Tetrahedron Letters,Vol.25,No.20,pp 2151-2154,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

REGIOSELECTIVE STANNYLMETALATION OF ACETYLENES IN THE PRESENCE OF TRANSITION-METAL CATALYST

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Abstract: The reaction of terminal acetylenes with $Bu_3SnMgMe$, $Bu_3SnAlEt_2$, or $(Bu_3Sn)_2Zn$ in the presence of various transition-metal catalysts provides vinylstannanes in good yields. Whereas copper catalyzed stannylmagnesation of 4-benzyloxy-1-butyne gives (E)-4-benzyloxy-1-tributylstannyl-1-butene exclusively, palladium catalyzed stannylzincation affords 4-benzyloxy-2-tributylstannyl-1-butene preferentially.

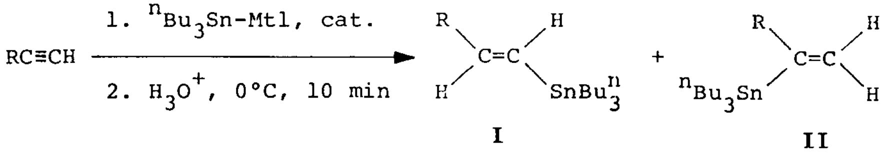
The reaction of the organometallic compounds prepared from $PhMe_2SiLi$ and MeMgI or Et_2AlCl with an acetylenic linkage affords simple and general access to the cis-addition products of the component atoms. The regio- and stereochemistry heavily depend on the nature of the transition-metal catalysts and the reaction is useful in synthetic work.[1] Here we wish to report that $Bu_3SnMgMe$, $Bu_3SnAlEt_2$, or $(Bu_3Sn)_2Zn$ reacts with terminal acetylenes to give vinylstannanes under good control of the regio- and stereoselectivity.[2,3]

An ethereal solution of methylmagnesium iodide (1.0 M, 3.0 ml, 3.0 mmol) was added to a THF solution of tributylstannyllithium[4], prepared from $SnCl_2$ (0.58 g, 3.0 mmol) and butyllithium (1.5 M, 6.0 ml, 9.0 mmol) at 0°C under argon atmosphere. After stirring for 15 min, CuCN (4 mg, 5 mol%) and 4-benzyloxy-1-butyne (0.16 g, 1.0 mmol) in THF (5 ml) was added and the whole was stirred for 30 min at 0°C. Aqueous workup and alumina column chromatography gave 4-benzyloxy-1-tributylstannyl-1-butene[5] (0.38 g, 88% yield) as a single product (Table 1, entry 2).

Many combinations of Bu_3SnMtl-transition-metal catalyst were examined. Whereas $Bu_3SnAlEt_2$-CuCN system provided a mixture of 1-tributylstannyl-1-alkene (I) and its regio isomer (II) in an 81:19 ratio (entry 4), $(Bu_3Sn)_2Zn$-$Pd(PPh_3)_4$ gave II predominantly (entry 6).

The reaction of $Bu_3SnMgMe$-CuCN with internal acetylene such as 5-benzyloxy-2-pentyne gave no addition product and the starting acetylene compound was recovered unchanged. As shown in Scheme 1, stannylmetalation proceeds in cis-fashion. Treatment of phenylacetylene with $Bu_3SnAlEt_2$ in the presence of CuCN gave isomeric two products which were separated by preparative GLPC (Silicone OV 17, 2 m, 200°C). The product III ($\underline{R}_t$ = 4 min) showed ^{1}H-NMR ($CDCl_3$) signals at δ 5.43 (d, $\underline{J}$ = 2.7 Hz, H_b), 6.03 (d, $\underline{J}$ =

Table 1. Transition-metal catalyzed stannylmetalation[a)]

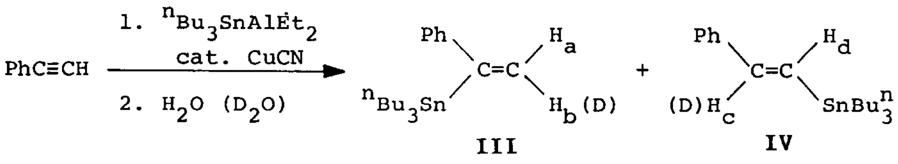


Entry	Substrate R =	Reagent	Catalyst	Yield[b)] (%)	Ratio[c)] of I/II I	II
1	$PhCH_2OCH_2CH_2$-	$(^{n}Bu_3Sn)_2CuCN$[d)]		75	36	64
2		$^{n}Bu_3SnMgMe$[e)]	CuCN	88	100	0
3		$^{n}Bu_3SnMgMe$	$CuBr \cdot SMe_2$	23	34	66
4		$^{n}Bu_3SnAlEt_2$[e)]	CuCN	86	81	19
5		$(^{n}Bu_3Sn)_2Zn$[f)]	CuCN	63	26	74
6		$(^{n}Bu_3Sn)_2Zn$	$Pd(PPh_3)_4$	81	14	86
7	Ph-	$^{n}Bu_3SnMgMe$	CuCN	89[g)]	>95	< 5
8		$^{n}Bu_3SnAlEt_2$	CuCN	88[g)]	79	21
9		$(^{n}Bu_3Sn)_2Zn$	$Pd(PPh_3)_4$	93[g)]	60	40
10		$(^{n}Bu_3Sn)_2Zn$	$PdCl_2(PPh_3)_2$	89[g)]	>95	< 5
11	$^{n}C_{10}H_{21}$-	$^{n}Bu_3SnMgMe$	CuCN	70[h)]	70	30
12		$^{n}Bu_3SnAlEt_2$	CuCN	87[h)]	38	62
13		$(^{n}Bu_3Sn)_2Zn$	$Pd(PPh_3)_4$	70[h)]	< 5	>95

a) Three mol of $^{n}Bu_3Sn$-Mtl reagent, one mol of acetylene compound, and 5mol% of catalyst were employed. b) Isolated yield unless otherwise noted. c) The ratios were determined by GLPC and ^1H-NMR spectra. d) A reagent was produced by mixing the stannyllithium with CuCN in a 2:1 ratio (see ref 2). e) Prepared from the stannyllithium and MeMgI (or Et_2AlCl) in a 1:1 ratio. f)Prepared from the stannyllithium and $ZnBr_2$ in a 2:1 ratio. g)GLPC yield using n-hexacosane as an internal standard. h) ^1H-NMR yield using dimethyl sulfoxide as an internal standard.

2.7 Hz, H_a). The other isomer **IV** having longer retention time ($\underline{R}_t$ = 7 min) gave ^1H-NMR ($CDCl_3$) absorption at δ 6.87 (s, 2H, H_c and H_d). The assignment of stereochemistry of H_a and H_b were based on ^1H-NMR spectral data of the hydrostannylation products.[6] Quenching the reaction mixture with D_2O provided an isomeric mixture whose ^1H-NMR shows only two signals in olefinic

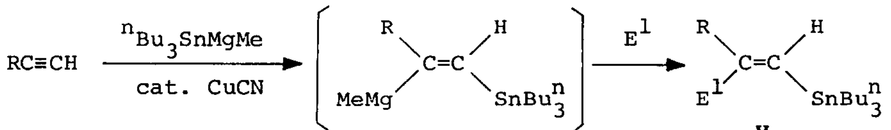
Scheme 1.



region at δ 5.98 and 6.82. Disappearance of higher field signal at δ 5.43 of the compound **III** is consistent with the cis-addition process.

The new reaction has provided not only simple vinylstannanes but also functionalized alkenylstannanes on treatment of an intermediary alkenylmetal species with various electrophiles. For instance, stannylmagnesation of 4-benzyloxy-1-butyne catalyzed by CuCN followed by the addition of MeI (large excess) gave **Vb** in 69% yield (Scheme 2).

Scheme 2.



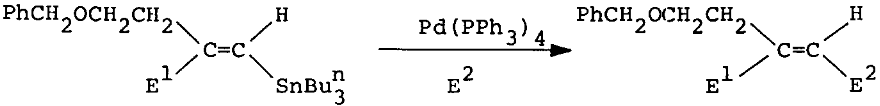
V

R = $PhCH_2OCH_2CH_2$-

a: E^1 = H (H_2O, 88%), b: E^1 = Me (MeI, 69%),
c: E^1 = Et (EtI, 73%), d: E^1 = CH_2=$CHCH_2$ (CH_2=$CHCH_2Br$, 78%),
e: E^1 = PhCH(OH) (PhCHO, 65%)(ref 7).

Combination of this reaction with the reported procedure for the transformation of vinylstannanes provided us with a simple route to regio- and stereoselective synthesis of trisubstituted ethenes. The compound **Vb** (0.45 g, 1.0 mmol) was treated with benzyl bromide (0.17 g, 1.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.06 g, 0.05 mmol)[8] in benzene under reflux for 4 h. Usual workup and purification by preparative TLC gave **VIc** (0.22 g) in 81% yield.[9]

Scheme 3.



V **VI**

VIa: E^1 = H, E^2 = PhCO (PhCOCl, 62%),
VIb: E^1 = Me, E^2 = CH_2=$CHCH_2$ (CH_2=$CHCH_2Br$, 87%),
VIc: E^1 = Me, E^2 = $PhCH_2$ ($PhCH_2Br$, 81%).

references and notes

1. H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, and H. Nozaki, J. Am. Chem. Soc., **105**, 4491 (1983). For the reaction with allenes, see Y. Morizawa, H. Oda, K. Oshima, and H. Nozaki, Tetrahedron Lett., in press.
2. Piers and his coworkers have showed that trimethylstannylcopper-dimethyl

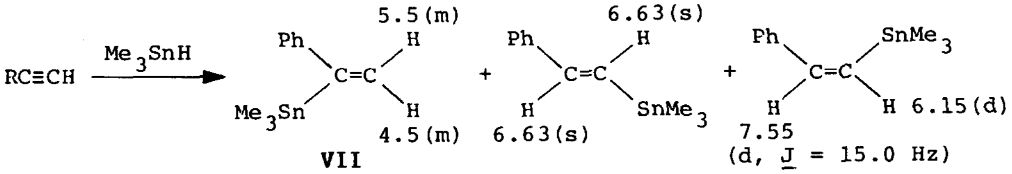
sulfide complex adds to triple bond. The reaction requires coexisting of proton donor such as methanol (E. Piers and J. M. Chong, *J. Chem. Soc. Chem. Comm.*, **1983**, 934. *idem*, *J. Org. Chem.*, **47**, 1604 (1982)). On the other hand, $Bu_3SnMgMe$, $Bu_3SnAlEt_2$, or $(Bu_3Sn)_2Zn$ in this work reacts without proton donor and various functionalized vinylstannanes could be prepared as shown in Scheme 2.

3. Other examples using Bu_3SnCu or $Bu_3SnCu(L)Li$, see S. D. Cox and F. Wudl, *Organometallics*, 2, 184 (1983). H. Westmijze, K. Ruitenberg, J. Meijer, and P. Vermeer, *Tetrahedron Lett.*, **23**, 2797 (1982). D. E. Seitz and S. -H. Lee, *Tetrahedron Lett.*, **22**, 4909 (1981). R_3SnMgR', see J. -P. Quintard, B. Elissondo, and M. Pereyre, *J. Organomet. Chem.*, **212**, C31 (1981).

4 C. Tamborski, F. E. Ford, and E. J. Soloski, *J. Org. Chem.*, **28**, 237 (1963). W. C. Still, *J. Am. Chem. Soc.*, **99**, 4836 (1977) and **100**, 1481 (1978). W. Kitching, H. A. Olszowy, and K. Harvey, *J. Org. Chem.*, **47**, 1893 (1982).

5. Bp 125°C (bath temperature)/0.1 Torr; ^{1}H-NMR ($CDCl_3$) δ 0.8-1.1 (m, 15H), 1.2-1.7 (m, 12H), 2.4-2.6 (m, 2H), 3.55 (t, *J* = 7.0 Hz, 2H), 4.55 (s, 2H), 6.00 (s, 2H), 7.3-7.4 (m, 5H); IR (neat) 1590, 1460, 1450, 1100, 990, 730, 690 cm^{-1}; Found: C, 61.29; H, 8.96%. Calcd for $C_{23}H_{40}OSn$: C, 61.22; H, 8.93%.

6. A. J. Leusink, H. A. Budding, and J. W. Marsman, *J. Organomet. Chem.*, **9**, 285 (1967). ^{1}H-NMR data was not available for the compound **VII** and we reexamined the reaction of trimethyltin hydride with phenylacetylene according to this literature. ^{1}H-NMR signals are as follows (δ value).



VII

7. After adding 4-benzyloxy-1-butyne to the reagent, the reaction mixture was cooled to -78°C and stirred for 1 min. Benzaldehyde (3 mol equivalent) was added in one portion.

8. M. Kosugi, Y. Shimizu, and T. Migita, *Chem. Lett.*, **1977**, 1423. J. W. Labadie, and J. K. Stille, *J. Am. Chem. Soc.*, **105**, 6129 (1983). D. Milstein and J. K. Stille, *J. Org. Chem.*, **44**, 1613 (1979). *Idem*, *J. Am. Chem. Soc.*, **101**, 4992 (1979) and **100**, 3636 (1978).

9. Bp 115°C (bath temperature)/0.1 Torr; ^{1}H-NMR ($CDCl_3$) δ 1.67 (s, 3H), 2.34 (t, *J* = 7.0 Hz, 2H), 3.32 (d, *J* = 8.0 Hz, 2H), 3.52 (t, *J* = 7.0 Hz, 2H), 4.45 (s, 2H), 5.37 (t, *J* = 8 Hz, 1H), 7.1-7.4 (m, 10H); IR (neat) 1590, 1490, 1440, 905, 725, 690 cm^{-1}; MS (rel intensity) m/z 266 (M$^+$, 4), 175 (22), 144 (36), 91 (100). Found: C, 85.67; H, 8.37%. Calcd for $C_{19}H_{22}O$: C, 85.65; H, 8.34%.

(Received in Japan 13 February 1984)