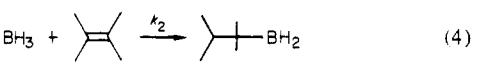
thexylchloroborane–methyl sulfide.[16] In our view, these results clearly establish that the hydroboration of alkenes with BH_3–Lewis base complexes must involve a prior dissociation of the complex followed by reaction of the free borane with the alkene.

As mentioned time and again,[10] kinetic studies of the reaction of BH_3–Lewis base complexes with simple alkenes such as 1-octene have been practically impossible due to the complexity of the reaction. However, the reaction of BH_3·SMe_2 with 2,3-dimethyl-2-butene (TME) stops at the first stage (RBH_2), making possible a rigorous kinetic analysis of the reaction. The rate equation for the dissociation mechanism (eq 3 and 4) derived

$$BH_3 \cdot SMe_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BH_3 + SMe_2 \qquad (3)$$



(4)

by steady-state treatment predicts complex kinetic behavior. The direct-attack mechanism, on the other hand, requires clean second-order kinetics to be exhibited. Our kinetic analysis of the rate data for the reaction of TME (0.200 M) with BH_3·SMe_2 (0.200 M) in toluene at 0 °C yielded second-order rate constants decreasing in magnitude with the progress of the reaction, as predicted by eq 5 (Table III). When the reaction is done in the

$$\frac{dp}{dt} = \frac{k_1 k_2[\mathrm{BMS}][\mathrm{TME}]}{k_{-1}[\mathrm{SMe_2}] + k_2[\mathrm{TME}]} \qquad (5)$$

presence of excess Me_2S, $k_{-1}[SMe_2] >> k_2[TME]$, simplifying the rate equation to eq 6.[17] Since Me_2S is in excess, its concentration will be fairly constant, leading to reasonable pseudo-second-order kinetic behavior. We observe this behavior. For the reaction of TME (0.200 M) with BMS (0.200 M) in the presence of excess Me_2S (0.400 M) in toluene at 0 °C, good second-order rate constants are observed (Table III).

$$\frac{dp}{dt} = \frac{k_1 k_2[\mathrm{BMS}][\mathrm{TME}]}{k_{-1}[\mathrm{SMe_2}]} \qquad (6)$$

It is interesting to note that these results can explain Pasto's results on the reaction of TME with BH_3·THF in THF at 0 °C.[12] Since the reaction was done in the presence of a large excess of THF (solvent), k_{-1}[THF] will be very large and thus be constant. A pseudo-second-order kinetics will obtain, as was indeed observed. (An expression similar to eq 6 should be applicable.)

Thus, our results on the reaction of 2,3-dimethyl-2-butene with BH_3·SMe_2 provide strong evidence for the dissociation mechanism.

We also wish to draw attention to the important observation made by Klein and co-workers.[18] They noted that the hydroboration of aged solutions of *m*-methoxystyrene with BH_3·THF exhibited a considerable induction period. They attributed this induction period to the diversion of a reactive intermediate by an impurity, probably peroxide. Only after all of the impurity had reacted would the hydroboration itself begin. This experiment clearly shows that the complex, BH_3·THF, is *not* the hydroborating species involved in the actual hydroboration step.

Thus, our present studies and that of Klein indicate that the mechanism of hydroboration of alkenes with BH_3–Lewis base complexes proceeds via a prior dissociation of the complex. They do not support the direct-attack mechanism proposed by Schleyer and co-workers on the basis of ab initio calculations.[14]

The rate studies were performed by monitoring the disappearance of the B–H stretching absorbance of the BH_3–Lewis base complex (~4.0–4.3 μm) using a quantiative IR procedure.[5,8]

(16) Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D. *J. Org. Chem.* **1982**, *47*, 863.

(17) The term k_2[TME] in eq 6 may still contribute to a minor extent, since a sufficiently large excess of Me_2S to eliminate the competition would have altered the medium. As a result, the observed pseudo-second-order rate constants k_2'' in Table III are not strictly inversely proportional to [Me_2S].

(18) Klein, J.; Dunkelblum, E.; Wolff, M. A. *J. Organomet. Chem.* **1967**, *226*, 57.

Asymmetric Addition to Chiral Naphthyloxazolines. A Facile Route to 1,1,2-Trisubstituted-1,2-dihydronaphthalenes in High Enantiomeric Excess

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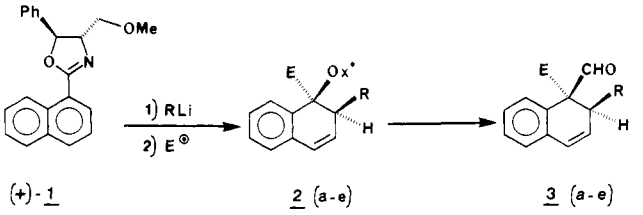
The increasingly important role of asymmetric synthesis has been manifested by the large number of reports on this subject over the past 10 years.[2] Prominent among these studies has been the use of chiral oxazolines as auxiliaries for a wide range of enantiomerically enriched compounds.[3] We now describe a novel asymmetric route to chiral 1,1,2-trisubstituted-1,2-dihydronaphthalenes with very high enantioselectivity.[4] The process involves the nucleophilic addition of various organolithium reagents to the chiral 1-naphthyloxazoline **1**[5] followed by trapping of the intermediate azaenolate with several electrophiles to furnish the dihydronaphthalene **2**. This tandem alkylation sequence affords



2 with a high degree of diastereofacial selectivity thus incorporating two asymmetric centers in a one-pot reaction.[6] Furthermore, a mild, high-yield procedure for removal of the oxazoline moiety is described, producing enantiomerically pure 1,2-dihydronaphthalene aldehydes **3**.

Treatment of a THF solution containing (+)-**1** (−45 °C) with an organolithium reagent followed by additin of an electrophile (−45 °C) produced the adducts **2a–e** as a mixture of diastereomers, whose ratios were readily assessed by HPLC analysis (Table I). In each example, the two diastereomers formed were the result of sequential trans addition,[7] thus the diastereomeric ratios reflect only the facial selectivity of the initial lithium nucleophile. The absolute configuration as well as the trans addition were confirmed by X-ray diffraction studies on pure **2c**. Since the oxazoline is known to contain the 4*S*,5*S* configuration,[8] the organolithium enters mainly at the β-face followed by electrophile entry at the α-face of the naphthalene ring. The diastereomers of **2** were easily separated by flash chromatography providing enantiomerically pure aldehydes **3** after removal of the oxazoline (vide infra).

(1) National Research Service Award Postdoctoral Fellow (NIH-IF-32CA07333).

(2) A comprehensive review on asymmetric synthesis has been compiled: Morrison, J. D. "Asymmetric Synthesis"; Academic Press: New York, 1983; Vol. 1–4, in press.

(3) Meyers, A. I.; Lutomski, K. A. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Part II, in press.

(4) Aryl borate anions have been shown to furnish *trans*-1,2-disubstituted-1,2-dihydronaphthalenes (Negishi, E.; Merrill, R. E. *Chem. Commun.* **1974**, 860.

(5) Prepared in 62% yield from 1-naphthoic acid following the procedure reported previously: Meyers, A. I.; Lutomski, K. A. *J. Am. Chem. Soc.* **1982**, *104*, 879. For other derivatives of aryloxazolines, see: Meyers, A. I.; Hanagan, M. A.; Trefonas, L. M.; Baker, R. J. *Tetrahedron* **1983**, *39*, 1991. $[\alpha]^{25}_D$ of **1** 53.0° (*c* 7.50, $CHCl_3$).

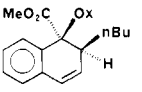
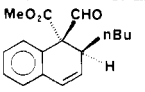
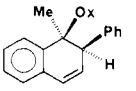
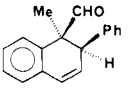
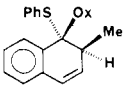
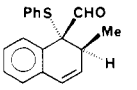
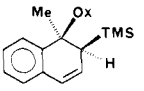
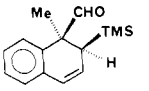
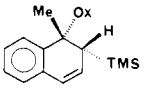
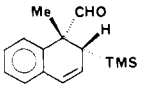
(6) Organolithium reagents add to simple, achiral naphthalene oxazolines and may be trapped to *trans*-1,1,2-trisubstituteddihydronaphthalenes (confirmed by X-ray analysis). Lutomski, K. A., unpublished results.

(7) The trans alignment of R to E in **2c** as well as the absolute configuration are given with the X-ray details in the supplementary material.

(8) Meyers, A. I.; Smith, R. K.; Whitten, C. E. *J. Org. Chem.* **1979**, *44*, 2250.

0002-7863/84/1506-1865$01.50/0

Table I. Asymmetric Addition to 1-Naphthyloxazolines

compd	RLi[a] (T, °C)	E[b] (T, °C)	2 (%)[c]	diast ratio[d]	3 (%)	$[\alpha]^{27}_D(CHCl_3)$[e]
a	*n*-BuLi (−45)	$MeCO_2Cl$ (−45)	 (99)	94:6	 (88)	*f*
b	PhLi (−45)	MeI (−45)	 (99)	83:17	 (88)	+201° (*c* 3.60)
c	MeLi (−45)	PhSSPh (−45)	 (56)	86:14	 (62)	+747° (*c* 4.35)
d	$[CH_3)_3SiLi$ (−78)	MeI (−78)		40:60	 (85)	+634° (*c* 0.58)
e			 (d + e, 69)		 (58)	−638° (*c* 0.85)

[a] Added to a 0.08 M solution of naphthyloxazoline at the indicated temperature. [b] Added to the reaction at the temperature shown. [c] Isolated yields of the diastereomeric mixture after flash chromatography; silica gel 60H, E. Merck. [d] Diastereomeric ratios were determined by HPLC, Zorbax Sil column (Du Pont), 10-20% THF–hexane as eluent, 1-1.5 mL/min. [e] Specific rotations of enantiomerically pure aldehydes isolated in the yields given. [f] The 94:6 ratio of enantiomers were not separated; see ref 15.

When (trimethylsilyl)lithium[9] was employed as the nucleophile the diastereoselectivity of **2d** and **2e** was greatly reduced to 4:6, respectively, presumably due to the HMPA present in the Me_3SiLi reagent. This was attributed to the inhibition of a chelate between the oxazoline and the lithium reagent. That the tandem alkylation still proceeded in a pure trans fashion was shown by separation of the adducts **2d** and **2e**, which, on oxazoline removal, confirmed that the two aldehydes were indeed enantiomers, not geometric isomers (Table I). Thus the HMPA present in the Me_3SiLi affects only the diastereofacial selectivity but not the trans addition of the nucleophile and the electrophile. Another interesting observation concerning this process was the modest yield of **2c** obtained (56%) when methyllithium was introduced followed by diphenyl disulfide giving a diasteromeric ratio of 86:14.[10] In an attempt to increase the efficiency of alkylation to **2c**, HMPA (2.0 equiv) was introduced prior to MeLi and Ph_2S_2 and gave complete reaction after 4 h. However, the yield of **2c** was unchanged but more significantly neither was the diastereomeric ratio. The conclusion, therefore, is that at least for alkyllithiums the use of cosolvents such as HMPA are without effect on the nucleophilic addition step, which is critical to the absolute stereochemical course of the reaction. This observation is contrary to earlier studies in other systems where HMPA, present prior to lithiation, strongly affects the stereochemical outcome.[11]

The removal of the chiral auxiliary, i.e., oxazoline, required milder conditions than the usual acid hydrolysis or reductive cleavage[12] due to the presence of the double bond, silyl groups, esters, and thioalkyl substituents. This was conveniently accomplished by addition of 2.0 equiv of methyl fluorosulfonate ("magic methyl")[13] to a dichloromethane solution of **2** to produce the *N*-methyl quaternary salt, which was reduced in situ with sodium borohydride (2.0 equiv, THF–MeOH, 4:1, 0 °C)[14] to afford the oxazolidines as a mixture of stereoisomers. The latter mixture was cleaved to the aldehyde **3** by using oxalic acid (THF, H_2O, 25 °C) in good to excellent yields (Table I).[15]

Although not yet taken to the dihydronaphthalenealdehydes **3**, several other organolithium reagents (1,3-dithianyl, *tert*-butyl) were added to **1** and trapped with methyl iodide to give **2** in comparable diastereomeric ratios and satisfactory overall yields. The versatility of this diastereofacial dialkylation is thereby demonstrated to possess the potential for reaching a variety of chiral products.[16]

Acknowledgment. Financial support for this work was provided by the National Institutes of Health. We are grateful to Professor O. P. Anderson and Cynthia Schauer for providing the X-ray data on a Nicolet R3m/E diffractometer (NSF-CHE 810 3011) and to the Colorado State University Regional NMR Center, funded by National Science Foundation Grant CHE-8208821.

Supplementary Material Available: Complete physical data on all new compounds, typical experimental details, and X-ray data for **2c** (8 pages). Ordering information is given on any current masthead page.

(9) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063.
(10) Reaction times in excess of 20 h were required to achieve this conversion, with **1** being recovered in addition to 10% 2,3-double-bond migration product.
(11) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. Meyers, A. I. *Acc. Chem. Res.* **1978**, *11*, 375.
(12) Meyers, A. I.; Himmelsbach, R.; Reuman, M. *J. Org. Chem.* **1983**, *48*, 4053.
(13) This substance is extremely toxic and should be handled with care.
(14) Oxazolines have been cleaved to aldehydes via initial quanternization with methyl iodide followed by borohydride reduction and acidic cleavage: Nordin, I. C. *J. Heterocycl. Chem.* **1966**, *3*, 531. And also by quaternization with methyl fluorosulfonate and $NaBH_4$: Corey, E. J.; Boger, D. L. *Tetrahedron Lett.* **1978**, 5.
(15) To further confirm that the minor diastereomers in **2** were indeed enantiomeric at the 1- and 2-naphthalene positions after oxazoline removal, the crude 94:6 mixture of **2a** was converted to the aldehyde mixture. The latter was reduced (>95%) to the primary alcohol ($NaBH_4$, MeOH, 0 °C) and was subjected to chiral shift studies with $Eu(hfc)_3$. Integration of the resolved CO_2Me singlet at 360 MHz showed the methyl singlets with a ratio of 93:7, in excellent agreement with the HPLC analysis of the mixture in **2a**.
(16) We have also observed that 2-naphthyloxazolines also undergo the tandem alkylations in high yield with diastereoselectivity in excess of 95% (Hoyer, D., unpublished results).
(17) **Note Added in Proof**: It has just come to our attention that magic methyl is no longer available from commerical sources. We have, however, found that trimethyloxonium fluoborate ("Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V), under exactly identical conditions as described above, readily quaternizes oxazolines in the cleavage procedure.