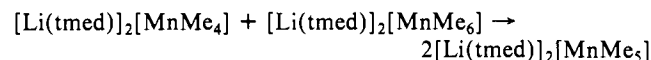


hexamethyl manganate $[\text{Li}(\text{tmed})]_2[\text{MnMe}_6]$ (**3**).¹² The +4 oxidation state of this species is confirmed by a magnetic moment of $3.9 \mu_B$ and by the ESR spectrum, which shows a strong sextet at 340 mT ($A_{\text{Mn}} = 0.0060 \text{ cm}^{-1}$) and a moderately intense "spin-forbidden" transition at 145 mT that are consistent with the presence of a nearly cubic ($D = \lambda = 0$) $S = 3/2$ ion.¹³ The X-ray crystal structure¹⁴ (Figure 1b) reveals an octahedral $[\text{MnMe}_6^{2-}]$ core that is capped by two "semi-face-bridging" Li-(tmed) cations; the molecular unit resides on a crystallographic inversion center. The average Mn-C distance of 2.12 Å is similar to those in $\text{MnMe}_4(\text{dmpe})$ of 2.08–2.12 Å, while the Li...H₃C-Mn contacts are divided into two short distances of 2.20–2.35 Å and one longer distance of 2.53 (2) Å. The coordination geometry about lithium may be best described as a distorted trigonal bipyramid, with C(7A) and N(2) in the axial positions.

Upon mixing solutions of the Mn^{II} and Mn^{IV} compounds $[\text{Li}(\text{tmed})]_2[\text{MnMe}_4]$ and $[\text{Li}(\text{tmed})]_2[\text{MnMe}_6]$ in a 1:1 ratio, comproportionation occurs to give the Mn^{III} pentamethyl man-



ganate $[\text{Li}(\text{tmed})]_2[\text{MnMe}_5]$ in nearly quantitative yield. Interestingly, however, the comproportionation reaction occurs relatively slowly ($t_{1/2} \sim 10$ min), presumably since methyl group transfer as well as electron transfer must take place. The three permethyl complexes form an unusual set of related organometallic species in three adjacent oxidation states.¹⁵

Preliminary results indicate that the tetravalent hexamethyl manganate, $[\text{Li}(\text{tmed})]_2[\text{MnMe}_6]$, reacts with internal acetylenes, $\text{RC}\equiv\text{CR}$, to give low yields of methylated olefins, $\text{MeRC}=\text{CRMe}$. Such cis-alkylation reactions of acetylenes are formally similar to the cis-hydroxylation of olefins by reagents such as OsO_4 .¹⁶ The potential utility of high-valent organomanganese compounds as synthetic reagents for the specific functionalization of organic compounds is under further investigation.

Acknowledgment. We thank the National Science Foundation (Grant CHE 85-21757), the Office of Naval Research under their Young Investigator Award Program, and Lubrizol for a fellowship to R.J.M. In addition, G.S.G. is the recipient of an A. P. Sloan Foundation Research Fellowship (1988–1990). We also thank Dr. Scott Wilson, Charlotte Stern, and Connie Odle of the University of Illinois X-ray Crystallographic Laboratory for carrying out the crystal structure determinations.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles for **1** and **3** (11 pages); tables of final observed and calculated structure factors for **1** and **3** (12 pages). Ordering information is given on any current masthead page.

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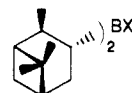
Enantioselective Ring Cleavage of *meso*-Epoxides with *B*-Halodiisopinocampheylboranes

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Asymmetric synthesis starting from *meso* compounds is an increasingly important method for the preparation of optically active compounds. Various chemical¹ and enzymatic² procedures have been utilized for such transformations. Surprisingly, not much attention has been given to the enantioselective ring cleavage of *meso*-epoxides that would lead to several classes of important compounds. We now report the synthesis of optically active 1,2-halohydrins using *B*-halodiisopinocampheylboranes, Ipc_2BX (**1a–c**).



1a: X = Cl
1b: X = Br
1c: X = I

The cleavage of carbon–oxygen bonds with boron reagents, in particular with trihaloboranes, is a well-documented and established procedure.³ However, the high Lewis acidity of trihaloboranes and their tridentate nature can result in the unwanted rupture of bonds in compounds containing other sensitive functional groups. To increase the selectivity in carbon–oxygen bond cleavage, monohaloboranes in which two of the halogens on boron are replaced by alkyl,⁴ alkoxy,⁵ thioalkyl,⁶ or nitrogen containing⁷ groups have recently been introduced. Such reagents indeed are selective and could by the proper choice of substituents cleave specific C–O bonds.⁷ Recently Guindon and co-workers reported⁴ the stereospecific ring cleavage of various cyclic ethers with *B*-bromodimethylborane. Of particular consequence in the cleavage of epoxides with these type of reagents is the fact that the halohydrin products are consistent with a predominantly S_N2 type mechanism proposed for such reactions.^{4,7,8} This suggests that the asymmetric version should proceed with a high degree of enantiotopic differentiation of the C–O bonds of suitable *meso*-epoxides. Recently, the enantioselective cleavage of cyclohexene oxide with thiols and azides in the presence of zinc or copper tartrates has been successfully accomplished.⁹ Except for this report, the cleavage of epoxides with chiral Lewis acids is an unexplored reaction. As part of our efforts in the field of asymmetric synthesis,¹⁰ we are currently exploring reactions involving boron based chiral Lewis acids. The present communication describes our investigations on the enantioselective ring opening of some *meso*-epoxides with *B*-halodiisopinocampheylboranes

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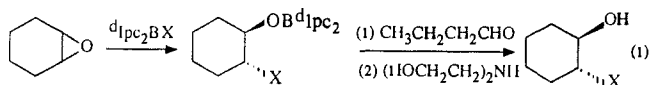
Table I. Optically Active 1,2-Halohydrins from *meso*-Epoxides and *B*-Halodiisopinocampheylboranes, ^dIpc₂BX^a

entry	epoxide	1,2-halohydrin	X	% yield ^b	bp, °C/mmHg or mp, °C	[α] _D ²³ ^c (c 5, CHCl ₃)	% ee ^c (1 <i>R</i> ,2 <i>R</i>)	abs config
1	cyclohexene oxide		Cl	70	75–80/15		22	<i>d</i>
2			Br	82	39–40	–26.9	84 (99) ^e	<i>f</i>
3			I	89	44–45	–31.6	91 (100) ^e	<i>g</i>
4	1,4-cyclohexadiene monoepoxide		Br	72	90–95/15	–42.0	63	<i>h</i>
5			I	75	37–38	–141.8	95 (100) ^e	<i>g</i>
6	cyclopentene oxide		I	63	65–70/0.5	–5.8	52	<i>c</i>
7	<i>cis</i> -2-butene oxide		Br	69	75–80/15	–3.4	61	<i>h</i>
8			I	67	80–85/15	–15.3	78	<i>h</i>
9	<i>cis</i> -3-hexene oxide		Br	71	90–95/15	+2.5	50	<i>h</i>
10			I	75	60–65/0.5	+11.8	69	<i>h</i>

^aThe superscript "d" indicates that the reagent is derived from (+)- α -pinene. ^bIsolated by column chromatography followed by crystallization, or bulb-to-bulb distillation. ^cAnalyzed as the corresponding acetates with Ni(HFB-1*R*-Cam)₂ capillary column. ^dBy analogy to the other examples. ^eOptical purity was upgraded by recrystallization from pentane. ^fBellucci, G.; Ingrosso, G.; Marioni, F.; Marsili, A.; Morelli, I. *Gazz. Chim. Ital.* 1974, 104, 69. ^gDetermined by X-ray crystallography. ^hElucidated through the corresponding dehalogenated product. See text.

(Ipc₂BX),¹¹ both enantiomers of which are readily available from either (+)- or (–)- α -pinene.

First we examined the reaction between cyclohexene oxide and ^dIpc₂BX (the superscript "d" indicates that the reagent is derived from (+)- α -pinene) under various conditions, i.e., temperature, solvent and molarity. Due to the labile nature of the products, a nonoxidative workup was developed (eq 1).

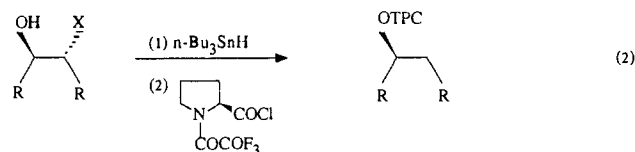


The course of the reaction was followed by ¹¹B NMR.¹² The reaction is very fast (<5 min) but proceeds with poor induction at 0 °C. Not surprisingly, an inverse relationship between enantiomeric excess (% ee) and the reaction temperature was found to exist. It was established that Ipc₂BCl, Ipc₂BBr, and Ipc₂BI require –78 °C/3 h, –100 °C/2 h, and –100 °C/0.5 h, respectively, to furnish good enantioselection. Furthermore, the reaction is independent of solvent or molarity. Since **1b** and **1c** provided superior results (at least in the case of cyclohexene oxide), we used these reagents subsequently for the preparation of optically active halohydrins (Table I).

In general [4.1.0]-oxaheptanes gave excellent initial optical yields of halohydrins.¹³ We also found that by simple recrystallization from pentane, these could be upgraded to products of essentially 100% ee. Cyclopentene oxide gave reduced chemical as well as optical yields. Simple acyclic epoxides were cleaved with optical inductions intermediate between those realized¹⁴ for

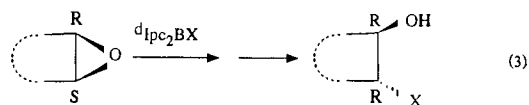
the oxides of cyclohexene and cyclopentene. The % ee of the halohydrins (as their acetates) was determined by using a chiral capillary GC column, Ni(HFB-1*R*-Cam)₂.¹⁵

The absolute configuration of the cyclic halohydrins was determined where possible by X-ray crystallography. The absolute configuration of the acyclic compounds was elucidated as follows in eq 2. Dehalogenation with tributyltin hydride gave the known



secondary alcohols¹⁶ which were analyzed as their TPC derivatives¹⁷ by using capillary GC. Since the *meso*-epoxides are opened in an antiperiplanar manner, determination of the absolute configuration of one asymmetric center establishes the configuration of the other as well.

Of particular significance of this procedure is the fact that in addition to high optical induction,¹⁸ the bond cleavage occurs in the same absolute sense to furnish (1*R*,2*R*)-halohydrins in all cases examined, with ^dIpc₂BX.¹⁹ These results are consistent with the cleavage occurring in an anti manner with inversion at the S carbon of the *meso*-epoxides (eq 3). In addition, closure of the



acyclic chiral non-racemic halohydrins yields the starting compounds, viz., a *cis*-epoxide, which would not be the case had the opening proceeded in a syn manner (eq 4).

In conclusion, the present methodology demonstrates the feasibility of cleaving *meso*-epoxides in an enantioselective manner either at the R or S carbon by selecting the appropriate chiral organoborane reagents. The transformation is general, providing

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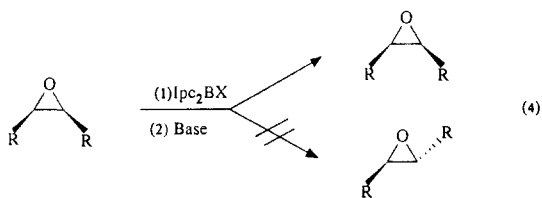
(19) The use of ^lIpc₂BX (derived from (–)- α -pinene) will obviously yield the corresponding (1*S*,2*S*)-halohydrins.

(11) Ipc₂BCl and Ipc₂BBr were prepared by passing HCl or HBr through a suspension of optically pure Ipc₂BH in pentane at 0 °C. Ipc₂BI was made by reaction with I₂. All the reagents were recrystallized and stored as stock solutions in pentane.

(12) The reaction is quenched with pyridine which coordinates with the unreacted haloborane (δ = 18–20 ppm) and not with the borinate (δ \approx 54 ppm) formed during the course of the reaction.

(13) The preparation of (1*R*,2*R*)-(-)-2-iodocyclohexanol: A 100-mL flask protected with a positive pressure of nitrogen was charged with Ipc₂BI (11 mmol, 0.25 M in pentane). The solution was cooled to –100 °C and treated dropwise with cyclohexene oxide (10 mmol) dissolved in pentane (2 mL). After the solution was stirred for 0.5 h at –100 °C, the reaction was quenched by the addition of butyraldehyde (1.8 mL, excess). The mixture was allowed to warm gradually to room temperature and stirred for an additional 1 h. By that time ¹¹B NMR indicated clean formation of boronate [R⁺OB(OEt)Ipc, δ = 31 ppm]. The reaction mixture was diluted with pentane (50 mL) and treated with diethanolamine (12 mmol, 4 M in THF). After the solution was stirred for 0.5 h, the precipitated boronate–diethanolamine complex was filtered off and the filtrate was washed with water and brine and dried over anhydrous Na₂SO₄. The solution was concentrated under reduced pressure, and the residue was purified by column chromatography followed by crystallization from pentane to provide the title compound (Table I, entry 3).

(14) No attempt was made to achieve optimum results.



highly valuable difunctionalized compounds in good to excellent enantiomeric purity from simple olefins. Synthesis of optically active halohydrins is but one of the many possible applications that we are currently exploring.

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Organometallic Chemical Vapor Deposition of III/V Compound Semiconductors with Novel Organometallic Precursors

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Compound semiconductors such as gallium arsenide (GaAs) and indium phosphide (InP) are important materials used in the fabrication of microelectronic and optoelectronic devices. Several techniques have been employed for the preparation of thin films of these materials, including organometallic chemical vapor deposition (OMCVD) and molecular beam epitaxy (MBE).¹ The OMCVD method is often preferred for larger scale processes and typically involves the reaction of a group III trialkyl such as Me₃Ga, with AsH₃ or PH₃ at elevated temperatures (600–700 °C) (eq 1).²



Apart from the potential environmental, safety, and health hazards of handling pyrophoric and toxic reagents under these conditions, the conventional OMCVD methodology also suffers from stoichiometry control problems, impurity incorporation (particularly carbon), and unwanted side reactions. Moreover, the high temperatures involved can promote interdiffusion of layers which prevents sharp heterojunctions from being achieved.

Attempts to grow superior films by modifications of the OMCVD process include low-pressure OMCVD,³ plasma-enhanced OMCVD,⁴ rapid thermal OMCVD,⁵ and hybrid MBE-

OMCVD systems.⁶ Several groups of workers have investigated the use of alternative sources of both the group III and group V components, e.g., Me₃P, Et₃P, *t*-BuPH₂,^{7,8} *t*-BuAsH₂,⁹ Et₂AsH,¹⁰ and group III triethyl derivatives.^{11,12} The use of adducts such as Me₃In·PEt₃ and Me₃In·NMe₃ has also been explored.¹³ Adducts are less air sensitive than their components and are thus easier to handle and purify. However, the donor-acceptor bonds in the adducts are generally considered to be relatively weak compared to the other bonds present (such as Ga–C or As–H).¹⁴ Ultimately these bonds have to be broken in order to form the III/V material. Dissociation of the adduct and loss of stoichiometry can occur, and typically excess PH₃ or AsH₃ is required for the production of good quality films.¹⁵

The ideal chemical solution to the problem is to cause the III–V bond to be as strong as, or stronger than, the other bonds in the molecule such that under film growth conditions the bonds between the group III and group V elements remain intact while the other bonds are broken. The obvious way to strengthen the III–V interaction is to replace the donor-acceptor linkage by a two-center, two-electron bond. Our initial studies have therefore focussed on the design and synthesis of organometallic molecules which feature σ bonding between the group III and group V elements.¹⁶ A further objective was to lower the deposition temperature by employing substituents that undergo facile hydrocarbon elimination.

We have found that compounds of type 1 are excellent single source precursors for the preparation of III/V compound semiconductor materials such as GaAs and InP under relatively mild conditions. A typical example is the use of [Me₂Ga(μ -*t*-Bu₂As)]₂ as the single source for the production of GaAs films. Film growth conditions involve the use of a cold-wall reactor, H₂ or He as the carrier gas, maintenance of the saturator containing the organometallic source at 130 °C, substrate temperatures of 450 to 700 °C, and a total system pressure of 1 × 10⁻⁴ to 10 Torr.

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