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 Ph$_3$SiSH 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 Ph$_3$SiSH 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.

**Synthetic Examples:**

- **Carbohydrate-derived examples:**
  - D-anhydrogalactose (82% yield)
  - D-anhydrogulose (82% yield)
  - L-digitoxoside (73% yield)
  - L-olivoside (73% yield)

- **Example from mixture of *cis*-diols:**
  - **OTMS** + **OTMS**
  - *dr* = 1.4:1
  - *major diastereomer not identified*
  - 69% yield

**Mechanism:**

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\text{MeCN, 456 nm LED} \quad \text{(Ir-PC)} (1 \text{ mol%}) \quad \text{DABCO (10 mol%)} \quad \text{Ph}_3\text{SiSH (30 mol%)} \quad \text{r.t.}
\]

\[
\text{Ir-PC} \quad \text{(Ir}[d\text{F(CF}_3\text{)ppy}\text{]}_2\text{dtbbpy})\text{PF}_6
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