Pergamon

Tetrahedron: Asymmetry, Vol. 8, No. 22, pp. 3711–3713, 1997

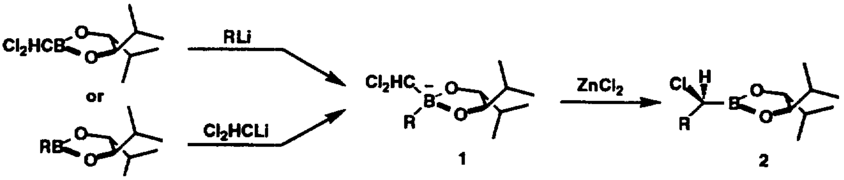
Printed in Great Britain
PII: S0957-4166(97)00528-4
0957-4166/97 $17.00 + 0.00

The mechanistic basis for diastereoselectivity in the Matteson rearrangement

E. J. Corey,* David Barnes-Seeman and Thomas W. Lee
Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, USA

Abstract: The diastereoselective rearrangement of α,α-dichloromethylboronate derivatives of chiral 1,2-diols (Matteson rearrangement) can be understood readily in terms of a bidentate interaction between the catalytic Lewis acid ($ZnCl_2$) and the substrate, leading to favored transition states such as **4** and **5**. © 1997 Elsevier Science Ltd

D. S. Matteson and coworkers have utilized boronate esters of chiral 1,2-diols for the enantioselective synthesis of a variety of chiral compounds, for example, alcohols, γ-lactones and β-hydroxy amines.[1] A key reaction in this methodology is illustrated in Scheme 1. The rearrangement of the intermediate **1** to the α-chloro boronate ester **2** is highly diastereoselective (up to 50:1) and provides a facile route to these versatile intermediates. The mechanistic basis for this remarkable diastereoselectivity, which has not been adequately explained, forms the subject of this communication.



Scheme 1.

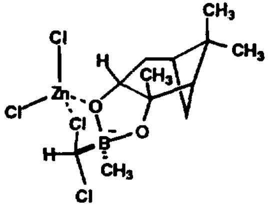
Previous papers from this laboratory have provided a clear and logical explanation of some 20 different enantioselective addition reactions of aldehydes (aldol, Diels–Alder, allylation, cyanation, etc.) under the influence of a variety of chiral Lewis acids.[2] An important feature of all these reactions is the occurrence of a formyl C–H···O hydrogen bond between the coordinated aldehyde and an oxygen ligand on the Lewis acid. Such a hydrogen bond is energetically favorable because the C–H of the coordinated aldehyde possesses enhanced electrophilicity while the ligand on the coordinated Lewis acid becomes more basic after substrate coordination. By the same principle, the Lewis acidic catalyst, $ZnCl_2$, for the conversion of **1** to **2** should be capable of binding to one of the two equivalent boronate oxygens in **1** which should then facilitate coordination to one of the diastereotopic chlorines in **1** to promote C–Cl heterolysis and rearrangement. This simple extension of the mechanistic arguments used earlier[2] leads to a unique explanation of the high diastereoselectivity of the Matteson rearrangement of **1** to **2** and also the preferred absolute stereochemical course.

Our analysis is summarized in Scheme 2. Coordination of $ZnCl_2$ to **2** will occur preferentially to the lone pair of oxygen which is *trans* to isopropyl for obvious steric reasons. Chelation to either of the diastereotopic chlorines of the dichloromethylboronate group is, in principle, possible. One chelation mode, shown in **3**, is clearly much less favorable than the other, shown in **4**, again for steric reasons. Reaction via the favored structure **4** in Scheme 2 leads to the observed predominating diastereomer by a stereoelectronically favorable rearrangement of antiperiplaner methyl from boron to carbon with

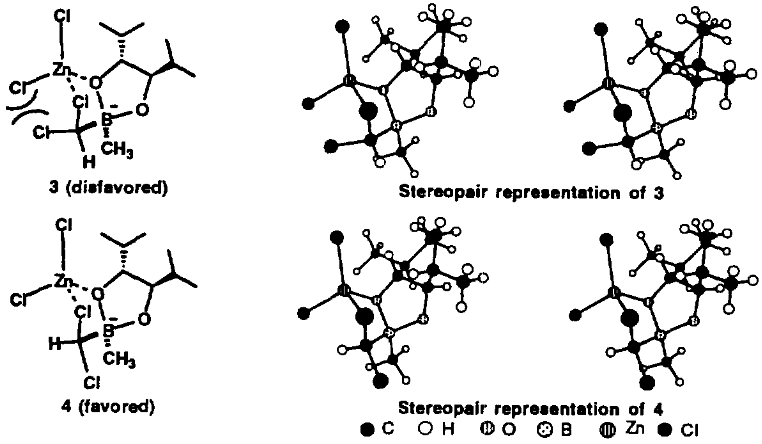
---

* Corresponding author. Email: corey@chemistry.harvard.edu

C–Cl cleavage. For a non-C$_2$-symmetric diol, such as pinanediol, which also can provide control,[1] the favored transition state (**5**, for pinanediol) is readily derived by our analysis.



5



3 (disfavored)

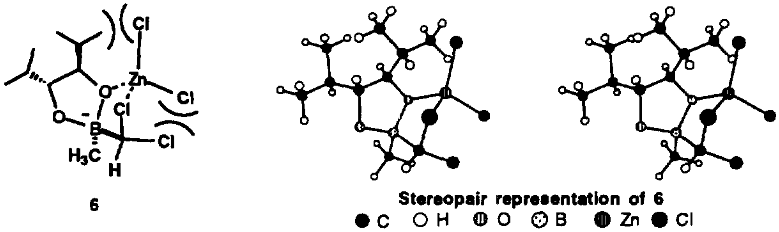
Stereopair representation of 3

4 (favored)

Stereopair representation of 4

Scheme 2.

Our analysis did not reveal any transition state as favorable as **4**. For example, the alternative shown in **6**[1d] can be dismissed, since it involves the severe repulsions which are shown in Scheme 3 and is clearly much less favorable than the arrangement shown in **4** of Scheme 2.



6

Stereopair representation of 6

Scheme 3. Example of a very disfavored transition state.

Our previous work in the significance of formyl C–H· · ·O hydrogen bonding[2] and the analysis in this paper make a strong case for the general importance of the bifunctional metal–ligand subunit (e.g. metal=B, Al, Ti) in determining the stereochemical course of numerous asymmetric reactions.[3,4]

References

1. (a) Matteson, D. S. *Acc. Chem. Res.* **1988**, *21*, 294. (b) Matteson, D. S. *Chem. Rev.* **1989**, *89*, 1535. (c) Matteson, D. S.; Hurst, G. D. *Heteroatom Chem.* **1990**, *1*, 65. (d) Matteson, D. S. in *Stereodirected Synthesis with Organoboranes*, Springer–Verlag, Berlin, 1995, Chapter 5.
2. (a) Corey, E. J.; Rohde, J. J.; Fischer, A.; Azimioara, M. D. *Tetrahedron Letters* **1997**, *38*, 33. (b) Corey, E. J.; Rohde, J. J. *Tetrahedron Letters* **1997**, *38*, 37. (c) Corey, E. J.; Barnes-Seeman, D.;

Lee, T. W. *Tetrahedron Letters* **1997**, *38*, 1699. (d) Corey, E. J.; Barnes-Seeman, D.; Lee, T. W. *Tetrahedron Letters* **1997**, *38*.

3. See also for oxazaborolidine-catalyzed reductions, (a) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551. (b) Corey, E. J.; Bakshi, R. K.; Shibata, S.; Chen, C. P.; Singh, V. K. *J. Am. Chem. Soc.* **1987**, *109*, 7925. (c) Corey, E. J.; Helal, C. J. *Tetrahedron Letters* **1995**, *36*, 9153. (d) Helal, C. J.; Magriotis, P. A.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 10938.
4. This research was supported by grants from the National Science Foundation and the National Institutes of Health. D.B.-S. and T.W.L. are Graduate Fellows of the National Science Foundation.

(Received in USA 19 September 1997)