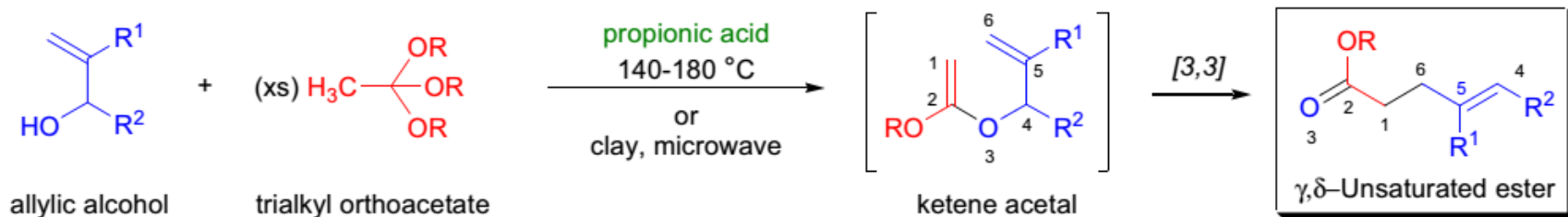


JOHNSON-CLAISEN REARRANGEMENT

—REPORTED BY W.S. JOHNSON

JOHNSON-CLAISEN REARRANGEMENT



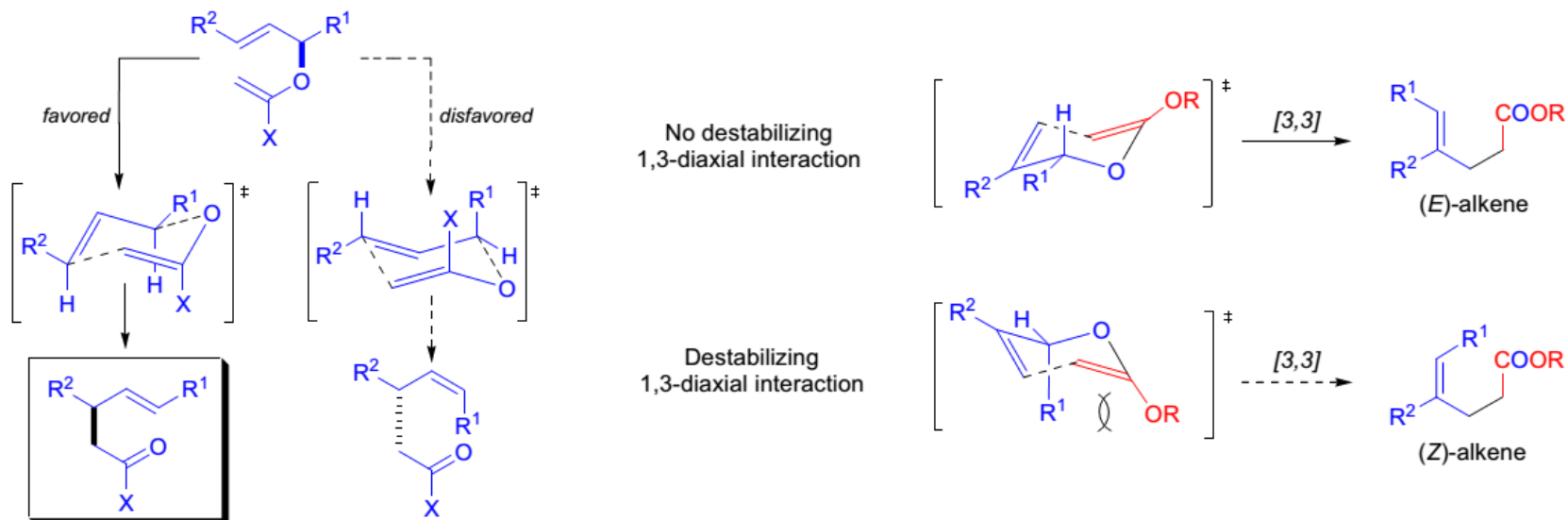
In 1970, W.S. Johnson reported a reaction in which allylic alcohols were heated in the presence of excess triethyl orthoacetate under weakly acidic conditions (e.g., catalytic amounts of propionic acid). The initial product was a ketene acetal that underwent a facile [3,3]-sigmatropic rearrangement to afford γ,δ -unsaturated esters. This method is a modification of the original Claisen rearrangement, and is referred to as the **Johnson-Claisen- or ortho ester Claisen rearrangement**.

IMPORTANCE

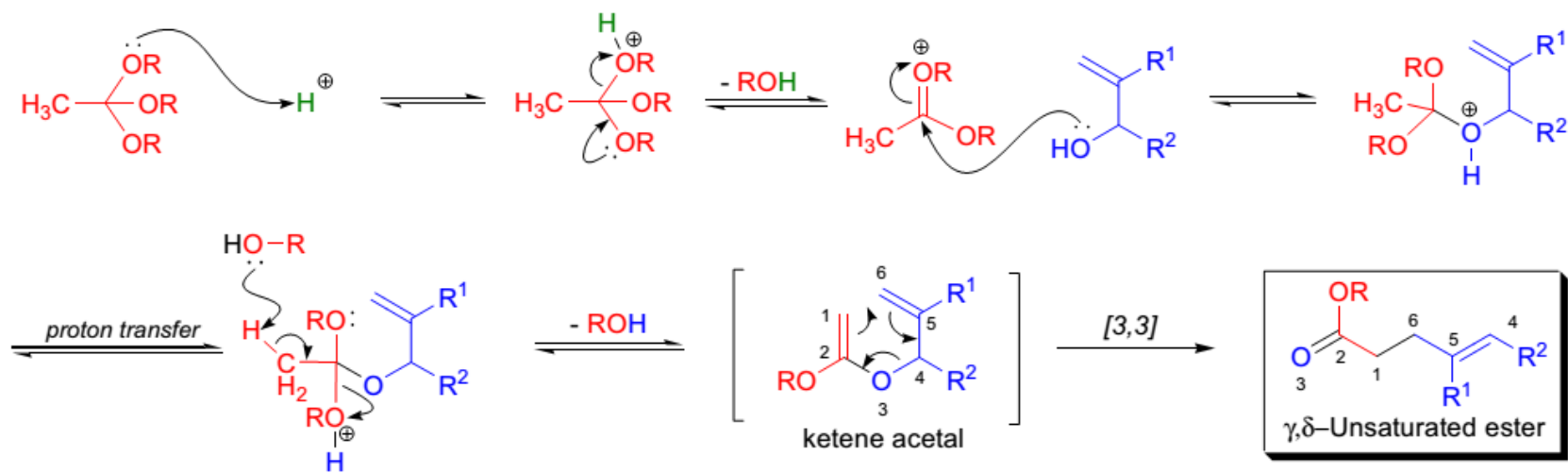
The reaction is highly stereoselective and is well-suited for the synthesis of trans-disubstituted olefinic bonds.

The temperature required for transformation is usually 100-180 °C. The rearrangement can be significantly accelerated by clay-catalyzed microwave thermolysis.

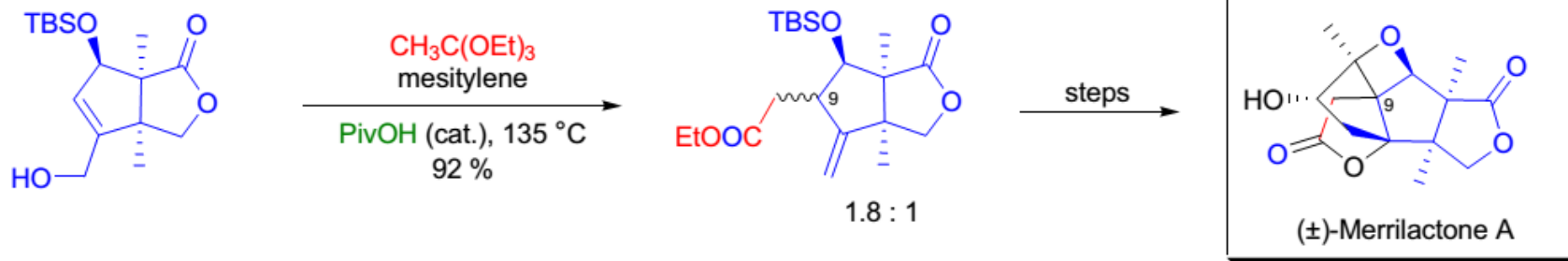
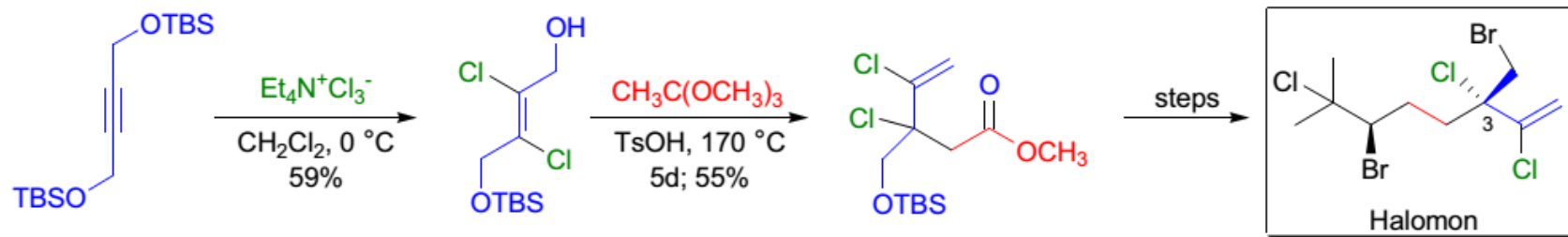
The Johnson-Claisen rearrangements of secondary allylic alcohols proceed with high (E)-selectivity due to the destabilizing 1,3-diaxial interactions in the transition state, which would lead to the (Z)-isomer.



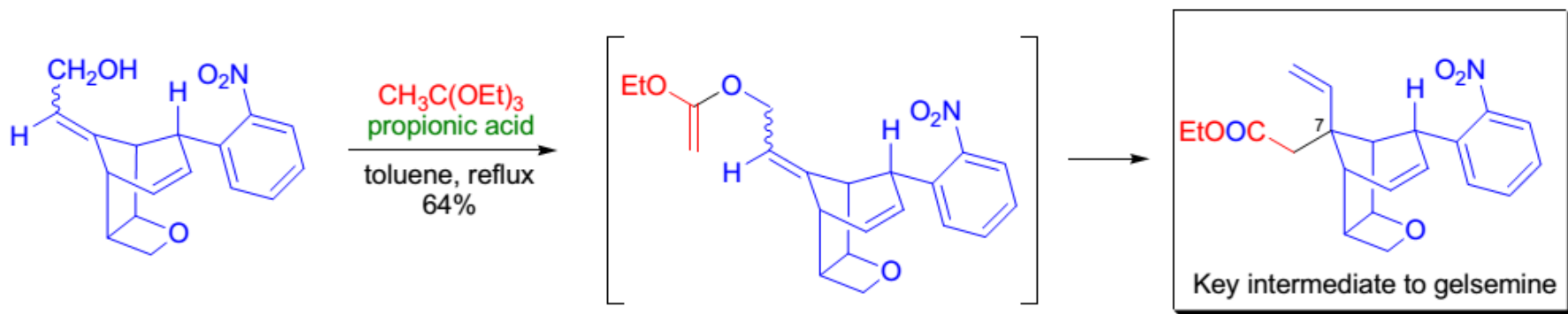
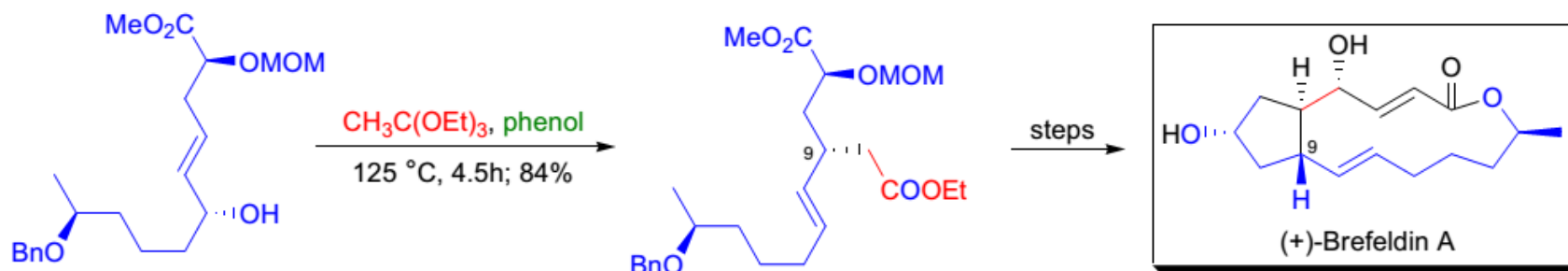
MECHANISM



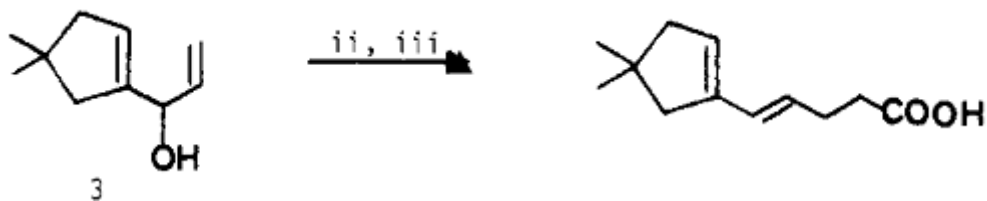
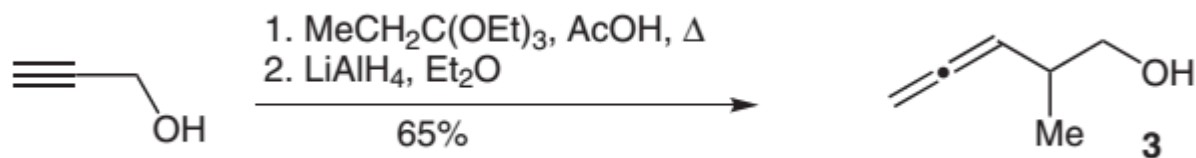
SYNTHETIC APPLICATIONS



SYNTHETIC APPLICATIONS



SYNTHETIC APPLICATIONS



Thanks