylene was obtained in good yield by the reaction of diphenylacetylene with phenyltributylstannane in the presence of a catalytic amount of palladium(II) salt using copper(II) chloride as a reoxidant.

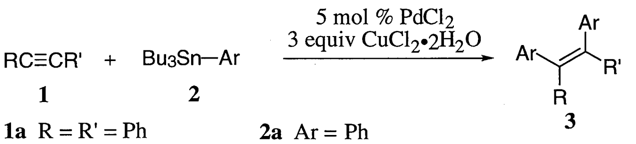
Various palladium(II) catalysts were effective using copper(II) chloride as a reoxidant (Table 1). The reaction was sensitive to solvent. Good results were obtained in THF and dioxane, whereas the yield of diphenylated product was markedly diminished in benzene, HMPA or chloroform. Manganese(IV) oxide and *p*-benzoquinone(BQ) in acetic acid was tolerable as the reoxidant, indicating that transmetallation from tin to copper seems not to be essential in this reaction.[5]

Table 1. Palladium-catalyzed reaction of **1a** with **2a**

Pd cat.	Reoxidant equiv	Solvent	Temp / °C	Time / h	Isolated Yield/ %
$PdCl_2$	$CuCl_2$ 3	THF	rt	2	65
$PdCl_2$	$CuCl_2$ 3	Et_2O	rt	3	59
$PdCl_2$	$CuCl_2$ 3	Dioxane	rt	2	85
$Pd(acac)_2$	$CuCl_2$ 3	THF	rt	2	67
$Pd(OAc)_2$	$CuCl_2$ 3	THF	rt	2	60
$Pd(dba)_2$	$CuCl_2$ 3	THF	rt	2	65
$Pd(OAc)_2$	MnO_2 25	HOAc	rt	5	62
$Pd(OAc)_2$	BQ 1.5	HOAc	60	2	38

We next explored other effective alkynes (Table 2). Terminal alkynes did not afford any addition product at all, regardless of substituents. Internal alkynes possessing phenyl, methoxycarbonyl or phenylthio[6] groups on both alkynyl carbons and any combination of the these were tolerable. Substitution either by alkyl group or silyl group resulted in no addition at all. X-ray structural analysis of the product obtained by the reaction of phenyltributyltin with dimethyl acetylenedicarboxylate suggested that the insertion underwent perfectly in *cis*-fashion, providing dimethyl (*Z*)-2,3-diphenyl-2-butenedioate as a single isomer.[7] Use of other organostannanes such as ethynylic, vinylic, allylic or benzylic derivatives resulted in their homo-coupling. No addition to alkyne was observed. *o*-Tolyl and 1-naphthylstannane gave low yields, probably due to steric hindrance.

Tetramethylstannane **4** reacted in a different manner from those described above.[8] The reaction with diphenylacetylene gave



1a R = R' = Ph
1b R = R' = CO_2Me
1c R = Ph, R' = CO_2Me
1d R = Ph, R' = PhS

2a Ar = Ph
2b p-MeC_6H_4
2c p-ClC_6H_4
2d o-MeC_6H_4
2e 1-naphthyl
2f 2-pyridyl
2g 2-furyl

Table 2. Palladium-catalyzed reaction of various alkynes with stannanes

Alkyne	Stannane	Solvent	Temp / °C	Time / h	Yield / %
1b	**2a**	THF	rt	2	66
1c	**2a**	Dioxane	60	2	66
1d	**2a**	Dioxane	60	2	59
1a	**2b**	Ether	rt	20	88
1a	**2c**	Dioxane	rt	22	48
1a	**2d**	THF	rt	2	trace
1a	**2e**	THF	rt	2	19
1a	**2f**	THF	rt	2	0
1a	**2g**	THF	rt	2	0

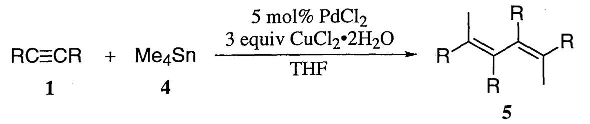


Table 3. Palladium-catalyzed reaction of **1** with tetramethylstannanes

Alkyne	Temp / °C	Time / h	Yield / %
1a	60	36	79
1b	rt	12	79

(Z,Z)-2,3,4,5-tetraphenyl-2,4-hexadiene in high yield as a single isomer (Table 3). (Z)-2,3-Diphenyl-2-butene was not detected at all. Though the reaction mechanism is not clear, we assume that alkenylpalladium species that is formed by *cis*-carbopalladation is the key intermediate and the following transmetallation from tin to palladium and insertion of the second diphenylacetylene are in competition. In the case of phenylstannane, the former was predominant, while the latter was in the methyl case. The change of the reaction course could be attributed to the slow transmetallation of the methyl group from methyltin species to palladium. The reaction of tetramethylstannane with dimethyl acetylenedicarboxylate under a mild condition gave tetramethyl (Z,Z)-2,4-hexadiene-2,3,4,5-tetracarboxylate again in high yield.

In summary, we found that palladium(II) catalyzed reaction of phenyltributylstannane and some internal alkynes affords tetrasubstituted alkenes stereoselectively. This reaction seems to be a convenient method to prepare *cis*-1,2-diphenylalkenes compared with using phenyl Grignard reagent. Use of tetramethylstannane instead of arylstannane dramatically altered the reaction to give dimerization-dimethylation product, stereoselectively.

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7 Colorless transparent crystals were grown from a dichloromethane/hexane mixture; $C_{18}H_{16}O_4$, M = 296.32, monoclinic, space group $P2_1/n$, a = 8.8515(5) Å, b = 8.6991(7) Å, c = 19.6374(6) Å, β = 94.143(4)°, V = 1508.1(1) Å^3, and Z = 4. The structure was solved by the direct method (SAPI91) and the final R factor is 0.048 (1394 reflections).

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