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Palladium (0) Catalyzed Hydrostannylation of Alkynes. Stereospecific Syn Addition of Tributyltin Hydride

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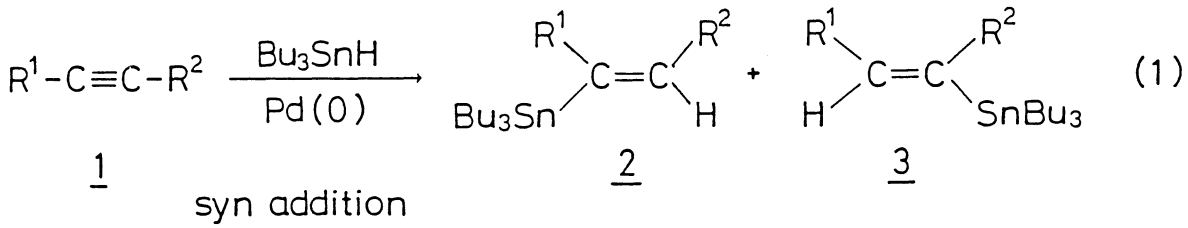
Tetrakis(triphenylphosphine)palladium(0) catalyzes the hydrostannylation of alkynes to give vinylstannanes in excellent yields. This reaction proceeds in syn manner.

Vinylstannane is one of the most useful reagents as both vinyl anion equivalent and as the precursor of vinyllithium[1] and vinylcuprate.[2] The most popular method for synthesizing vinylstannanes involves the hydrostannylation of alkynes. The hydrostannylation takes place readily in the presence of a catalytic amount of radical initiator such as azobis(isobutyronitrile) (AIBN). However, this method often requires long reaction time and high temperature, and the yield is sometimes low.

Recently, Utimoto and coworkers have reported that triethylborane, which acts as radical initiator, catalyzes the hydrostannylation of alkynes, under low temperature.[3] However, although addition of triphenyltin hydride to the alkynes proceed in good yield, that of tributyltin hydride proceeds in lower yield and requires longer reaction time.



1 2 3 (1)

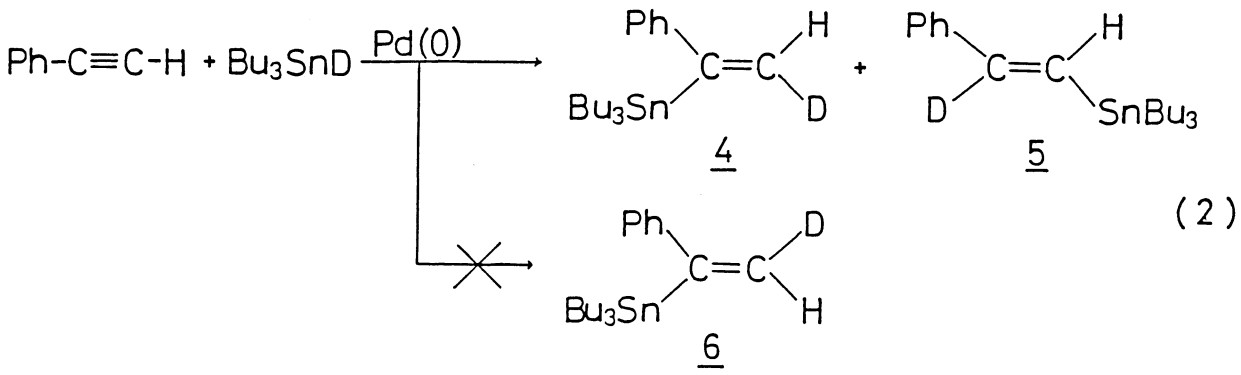
Now, we wish to report that Pd(0) compounds promoted syn addition of tributyltin hydride to alkynes. Although transition metal catalyzed hydrostannylation of alkynes was already reported, the reported methods are not always satisfactory in stereoselectivity and chemical yield.[4] When 2 mol% of $Pd(Ph_3P)_4$ was used as catalyst, the reaction proceeded smoothly and completed within 30 minutes at room temperature (Eq. 1). Results were shown in Table 1. Not only the hydrostannylation of terminal alkynes, but that of internal alkynes also proceeded smoothly in excellent yields (entries 10-14). The alkynes, which have the various kind of reactive functional groups, also reacted chemoselectively with tributyltin hydride to give vinylstannanes in excellent yields. For example, the alkynes which have hydroxyl group or carbon-carbon double bond are hydrostannylated without affecting those functional groups. And 1,4-bis(phenylthio)-2-butyne, which is expected to eliminate phenylthio group during the course of the free radical method, do not eliminate it in our method (entry 13).

Not only $Pd(Ph_3P)_4$, but $Pd(n\text{-}Bu_3P)_4$ was also effective for hydrostannylation of alkynes. However, it was not so effective as $Pd(Ph_3P)_4$. It requires longer reaction time (0.5-1 hour), and the yields of vinylstannanes were somewhat lower. On the other hand, $Pd(Ph_2PCH_2CH_2PPh_2)$ was not effective.

While the hydrostannylation of terminal alkyne in the presence of radical initiator gave 1-(tributylstannyl)-1-alkene predominantly, our method gave considerable amount of 2-(tributylstannyl)-1-alkene, and often gave it predominantly. Especially, the hydrostannylation of ethyl propynoate gave ethyl 2-(tributylstannyl)propenoate exclusively; ethyl 3-(tributylstannyl)propenoate was not obtained (entry 9). However, in the other cases, the regio selectivity was lower.

On the other hand, the regioselectivity of some internal alkynes were relatively higher than that of terminal alkynes (entries 10, 11). Further study about the factors which control the regioselectivity is now in progress.

Palladium (0) catalyzed hydrostannylation of alkyne is highly stereospecific.[5] When phenylacetylene was treated with tributyltin deuteride in the presence of $Pd(Ph_3P)_4$, deuterostannylated products 4 and 5 were obtained. However, anti adduct 6 was not obtained at all (Eq. 2). This result supports the syn addition process. According to Nozaki and coworkers' report, resemble results were observed in the palladium catalyzed stannylmetalation of alkynes.[6]



(2)

Table 1. Pd(0) Catalyzed Hydrostannylation of Alkynes

Entry	R^1	R^2	Catalyst[a]	Yield of 2/%[b]	Yield of 3/%[b]
1	Ph-	H-	A	48[c]	48[c]
2	$HOCH_2$-	H-	A	58	37
3			B	46	34
4	$PhCH_2OCH_2$-	H-	A	62	33
5			B	44	43
6	$HOCH_2CH_2$-	H-	A	44	50
7	$CH_3CH(OH)$-	H-	A	28	66
8	$C_2H_5OC(=O)$-	H-	A	83	0
9	$(CH_3)_2C=CHCH_2OCH_2$-	H-	A	57	36
10	Ph-	CH_3-	A	90	trace
11	$HOCH_2$-	CH_3-	A	74	14
12	$AcOCH_2$-	$AcOCH_2$-	A	93	
13	$PhSCH_2$-	$PhSCH_2$-	A	97	
14	$PhCH_2OCH_2$-	$PhCH_2OCH_2$-	A	95	

a) A: $Pd(Ph_3P)_4$ (2 mol%), B: $Pd(n\text{-}Bu_3P)_4$ (2 mol%). b) Isolated yields.
c) Isolated as a mixture of 2 and 3. The ratio of isomers was determined by GLC.

Hydrostannylation of 1,4-diacetoxy-2-butyne (entry 12) was shown as follows as typical procedure: To a stirring solution of 1,4-diacetoxy-2-butyne (0.51 g, 3.0 mmol) and $Pd(Ph_3P)_4$ (0.069 g, 0.06 mmol) in benzene (10 ml) at room temperture was added Bu_3SnH (1.13 g, 3.9 mmol) in benzene (5 ml). The mixture was stood at room temperature for 10 minutes. Solvent was removed under reduced pressure. The crude material was purified by flash chromatography on silica gel (dichloromethane) to give (*E*)-1,4-diacetoxy-2-(tributylstannyl)-2-butene (1.29 g, 2.80 mmol).

References

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3) K. Nozaki, K. Oshima, and K. Utimoto, J. Am. Chem. Soc., 109, 2547 (1987).

4) Y. Ichinose, H. Oda, K. Oshima, and K. Utimoto, Bull. Chem. Soc. Jpn., 60, 3468, (1987); K. Kikukawa, H. Umekawa, F. Wada, and T. Matsuda, Chem. Lett., 1988, 881.

5) C. Nativi and M. Taddei, J. Org. Chem., 53, 820 (1988); The ^{1}H-NMR spectral data of 2-(tributylstannyl)-2-butene-1-ol (entry11, 2) was shown in this paper. The ^{1}H-NMR spectral data of other hydrostannylated propargyl alcohols in this paper also support the structure of vinylstannanes of entries 10-14.

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