Thermodynamic Control Enables trans-Selective Isomerization of Vicinal Diols via Iridium Photocatalysis

**Significance:** The Wendlandt group reports a selective catalytic isomerization of cis-1,2-diols to trans-diequitorial-1,2-diols via photoredox catalysis. The use of Ph₃SiSH was found to be essential, as the nature of the silanethiol catalyst influenced the product distribution of the two isomers. The reaction was amenable to a variety of 1,2-diols and as well as mixtures of diastereomers, giving a single product isomer.

**Comment:** A series of mechanistic experiments revealed that, under the optimal conditions, the H-atom abstraction and donation steps were mediated by the Ph₃SiSH catalyst. The amine additive served as a base, not as a H-atom abstractor. The authors conclude that since the H-atom abstraction process is reversible, the equilibrium ratio represents the thermodynamic product distribution of the isomers.

**Selected examples:**

- 51% yield
- 68% yield
- 80% yield
- 73% yield
- 57% yield

**Carbohydrate-derived examples:**

- D-anhydrogalactose
- D-anhydrogulose 82% yield
- L-digitoxoside
- L-olivoside 73% yield

**Example from mixture of cis-diols:**

\[ \text{OTMS} + \text{OTMS} \rightarrow \text{OTMS} \]

\[ \text{dr} = 1.4:1 \]

*major diastereomer not identified

\[ \text{69% yield} \]