

Stereocontrol using a Heterosubstituted Allylic Carbanion. Regio- and Stereo-selective Reactions of Trimethylsilyl Allylic Carbanions with Aldehydes

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Regio- and stereo-selective coupling between trimethylsilyl allyl carbanions and aldehydes is achieved in the presence of an additive, 'M'; use of R_2BCl or $EtAlCl_2$ as the additive gives the *threo* isomer (**3**) predominantly, while use of $Bu_3SnCl-BF_3$ affords the *erythro* isomer exclusively.

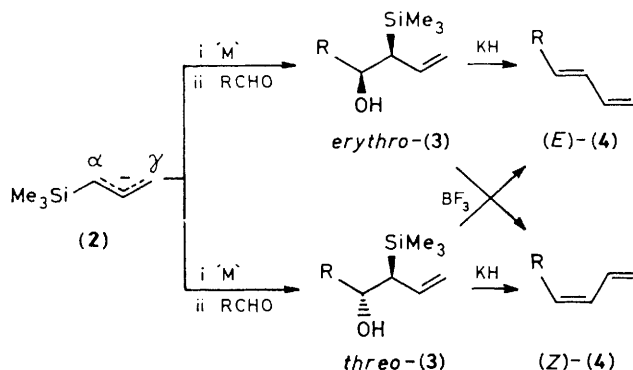
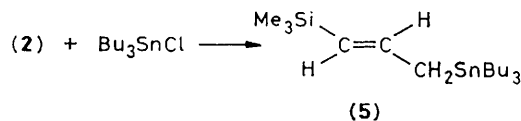
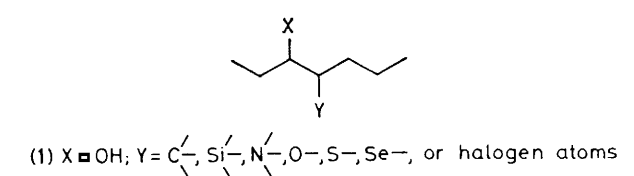
Diastereocontrol between two adjacent substituents in acyclic systems (**1**), where $X = OH$ and $Y = Me$, is achieved *via* a number of methods.¹ Such control between two heterosubstituents, in which $X = OH$ and $Y = Si=, N=, O-, S-, Se-,$ or

halogen atoms, appears to be highly desirable from the synthetic point of view. We now report a new method for diastereocontrol between $X = OH$ and $Y = SiMe_3$. Our method is based on regio- and diastereo-selective reactions between

Table 1. Regio- and diastereo-selective reactions of (2) with aldehydes.^a

| RCHO | 'M' | Yield of <i>threo</i> -(3), % | Yield of <i>erythro</i> -(3), % | Yield of γ -adduct, % ^b |
|---------------------------------------|--|-------------------------------|---------------------------------|---|
| Me ₂ CHCHO | (CH ₂ [CH ₂] ₃ CH) ₂ BCl ^c | ca. 100 | — | — |
| MeCH ₂ CH ₂ CHO | EtAlCl ₂ | ca. 100 | — | — |
| n-C ₉ H ₁₉ CHO | Bu ₃ SnCl-BF ₃ ^d | — | ca. 100 | — |
| CH(Me):CH(CHO) | EtAlCl ₂ | 86 | 14 | — |
| PhCHO | EtAlCl ₂ | 88 | 4 | 7 |
| " | Et ₂ AlCl | 58 | — | 42 |
| " | (CH ₂ [CH ₂] ₃ CH) ₂ BCl ^c | 79 | 15 | 6 |
| " | (CH ₂ [CH ₂] ₃ CH) ₂ BCl ^e | 71 | — | 29 |
| " | Bu ₃ SnCl-BF ₃ ^d | — | ca. 100 | — |

^a All reactions were carried out on a 1 mmol scale as described in the text. The products were identified by ¹H n.m.r., i.r., and mass spectra, and/or comparison with authentic materials. ^b Me₃SiCH=CHCH₂CH(OH)R. ^c The boron reagent and the aldehyde were added at -78 °C. ^d *Erythro*-(3) was prone to deoxysilylation by BF₃ present in the reaction mixture. ^e The boron reagent and the aldehyde were added at -30 °C.



the trimethylsilyl allylic carbanion (2) and aldehydes (Scheme 1). Although (2) reacts with aldehydes at the γ -position under normal conditions, this γ -regioselectivity can be changed completely to α -selectivity by the addition of an additive 'M'.² Use of dicyclopentylboron chloride or ethylaluminum dichloride as an additive gives *threo*-(3),³ while use of tributyltin chloride-BF₃ affords *erythro*-(3) exclusively.⁴ The results are summarized in Table 1.

The reaction of aliphatic aldehydes proceeds with very high stereo- and regio-selectivity, while that of aromatic and vinyl aldehydes proceeds with moderate *threo* selectivity. Since it is known that (2) reacts with R₃SiCl or RI at the γ -position,^{2b} additives 'M' such as Bu₃SnCl, R₂BCl, or AlCl₂ may react similarly at the γ -position. In fact, (5) was isolated from the reaction of (2) with Bu₃SnCl and its n.m.r. spectra revealed the *trans* geometry of the double bond; ¹H n.m.r. (CCl₄, Me₄Si) δ 0 (Me₃Si), 1.81 (d, *J* 8 Hz, 2H), 5.15 (d, *J* 18

Hz, 1H), 5.97 (dt, *J* 18 and 8 Hz, 1H). Under the influence of BF₃, (5) reacted with PhCHO to give *erythro*-(3)[†] exclusively as expected from the previous observation.⁴ Although an intermediate organometallic compound was not isolated owing to lack of stability, boron and aluminium additives must produce γ -trimethylsilylsubstituted allylic boron and aluminium compounds with *trans* configuration which subsequently react with aldehydes to afford *threo*-(3) either exclusively or predominantly.

Irrespective of the precise mechanism, the present method provides a convenient procedure for acyclic stereocontrol between OH and SiMe₃ substituents. Further, *erythro*- or *threo*-(3) can be stereoselectively converted into (*E*)- or (*Z*)-1,3-dienes (4) by a known method (Scheme 1).⁵ Consequently, our reaction may also complement the Wittig type terminal 1,3-diene synthesis, since the latter reaction is frequently accompanied by complications.[‡]

The general procedure for the synthesis of (3) is as follows. The carbanion (2) was generated from the reaction of the allyltrimethylsilane (1 mmol) with Bu^tLi (1.1 mmol)-hexamethylphosphoric triamide (1.1 mmol) in tetrahydrofuran (5 ml) at -78 °C for 2 h. Additive 'M' (1.1 mmol) was added at the same temperature, and the aldehyde was added after a few minutes. The reaction mixture was allowed to warm to room temperature and quenched with aqueous NH₄Cl. The usual work-up gave the desired isomer. In the case of the reaction with Bu₃SnCl-BF₃, Bu₃SnCl was added first and the

[†] ¹H N.m.r. (CCl₄, Me₄Si) *erythro*-(3) (R = Ph): δ 0.08 (s, 9H), 2.09 (dd, *J* 9.0 and 10.0 Hz, 1H), 1.88 (br. s, 1H), 4.71 (dd, *J* 16.5 and 2 Hz, 1H), 4.73 (d, *J* 9 Hz, 1H), 4.83 (dd, *J* 10.0 and 2 Hz, 1H), 5.58 (ddd, *J* 10.0, 10.0, and 16.5 Hz, 1H), and 7.15 (s, 5H); *threo*-(3) (R = Ph): δ 0.09 (s, 9H), 2.09 (dd, *J* 10.5 and 6.5 Hz, 1H), 2.20 (br. s, 1H), 4.96 (d, *J* 6.5 Hz, 1H), 5.01 (dd, *J* 16.5 and 2 Hz, 1H), 5.15 (dd, *J* 10.5 and 2 Hz, 1H), 6.01 (ddd, *J* 10.5, 10.5, and 16.5 Hz, 1H), and 7.15 (s, 5H).

[‡] Matteson's method requires the isolation of boronates and long reaction times.³ We are grateful to Professor Matteson for providing us with n.m.r. spectra of (4).

aldehyde and BF_3 were added after a few minutes. Total yields were usually in the range 50–70%.§

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References

- 1 For example, see the following reviews: P. A. Bartlett, *Tetrahedron*, 1980, **36**, 3; Y. Yamamoto and K. Maruyama, *Heterocycles*, 1982, **18**, 357.
- 2 For a review, E. W. Colvin, 'Silicon in Organic Synthesis,' Butterworth, London, 1981, p. 119. R. Corriu and J. Masse, *J. Organomet. Chem.*, 1973, **57**, C5; K. Yamamoto, M. Ohta, and J. Tsuji, *Chem. Lett.*, 1979, 713; E. Ehlinger and P. Magnus, *J. Am. Chem. Soc.*, 1980, **102**, 5004; P. W. K. Lau and T. H. Chan, *Tetrahedron Lett.*, 1978, 2383; the addition of MgBr_2 to (2) produces α -selectivity, but the diastereoselectivity is low.
- 3 The *threo* isomer is obtained *via* an allylic boronate derivative; D. J. S. Tsai and D. S. Matteson, *Tetrahedron Lett.*, 1981, 2751. *Threo* and *erythro* nomenclature is based on Heathcock's convention.
- 4 Y. Yamamoto, H. Yatagai, Y. Naruta, and K. Maruyama, *J. Am. Chem. Soc.*, 1980, **102**, 7107.
- 5 P. F. Hudrik and D. Peterson, *J. Am. Chem. Soc.*, 1975, **97**, 1464.

§ F. Sato, *et al.* reported at the 45th Annual Meeting of the Chemical Society of Japan, 1982, that *threo*-(3) was also obtained *via* the reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^3\text{-C}_3\text{H}_4\text{SiMe}_3)$ with aldehydes.