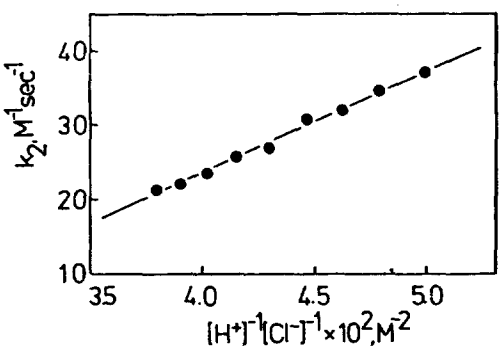

Figure 2. [HCl] and [Cl^-] dependence of second-order rate constants for dimerization of $MoOCl_5^{2-}$ at 5°C. [$MoOCl_5^{2-}$] = 3.10 × 10^{-3} M, [Cl^-] = 6.0M.

$$-d[MoOCl_5^{2-}]/dt = k_2[MoOCl_5^{2-}]^2 = k[HCl]^{-1}[Cl^-]^{-1}[MoOCl_5^{2-}]^2 \quad (1)$$

From equation (1) $k_2 = k[HCl]^{-1}[Cl^-]^{-1}$. A straight line of Figure 2 gives k to be negative first-order function of $[HCl]^{-1}$ and $[Cl^-]^{-1}$, respectively.

The form of the rate equation (1) is consistent with the following mechanism.

$$MoOCl_5^{2-} + H_2O \overset{K_1}{\rightleftharpoons} MoOCl_4(H_2O)^- + Cl^-$$

$$MoOCl_4(H_2O)^- + MoOCl_5^{2-} \overset{K_2}{\rightleftharpoons} Cl_4Mo(O)-OH-Mo(O)Cl_5^{4-} + H^+ \quad (I)$$

$$I + H_2O \overset{k}{\rightarrow} Cl_4Mo(O)-OH-Mo(O)Cl_4(H_2O)^{3-} + Cl^- \quad (II)$$

$$II + H_2O \overset{fast}{\longrightarrow} Cl_4Mo(O)-(OH)_2-Mo(O)Cl_4^{4-} + H^+$$

Rate determining step is process of the formation of the aqua complex by displacement of second water coordinated to molybdenum of I. If K_1 and K_2 were small, then rate = k[I] = $k K_1K_2$ [$MoOCl_5^{2-}$]^2 [HCl]$^{-1}$ [Cl^-]$^{-1}$ and $k_2 = k K_1K_2$.

Although the final product is not isolated as crystals from solutions we are considered that predominant compound in 6M hydrochloric acid is bis-(μ-hydroxooxomolybdenum(V)), Mo(O)-$(OH)_2$-Mo(O) known as paramagnetic dimer. There is ample evidence for di-μ-hydroxo dimeric M-$(OH)_2$-M with certain transition metals.[8]

Mechanisms of these reactions deserve further attention and should be the subject of future investigations.

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A Synthesis of 1,2-O-Isopropylidene-(S)-Glyceraldehyde

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1,2-O-Isopropylidene-(S)-glyceraldehyde(**1**) and 1,2-O-isopropylidene-(R)-glyceraldehyde(**2**) (Figure 1) have been extensively used as chiral starting materials for the synthesis of optically active natural products.[1] The (R)-enantiomer, 1,2-O-isopropylidene-(R)-glyceraldehyde(**2**) is readily available from inexpensive natural D-mannitol.[2] However, the (S)-enantiomer(**1**) was prepared from unnatural L-mannitol or L-arabinose in several steps.[3] Recently, the synthesis of (S)-enantiomer (**1**) from L-galactono-1,4-lactone[4] and L-tartaric acid[5] has been reported. Now we wish to report an asymmetric synthesis of (S)-enantiomer(**1**) from readily available allylic alcohol (Scheme 1).

Sharpless' (+)-tartrate-mediated asymmetric epoxidation[6] of allyl alcohol afforded (S)-epoxyalcohol(**3**),[7] which was directly used for the next step without further purification. The crude epoxide(**3**) was treated with thiophenol and NaOH (reflux, 3h) to give (S)-1-(phenylthio)-2,3-propanediol(**4**). Recrystallization from petroleum ether gave the diol(**4**)[8] as a white solid(71%). Isopropylidination of the diol(**4**) was effected with 2,2-dimethoxypropane and D-camphorsulfonic acid to give phenylthio acetonide(**5**)[8] in 95% yield, which was separated by flash chromatography using 20% ether-hexane as eluents(Rf 0.62). The phenylthio compound(**5**) was oxidized with m-chloroperoxybenzoic acid to give the sulfoxide(**6**)[8] in 89% yield, which was separated by flash chromatography

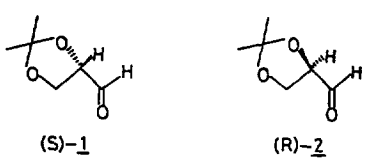
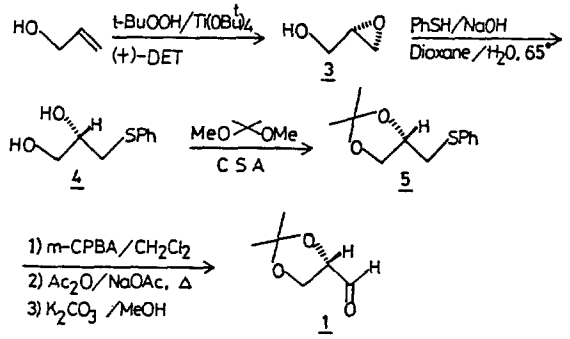


Figure 1.



Scheme 1.

using 25% hexane-ether as eluents(Rf 0.26). The sulfoxide(**6**) was subjected to Pummerer rearrangement[9] (Ac_2O/NaOAc, reflux, 11h) and purified on TLC plate (eluted with 25% ether-hexane, Rf 0.37) to give the α-acetoxy sulfide(**7**)[8] in 81% yield. Treatment of α-acetoxy sulfide(**7**) with K_2CO_3/MeOH (reflux, 2h) afforded 2,2-dimethyl-1,3-dioxolane-4-carboxaldehyde, the (S)-enantiomer(**1**)[8]; bp45-47°C/15mmHg (lit.,[2] bp40.5-41.5°C/11mmHg); $[\alpha]_D^{20}$ -19.6°(c=0.34, MeOH). The compound synthesized was identical in all respects (TLC, IR, NMR, MS) with the compound reported in the literature.

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7. In the reference 6(a), Sharpless reported that allyl alcohol afforded 2(S)-glycidol, ca 15% yield, 73% ee performed at 0°C by using (+)-diisopropyl tartarate and $Ti(OiPr)_4$.
8. Satisfactory physical properties and spectroscopic data(^{1}H-NMR, IR, MS) were obtained for the compounds: diol(**4**); mp 61-64°C; TLC Rf 0.31(20% hexane-ether); IR(KBr, pellet) 3410, 3060, 1585, 1485cm^{-1}; ^{1}H-NMR(80 MHz, $CDCl^3$)δ 3.13(1H), 3.23(1H), 3.53(3H,m), 7.2-7.4(5H,m); MS 184(M^+), 109(Base). Phenylthio acetonide(**5**); IR(NaCl, neat) 3060, 1585, 1480cm^{-1}; ^{1}H-NMR δ 1.42 (3H,s) 1.43 (3H,s), 3.15 (2H,d), 3.73-4.45 (3H, m), 7.23-7.38 (5H,m). Sulfoxide(**6**); IR(NaCl, neat) 3060, 1585, 1050cm^{-1}; ^{1}H-NMR δ 1.42 (3H,s), 1.44 (3H,s), 2.95-3.10 (2H,d), 3.67-4.35 (3H,m), 7.23-7.38(5H,m). α-acetoxy sulfide(**7**); IR(NaCl, neat) 3060, 1735, 1585, 1190 cm^{-1}; ^{1}H-NMR δ 1.34(3H,s), 1.42(3H,s), 2.10(3H,s), 3.85-4.35(3H,m), 5.91-6.15(1H,d), 7.25-7.61(5H,m). (S)-enantiomer(**1**); IR(NaCl, neat) 2850, 2750, 1725 1180 cm^{-1}; ^{1}H-NMR δ 1.35 (3H,s), 1.46 (3H,s), 4.01-4.18 (2H,d), 4.24-4.39 (1H,m), 9.85 (1H,s).
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Selective Hydroboration of Alkenes and Alkynes with Thexyl-2-butoxyborane in the Presence of Ketones

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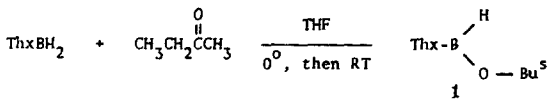
Various borane derivatives hydroborate alkenes and alkynes to produce organoboranes.[1] However these reagents also react fast with ketones.[2] Thus, in the presence of ketones, selective hydroborations of alkenes and alkynes, to our best knowledge, have never been achieved.

Recently, thexyl-2-butoxyborane, **1**, was prepared from the reaction of thexylborane ($ThxBH_2$) with an equimolar amount of 2-butanone (eq 1).



^{11}B nmr spectrum of **1** shows a doublet (J_{B-H}=146 Hz) at δ=50.6 ppm, whereas ^{11}B nmr chemical shift of $ThxBH_2$ is known to be 24.0 ppm.[3] The ir spectrum of $ThxBH_2$[4] shows the bridge-hydrogen band at 1565 cm^{-1} and the terminal boron-hydrogen band at 2640 cm^{-1}. However their spectrum of **1** in THF shows no bridge hydrogen band, but only the terminal boron-hydrogen band at 2413cm^{-1}. Apparently **1** exists as a monomeric species.

In the study of the reducing characteristics of **1** for representative functional groups, we have found that this new reagent reacted with aldehydes, terminal alkenes and alkynes