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ERYTHROSELECTIVITY IN ADDITION OF γ-SUBSTITUTED ALLYLSILANES TO ALDEHYDES IN THE PRESENCE OF TITANIUM CHLORIDE

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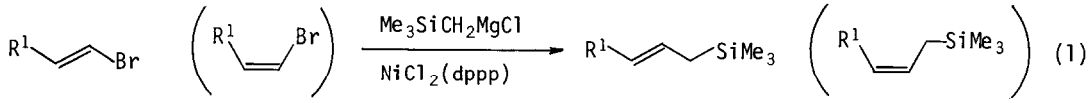
Summary: (*E*)-Crotyltrimethylsilane and (*E*)-cinnamyltrimethylsilane were allowed to react with aldehydes (RCHO: R = *t*-Bu, *i*-Pr, Et, Me) in the presence of titanium chloride to give erythro homoallyl alcohols with over 93% selectivity. Lower erythroselectivity was observed in the reaction of (*Z*)-allylsilanes.

There has been intense interest recently in controlling stereochemistry in addition of γ-substituted allylic organometals to aldehydes from both mechanistic and synthetic viewpoints.[1-3] For the reaction of allylic organometals containing lithium, boron, aluminum, titanium, zirconium, and chromium, it has been observed that *Z*-allylic isomers led to erythro adducts while *E*-isomers to threo ones, and the selectivity is generally accepted to be determined in the six-membered transition states.[2] Reaction of crotyltrialkyltins with aldehydes in the presence of $BF_3 \cdot Et_2O$ has been reported to proceed via acyclic transition states to give erythro products regardless of the geometry of the double bond.[3] We report here the first stereochemical results obtained for the reaction of (*E*)- and (*Z*)-allylsilanes in the presence of titanium chloride.[4,5]

The γ-substituted allylsilanes, (*E*)- and (*Z*)-crotyltrimethylsilane (**1a**) and (*E*)- and (*Z*)-cinnamyltrimethylsilane (**1b**) were prepared in 70-80% yield by cross-coupling[6] of trimethylsilylmethylmagnesium chloride with (*E*)- and (*Z*)-bromopropene (**2a**)[7] and (*E*)- and (*Z*)-bromostyrene (**2b**), respectively, in the presence of dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) as a catalyst (eq. 1).[8]

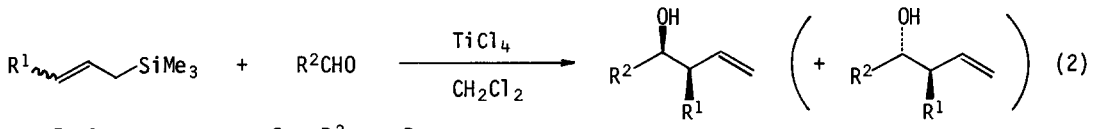


(1)

R^1 = Me: (*E*)-**2a** (*Z*)-**2a** R^1 = Me: (*E*)-**1a** (*Z*)-**1a**

R^1 = Ph: (*E*)-**2b** (*Z*)-**2b** R^1 = Ph: (*E*)-**1b** (*Z*)-**1b**

The allylsilanes **1a** and **1b** were allowed to react with pivalaldehyde (**3a**), isobutyraldehyde (**3b**), propionaldehyde (**3c**), and acetaldehyde (3d) in the presence of titanium chloride in dichloromethane (eq. 2). Homoallyl alcohols were obtained in high yields in the reaction at -78°C and 0°C for **1a** and **1b**, respectively. The reaction conditions and results are summarized in Table 1. The stereochemistry (erythro or threo) of the alcohols was determined by converting them into known β-hydroxy acids[9] by oxidative cleavage of the olefinic double bond ($KMnO_4/NaIO_4$).



(2)

1a,b

3a: R^2 = *t*-Bu
3b: R^2 = *i*-Pr
3c: R^2 = Et
3d: R^2 = Me

4 (erythro) **5** (threo)

As is seen from the Table, (*E*)-crotylsilane (**1a**) afforded erythro homoallyl alcohols **4** with high stereoselectivity, the selectivity being >99%, 97%, and 95% for **3a**, **3b**, and **3c**, respectively. Lower erythroselectivity was observed in the reaction of (*Z*)-**1a** where threo alcohols **5** were formed in 31-36% as by-products. Similar results were obtained with (*E*)- and (*Z*)-cinnamylsilane (**1b**). Thus, (*E*)-**1b** led to erythro alcohols **4** with over 93% selectivity while (*Z*)-**1b** to both **4** and **5** in a ratio of about three to one.

Studies on S_E' reactions of optically active allylsilanes[10] have demonstrated that the S_E' reactions proceed with anti stereochemistry and therefore the present reaction must proceed via an acyclic linear transition state, not via a cyclic six-membered transition state. The erythroselectivity of the allylsilanes may be illustrated by the mechanism shown in Scheme I. In the case of (*E*)-allylsilanes, the transition state **A** leading to an erythro alcohol is sterically favored over the diastereomeric transition state **B** which suffers steric repulsion between R^1 and R^2 (gauche interaction). On the same ground, **C** is considered to be favored over D for the reaction of (Z)-allylsilanes. It is rather surprising that the erythroselectivity observed with (*E*)- and (*Z*)-allylsilanes is different greatly from each other. The mechanism in

Scheme I

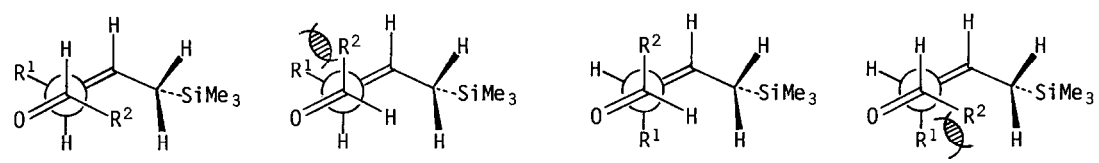


Table 1. Reaction of (*E*)- and (*Z*)-Allylsilanes **1** with Aldehydes **3** in the Presence of Titanium Chloride.[a]

allylsilane **1** (*E*/*Z*)	aldehyde **3**	reaction conditions temp (°C)	time (h)	yield (%)[b] **4** and **5**	ratio[c] **4**/**5**
(*E*)-**1a** (R^1 = Me) (>99/<1)	**3a** (R^2 = *t*-Bu)	-78	1	98	>99/<1
	3b (R^2 = *i*-Pr)	-78	1	92	97/3
	3c (R^2 = Et)	-78	1	91	95/5
(*Z*)-**1a** (R^1 = Me) (3/97)	**3a** (R^2 = *t*-Bu)	-78	0.5	87	65/35
	3b (R^2 = *i*-Pr)	-78	0.5	98	64/36
	3c (R^2 = Et)	-78	0.5	98	69/31
(*E*)-**1b** (R^1 = Ph) (>99/<1)	**3a** (R^2 = *t*-Bu)	0	3	78	>99/<1
	3c (R^2 = Et)	0	2	76	94/6
	3d (R^2 = Me)	0	1	76	93/7[d]
(*Z*)-**1b** (R^1 = Ph) (6/94)	**3a** (R^2 = *t*-Bu)	0	3	74	75/25
	3c (R^2 = Et)	0	2	68	71/29
	3d (R^2 = Me)	0	1	50	72/28[d]

[a] Titanium chloride (1.2 eq) was added at -78°C to a mixture of an allylsilane (1.2-1.5 eq) and an aldehyde (1.0 eq) in dichloromethane. The mixture was stirred at -78°C or 0°C and quenched with water. [b] Isolated yields for the reaction of **1b**, and GLC yields for the reaction of **1a**. [c] The ratio was determined by GLC analysis unless otherwise noted. [d] Determined by ^{1}H NMR.

Scheme I does not seem to account for the difference. It might be necessary to consider a modified transition state such as one involving synclinal geometry.

The erythroselectivity obtained here with (*E*)-allylsilanes is one of the highest for the reaction of γ-substituted allylic organometals,[1-3] and hence the present erythroselective reaction must find useful applications in control of stereochemistry in acyclic systems. Recent development of methods[8,11] for synthesis of allylsilanes with definite configuration will support their synthetic utility.

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