Non-*ipso* Electrophilic Substitution of Vinylstannanes and Silanes

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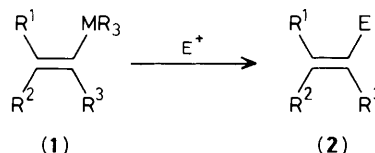*Fachbereich Chemie der Universität, Hans-Meerwein-Strasse, 3550 Marburg, Federal Republic of Germany*

Vinyl-stannanes and -silanes having a substituent at the 1-position react with carbon electrophiles at the terminal position, *i.e.*, the normal *ipso* electrophilic substitution based on the β-effect is not observed.

It is generally accepted that the reactions of vinyl-stannanes (**1a**) and -silanes (**1b**) with electrophiles occur with *ipso*-substitution, *i.e.*, the electrophiles attack the tin (silicon)-bearing vinyl carbon atom regioselectively to produce (**2**).[1,2] In this Communication we report that this does not hold for compounds (**1**) in which R^1 and R^2 are hydrogen. The results help to define the limits of the β-effect which normally dictates the reaction course (**1**) → (**2**).[1,2]

Upon reaction of (**3a**) with pivaloyl chloride in the presence of $TiCl_4$ in dry CH_2Cl_2 −78 → −35 °C, the substitution product (**4a**) was isolated as an 80:20 mixture of *E/Z* isomers.† The *ipso*-substitution product could not be detected. The same reactivity pattern pertains in other acylation reactions (Table 1).† Complete regioselective attack at the terminal carbon atom also occurs in the $TiCl_4$ mediated addition of aldehydes to (**3**) to form homoallylic alcohols (**5**) (Table 2).†‡ Finally, a 1:1:1 mixture of (**3b**), t-butyl chloride, and $TiCl_4$ at −10 °C leads to a 40% yield of $Bu^tCH_2CH=CH-Bu^t$ as a 1:1 *E/Z* mixture.

The results are consistent with *terminal* attack of the

C-electrophile, producing a tertiary α-stannyl carbocation (**6**),[3] followed by regioselective 1,2-hydride shift with formation of the β-stannyl carbocation (**7**). The latter undergoes destannylation to the products (**4**)/(**5**). The methylene unit bearing the *E*-group in (**6**) does not participate in a hydride shift owing to inductive effects. The 'normal' *ipso* attack would lead to a *primary* β-stannyl carbocation (**8**). Apparently, the magnitude of the β-effect[4] in (**8**) is less than the stabilization of the cation (**6**) by alkyl and stannyl groups.[3] However, it is difficult to assess electronic effects in the present system since steric factors are also likely to be important (the terminal position is less shielded). Relevant is the observation that protodestannylation[1,5] of (**3b**) with 3.5 M HCl occurs solely in an *ipso*-manner.
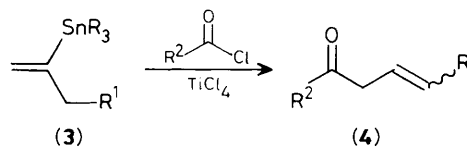
Table 1. Acylation of vinylstannanes (**3**).

Stannane	Acid chloride	Yield (4) (%)	E:Z
(**3a**)	$R^2 = Bu^t$	85 (**4a**)	80:20
(**3a**)	$R^2 = Me$	38 (**4b**)	69:31
(**3a**)	$R^2 = Et$	42 (**4c**)	77:23
(**3c**)	$R^2 = Bu^t$	61 (**4d**)	37:63

† Generally, a 2:1:2 mixture of (**3**), electrophile, and $TiCl_4$ was used. The reason for the moderate yields in some cases has to do with isolation problems (usually chromatography over silica gel using light petroleum/ethyl acetate) and/or volatility of the products. The reactions also occur if 1:1:1 mixtures are used, but the yields are about 10—20% lower. Other Lewis acids such as $BF_3 \cdot OEt_2$ and $SnCl_4$ are ineffective under these conditions. The vinylstannanes were prepared in yields of 77—80% by the reaction of the corresponding vinyl-lithium reagents with R_3SnCl.

‡ Formally, these processes are ene reactions. However, under the same conditions metal-free alkenes such as 2,4,4-trimethylpent-1-ene or 3-phenylprop-1-ene do *not* react with heptanal.

(1) → (2)

a; M = Sn
b; M = Si

(3) → (4)

a; R = Me; R^1 = Pr^n
b; R = Me; R^1 = Bu^t
c; R = Bu^n; R^1 = Bu^t

a; R^1 = Pr^n; R^2 = Bu^t
b; R^1 = Pr^n; R^2 = Me
c; R^1 = Pr^n; R^2 = Et
d; R^1 = Bu^t; R^2 = Bu^t

(3) $\xrightarrow[TiCl_4]{R^2CHO}$ (5)
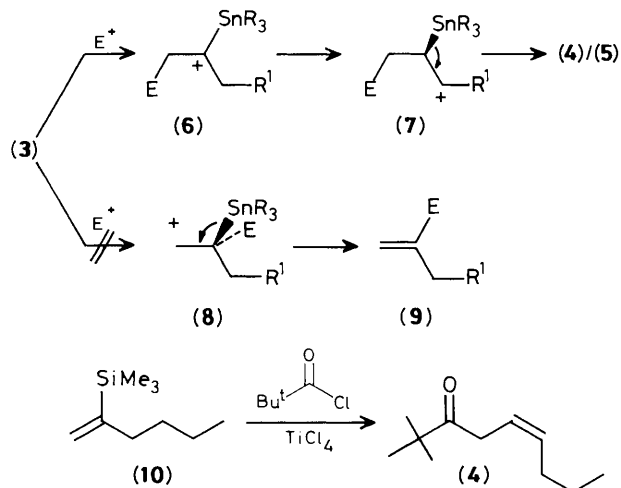
Table 2. Regioselective addition of vinylstannanes (3) to aldehydes.

Stannane	R^2	Temp./°C (t/h)	Yield (5) (% isolated)	$E:Z$
(3a)	Pr^n	$-50(4)$	65	83:17
(3a)	Pr^i	$-45(4)$	71	79:21
(3a)	Bu^t	$0(5)$	37	86:14
(3a)	n-Hexyl	$-30(4)$	44	83:17
(3b)	Pr^n	$-30(4)$	57	50:50
(3b)	Pr^i	$-10(5)$	77	35:65
(3b)	Bu^i	$-40(4)$	67	50:50
(3b)	n-Hexyl	$-30(4)$	43	56:44

a All reactions were initiated at $-78\,°C$ in dry CH_2Cl_2 using $2:1:2$ mixtures of (3), aldehyde, and $TiCl_4$, respectively; the temperature was then allowed to rise to the value given.

The above reactivity pattern appears to hold for the related vinylsilanes as well. Thus, preliminary studies involving (10) point to preferred terminal attack. For example, acylation using pivaloyl chloride/$TiCl_4$ at $-30\,°C$ afforded (4a) (80% yield; $E:Z$ 15:85). The reason for the reversal of E/Z selectivity in going from the tin to the silicon system is currently unclear.

In summary, we have shown that the classical *ipso* substitution rule does not hold for the reaction of carbon electrophiles with 1-substituted vinylsilanes and vinylstannanes.

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References

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2 Exceptions are certain sterically controlled intramolecular acylations of vinylsilanes (K. Mikami, N. Kishi, and T. Nakai, *Tetrahedron Lett.*, 1983, **24**. 795) as well as α-silylated enol ethers which show typical enol-like behaviour (T. Sato, T. Abe, and I. Kuwajima, *Tetrahedron Lett.*, 1978, **19**, 1383; see also J. A. Soderquist and A. Hassner, *ibid.*, 1988, **29**, 1899).

3 Soderquist and Hassner[2] have determined the relative stabilization of carbocations by alkyl or metal groups to be as follows: $CMe_3 > SnMe_3 > GeMe_3 > SiMe_3$; see also G. A. Olah, A. L. Berrier, L. D. Field, and G. K. Surya Prakash, *J. Am. Chem. Soc.*, 1982, **104**, 1349; A. C. Hopkinson and M. H. Lien, *J. Org. Chem.*, 1981, **46**, 998.

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