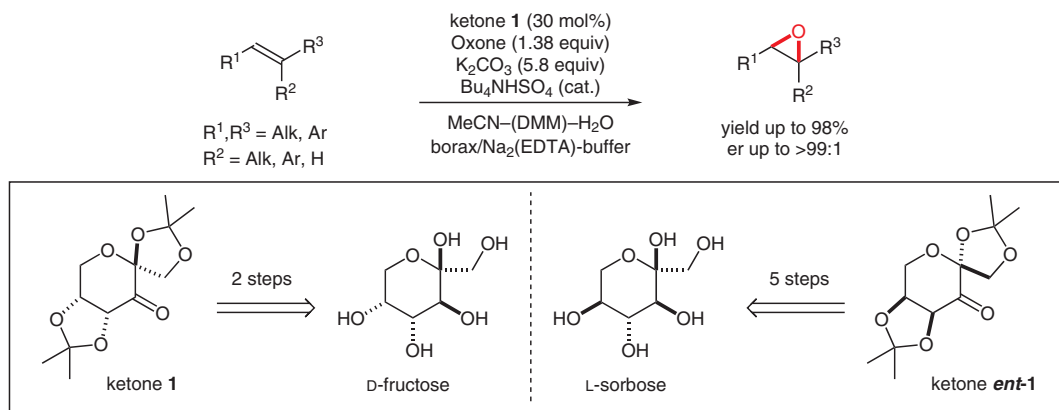


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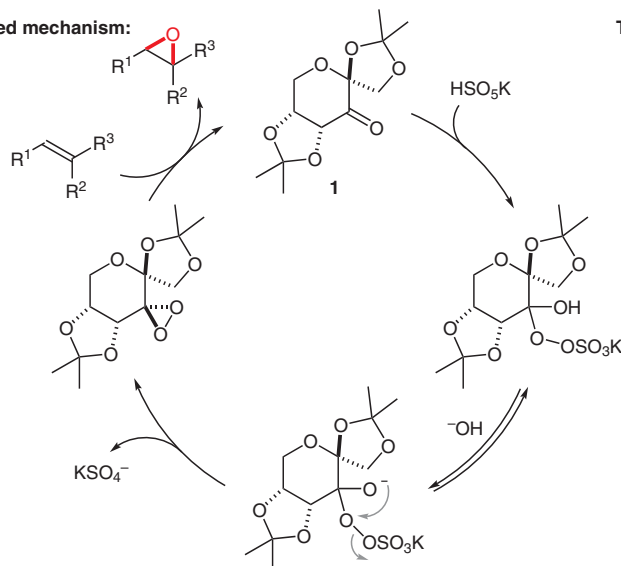
An Efficient Catalytic Asymmetric Epoxidation Method

*J. Am. Chem. Soc.* **1997**, *119*, 11224–11235.

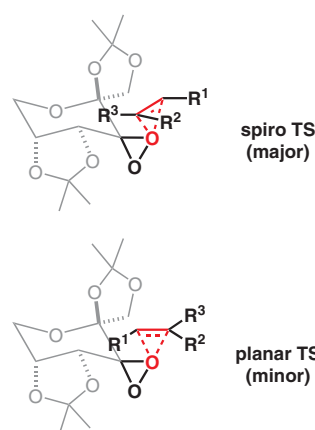
## The Shi Epoxidation



Proposed mechanism:



Transition-state model:



**Significance:** In the late 1990s, the research group of Shi developed the first general effective organic catalyst for the asymmetric epoxidation of nonactivated *trans*-olefins or trisubstituted olefins with potassium peroxomonosulfate (Oxone). Ketone **1** and its enantiomer **ent-1** are readily available from the inexpensive carbohydrates D-fructose and L-sorbose, respectively. Even though terminal olefins and *cis*-olefins are due to the lack of steric repulsion in the transition state unsuitable substrates in the Shi epoxidation, the method has found wide application in organic synthesis.

**Comment:** Deliberate tuning of the pH is necessary for the reaction to proceed without substantial decomposition of the catalyst through a Baeyer–Villiger oxidation. Thus, an elaborate solvent/buffer system (including metal salts) is required. However, in contrast to the Jacobsen or Sharpless methodologies, the Shi epoxidation does not use transition metals in its catalytic cycle. In addition, the authors developed a further variant that only requires hydrogen peroxide as the oxidant (*Tetrahedron Lett.* **1999**, *40*, 8721).

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