

Regioselective Hydrostannation of Terminal Acetylenes
under Transition Metal Catalysis

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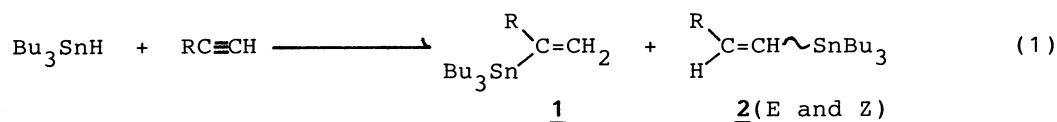
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Rhodium complexes (RhClL_3 , $\text{RhCl}(\text{CO})\text{L}_2$, $[\text{RhCl}(\text{COD})]_2$; $\text{L}=\text{PPh}_3$) catalyze hydrostannation of terminal acetylenes ($\text{RC}\equiv\text{CH}$; $\text{R}=\text{Ph}$, Me_3Si , $\text{R}^1\text{OC}(\text{R}^2)(\text{R}^3)$, and $\text{R}^1\text{OCH}_2\text{CH}_2$; $\text{R}^1=\text{THP}$, OAc ; $\text{R}^1, \text{R}^2=\text{H}$, Me) with Bu_3SnH to produce $\text{R}(\text{Bu}_3\text{Sn})\text{C}=\text{CH}_2$ selectively. Other transition metal complexes $[\text{MCl}_2\text{L}_2 (\text{M}=\text{Ni}, \text{Pd}, \text{Pt}, \text{Co})]$ are also active for the hydrostannation, but with less selectivity.

The hydrostannation of acetylenes producing alkenylstannanes is of particular synthetic interest, since the alkenyl group of such products can be transferred from tin to various other atoms including Li.^{1,2)} The hydrostannation takes place considerably more readily than the corresponding hydrosilation, and is considered to follow a polar or a free radical way depending on substituents and conditions.³⁻⁵⁾ However, few regio- and stereoselective hydrostannations have been known. The applicability of various catalysts, such as those used in the hydrosilation reaction, has not been well investigated. Here we report the transition metal-catalyzed regioselective hydrostannation of terminal acetylenes.

The terminal acetylenes used here spontaneously reacted with Bu_3SnH at 60 °C and Bu_3Sn group generally added to terminal acetylenic carbon to give 2 (Eq. 1 and Table 1). Radical initiator, AIBN, showed little effect.⁶⁾



An addition of 1 mol% of a rhodium, a nickel, a palladium or a platinum complex to the reaction mixtures drastically accelerated the rate and completed the hydrostannation within a half hour even at 0 °C, and Bu_3Sn group added considerably to internal acetylenic carbon to give 1. Especially rhodium complexes not only accelerated the rate but also produced 1 selectively. Sometimes violent exothermic reactions were observed. Toluene or THF was examined to control the reaction temperature, but the regio- and stereoselectivity could not be improved. Since palladium complexes easily react with trialkylstannanes to give

Table 1. Transition Metal-Catalyzed Hydrostannation of Acetylenes(Eq. 1)^{a)}

R in RC≡CH	Catalyst	Temp	Time	Yields ^{b)}	Products(% ratio) ^{c)}	
		°C	h	%	<u>1</u>	<u>2(E/Z)</u>
Ph	-	60	11	71	0	100(48/52)
Ph	AIBN	60	20	81	0	100(67/33)
Ph	RhCl(PPh ₃) ₃	r.t.	0.5	86	88	12(100/0)
Ph	RhCl(CO)(PPh ₃) ₂	0	0.5	99	78	22(91/9)
Ph	[RhCl(COD)] ₂	0	0.5	66	81	19(32/68)
Pn	[Rh(COD)(PPh ₃) ₂] ⁺ PF ₆ ⁻	0	2 ^{d)}	70	80	20(55/45)
Ph	NiCl ₂ (PPh ₃) ₂	r.t.	0.2	80	45	55(91/9)
Ph	PdCl ₂ (PPh ₃) ₂	0	0.5	88 ^{e)}	43	51(100/0)
Ph	PtCl ₂ (PPh ₃) ₂	r.t.	0.2	73	34	66(82/18)
Ph	CoCl ₂ (PPh ₃) ₂	0	4	40	43	57(84/16)
Ph	RuCl ₂ (PPh ₃) ₄	r.t.	68	78	11	89(47/53)
CH ₃ OCH ₂	-	r.t.	0.5	50	16	84(98/2)
CH ₃ OCH ₂	RhCl(CO)(PPh ₃) ₂	0	0.5	90	49	51(84/16)
CH ₃ OCH ₂	[Rh(COD)(PPh ₃) ₂] ⁺ PF ₆ ⁻	0		no reaction ^{f)}		
THPOCH ₂	-	60	44	98	53	47(100/0)
THPOCH ₂	RhCl(PPh ₃) ₃	0	0.5	68	88	12(100/0)
THPOCH ₂	RhCl(CO)(PPh ₃) ₂	0	0.5	72	94	6(100/0)
THPOCH ₂	NiCl ₂ (PPh ₃) ₂	0	0.5	92	88	12(100/0)
THPOCH(Me)	-	60	10	64	0	100(64/36)
THPOCH(Me)	RhCl(CO)(PPh ₃) ₂	r.t.	2	70	90	10(100/0)
THPOC(Me) ₂	-	60	46	75	t	>99(100/0)
THPOC(Me) ₂	RhCl(CO)(PPh ₃) ₂	r.t.	3	69	76	24(>99/t)
THPOCH ₂ CH ₂	-	60	5	77	5	95(>99/t)
THPOCH ₂ CH ₂	RhCl(CO)(PPh ₃) ₂	r.t.	2	82	72	28(>99/t)
AcOCH ₂	-	60	4	93	t	>99(>99/t)
AcOCH ₂	RhCl(CO)(PPh ₃) ₂	r.t.	0.5	71	73	27(>99/t)
AcOCH(Me)	-	60	19	92	t	>99(84/16)
AcOCH(Me)	RhCl(CO)(PPh ₃) ₂	r.t.	19	60	74	26(>99/t)
AcOC(Me) ₂	-	60	24	96	t	>99(39/61)
AcOC(Me) ₂	[RhCl(COD)] ₂	r.t.	4	60	76	24(>99/t)
AcOCH ₂ CH ₂	-	60	20	81	t	>99(>99/t)
AcOCH ₂ CH ₂	RhCl(CO)(PPh ₃) ₂	0	20	69	65	35(>99/t)
Me ₃ Si	-	r.t.	2	76	0	100(100/0)
Me ₃ Si	RhCl(CO)(PPh ₃) ₂	0	6	91	76	24(100/0)

a) The reactions were carried out with 1 mol% of a catalyst and 5-10% excess of a RC CH under nitrogen. The consumption of Bu₃SnH was monitored by GLC.

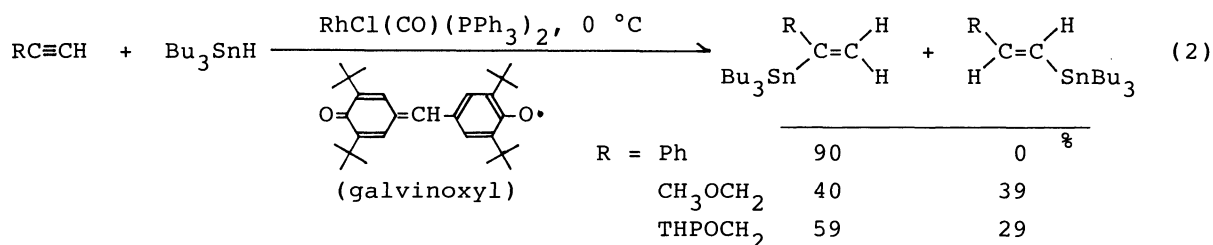
b) Isolated yields by short pass distillation based on Bu₃SnH. c) Determined by GC. t; trace d) After 1 day 25% of Bu₃SnH was still retained.

e) Bu₃SnSnBu₃ (6%) was contaminated. f) Bu₃SnH was recovered.

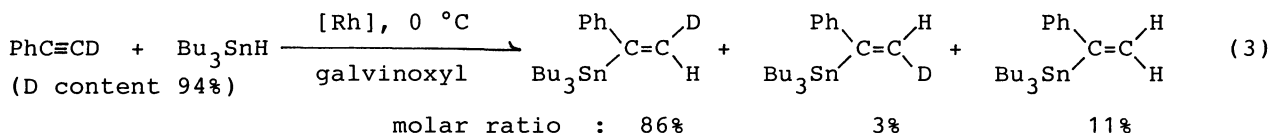
distannanes,⁷⁾ the palladium complexes should be mixed with acetylenes before the addition of Bu_3SnH . It is still difficult to obtain reproducible results with the palladium complexes. In the hydrostannation of acetylenes with Ph_3SnH , the palladium catalysts were successfully used by K. Utimoto and coworkers, although the regiochemistry was considerably different from that of present hydrostannation.⁸⁾ The rhodium complexes, however, should be mixed with Bu_3SnH before the addition of acetylenes to obtain reproducible results.⁹⁾ Moderate and small effects were observed with cobalt and ruthenium complexes, respectively.

Interestingly the rhodium complexes involving Rh-Cl bond caused violent exothermic reactions and completely consumed Bu_3SnH within a few minutes. Cationic rhodium complex, $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]^+\text{PF}_6^-$, however, only moderately catalyzed the hydrostannation of phenylacetylene and was inactivated after 2 h when 75% of Bu_3SnH was consumed. Furthermore the cationic complex exhibited no catalytic activity in the reaction with $\text{CH}_3\text{OCH}_2\text{C}\equiv\text{CH}$.

A combination of galvinoxyl (radical inhibitor) and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ in the hydrostannation of phenylacetylene completely suppressed the formation of 2 (R=Ph) and produced 1 (R=Ph) in an excellent yield. The radical inhibitor, however, had little effect on the regiochemistry of propargyl ethers but suppressed the formation of (Z)-2 (R= CH_3OCH_2) (Eq. 2). The formation of 2 (R=Ph) can be attributed



to a spontaneous free radical pathway. A. J. Leusink and coworkers have disclosed the trans-addition of Sn-H to C-C triple bond in either a free radical or a polar (nucleophilic) hydrostannation, i.e., (Z)-2 should be kinetic products in the spontaneous hydrostannation.^{4,5)} Therefore, the formation of (E)-2 of propargyl ethers may come from the transition metal-catalyzed reactions, although a polar pathway can not be excluded. The rhodium catalyst system proved to give (E)- $\text{Ph}(\text{Bu}_3\text{Sn})\text{C}=\text{CHD}$ stereoselectively in the reaction of $\text{PhC}\equiv\text{CD}$ with Bu_3SnH (eq. 3).¹⁰⁾



This result clearly showed the cis-addition of Sn-H in the present transition metal-catalyzed hydrostannation. The cis-stereochemistry is commonly observed in the transition metal-catalyzed hydrosilation reaction.^{11, 12)}

Although the mechanism of present hydrostannation may not so different from that of transition metal-catalyzed hydrosilation, there is no clear-cut explana-

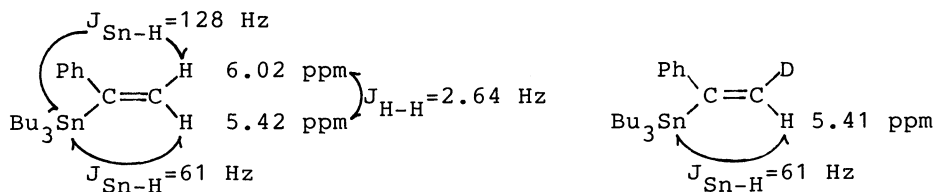
tion for the present unusual regiochemistry.

H. Nozaki and coworkers reported an excellent procedure for regio- and stereoselective preparation of alkenylstannanes through a stannylmetallation of C-C triple bond.¹³⁾ The present hydrostannation provides a simple method for the preparation of $R(R'_3Sn)C=CH_2$ with respect to starting materials and procedure, although the stereoselective preparation of $RCH=CHSnR'_3$ is still problem.

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- 9) In the absence of Bu_3SnH , the rhodium complexes changed terminal acetylenes to polymeric compounds.
- 10) The isomer ratio was determined by NMR spectra with the following assignment (see Ref. 3).



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