

A STEREO- AND REGIO-SPECIFIC ADDITION OF η^3 -TRIMETHYL-
SILYLALLYLTITANIUM COMPOUND WITH ALDEHYDES. A FACILE
AND STEREOCONTROLLED SYNTHESIS OF E- AND Z-TERMINAL DIENES

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Summary: η^3 -Trimethylsilylallyltitanium compound,
(η^5 -C₅H₅)₂Ti(η^3 -1-trimethylsilylallyl), reacts with aldehydes to give
(\pm)-(R,S)-3-trimethylsilyl-4-hydroxy-1-alkenes in excellent yields,
which can be deoxysilylated to either E- or Z-1,3-dienes.

The chemistry of allylic anions containing α -heteroatom substituents has been intensively investigated in recent years and has led to the development of many new synthetic methods.¹ Regio- and stereo-chemical control in reactions of these ambident anions with electrophiles is crucial to the utility of these methods.^{2,3}

Recently, Tsai and Matteson reported that the regio- and stereo-chemistry in reactions of trimethylsilylallyl anion with aldehydes is highly controlled via E-1-trimethylsilyl-1-propene-3-boronate, and that the resulting (\pm)-(R,S)-3-trimethylsilyl-4-hydroxy-1-alkenes can be deoxysilylated stereospecifically by the methods of Hudrlik and Peterson to either E- or Z-terminal dienes in excellent yields.³ As the Wittig reaction to produce 1,3-dienes is replete with complication, this reaction seems to be useful to have a simple alternative. However, this method has certain drawbacks such as low over-all yields, long reaction periods or multi-step procedure.

In the previous report, we have shown that η^3 -crotyltitanium compound $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^3\text{-crotyl})$ reacts regio- and stereo-selectively with aldehydes to form threo- β -methylhomoallyl alcohols in excellent yields.⁴ We have now found that η^3 -trimethylsilylallyltitanium compound $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^3\text{-1-trimethylsilylallyl})$ (**1**), formed in situ by reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}$ and trimethylsilylallyllithium, reacts with various aldehydes such as primary, secondary or tertiary alkyl aldehydes, or aryl aldehydes to yield (\pm)-(R,S)-3-trimethylsilyl-4-hydroxy-1-alkenes (**2**) in excellent yields, thus providing a simple and a high-yield procedure for the synthesis of either E- or Z-terminal dienes. Trimethylsilylallyllithium in tetrahydrofuran⁵ at -78°C was treated with a slight excess of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}$ formed in situ by reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ and isobutylmagnesium chloride in tetrahydrofuran⁶, and the mixture was stirred for 30 min. To this solution was added 0.9 equivalent of an aldehyde, and the mixture was stirred for 1 h at -78°C . The reaction mixture was brought to room temperature gradually and then stirred for 1 h. Quenching the reaction mixture with 4N-HCl (2 equivalents of the amount) followed by oxidation with air⁴ afforded **2** in the yields given in Table 1 and $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ in 80-88% yields.

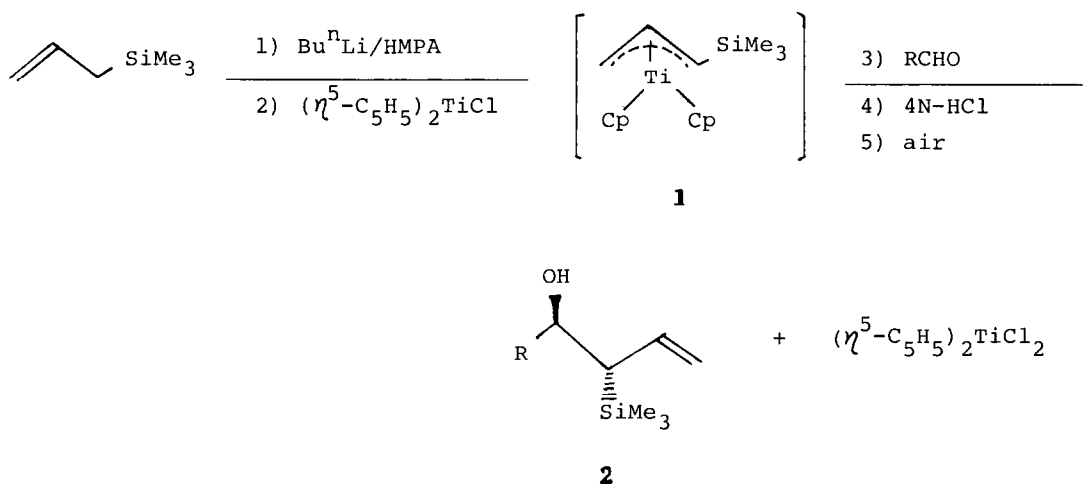






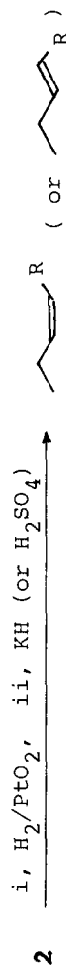
Table 1. Reaction of Complex **1** with Aldehydes RCHO, and Deoxysilylation of the Resulting Products **2**

Run	R in RCHO	Yield of 2 ^a (%)	Deoxysilylation conditions	Diene ^b	(yield, %) ^c
1	Et	86 ^d			
2	Pr ⁱ	88 ^d			
3	Bu ^t	98 ^d			
4	Ph	95 ^e	KH in THF, 10 min.		(88)
5			H ₂ SO ₄ in THF, 10 min.		(86)
6	BrCH ₂ CH ₂ CH ₂ CH ₂	92 ^e	KH in THF, 10 min.		Br (84)
7			H ₂ SO ₄ in THF, 10 min.		Br (89)

^a Isolated yield by column chromatography, based on RCHO. ^b The products were identified by

¹H n.m.r. (200 MHz).⁷ In each case no detectable amounts of stereo isomer were detected.

^c Isolated yield by distillation, based on **2**. ^d Products **2** were converted to E- and Z-3-alkenes as shown below and configuration was determined by g.l.c.; In each case, no detectable amounts of regio- and stereo-isomer were detected.



^e Configuration was determined by converted to dienes.

Competitive reactions to test the chemoselectivity showed that **1** exhibits remarkable chemoselectivity for the reaction with aldehydes in the presence of ketones, nitriles, esters or halides. For example, **1** reacted selectively with propionaldehyde (98-100% selectivity) in the presence of 2-pentanone (<2%), methyl acetate (0%), propionitrile (<1%) or butyl bromide (0%). This remarkable functional group tolerance of **1** should permit its use for preparation of E- and Z-terminal dienes containing various functional groups, such as shown in runs 6 and 7 in the table.

References

1. For reviews see: M. Schlosser, *Angew. Chem. Internat. Ed.*, **13**, 701 (1974).
D. Seebach and K.H. Geiss, *J. Organometal. Chem. Library*, **1**, 1 (1976).
2. (a) For review see: Y. Yamamoto and K. Maruyama, *J. Syn. Org. Chem. Jpn.*, **40**, 332 (1982).
(b) M. Yamaguchi and T. Mukaiyama, *Chem. Lett.*, 1279 (1979).
(c) R.W. Hoffmann and B. Kemper, *Tetrahedron Lett.*, 4883 (1980).
(d) M. Yamaguchi and T. Mukaiyama, *Chem. Lett.*, 993 (1980).
(e) Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Org. Chem.*, **45**, 195 (1980).
(f) M. Yamaguchi and T. Mukaiyama, *Chem. Lett.*, 1005 (1981).
(g) Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Am. Chem. Soc.*, **103**, 3229 (1981).

3. D.J.S. Tsai and D.S. Matteson, *Tetrahedron Lett.*, **22**, 2751 (1981).
4. F. Sato, S. Iijima, and M. Sato, *Tetrahedron Lett.*, **22**, 243 (1981).
5. P.W.K. Lau and T.H. Chan, *Tetrahedron Lett.*, 2383 (1978).

6. H.A. Martin and F. Jellinek, *J. Organometal. Chem.*, **12**, 149 (1968).

7. 200 MHz ^1H n.m.r. data for $\text{H}^1\text{H}^2\text{C}=\text{CH}^3-\text{CH}^4=\text{CH}^5-(\text{CH}_2)_4-\text{Br}$ (in CDCl_3).

Compound	δ : H^1	H^2	H^3	H^4	H^5	CH_2Br	$J_{1,3}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	J_{5,CH_2} (Hz)
E-isomer	5.00	5.12	6.35	6.09	5.70	3.42	10.0	16.6	10.0	15.2	8.0
Z-isomer	5.13	5.23	6.64	6.05	5.46	3.42	10.0	16.6	10.5	10.8	8.0

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