

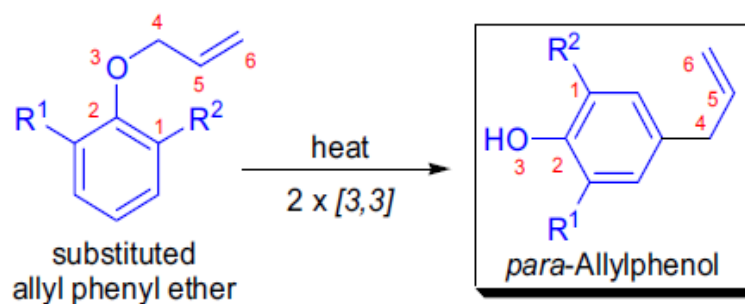
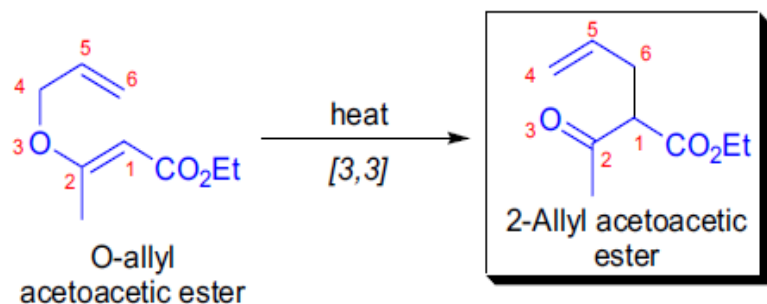
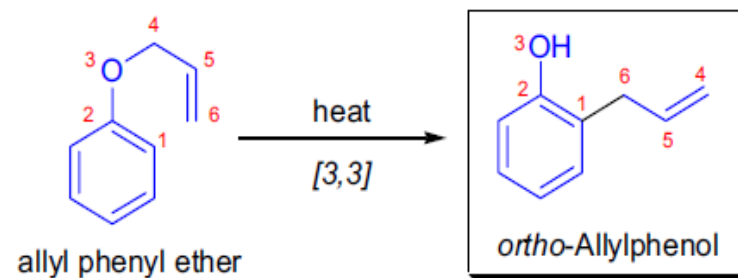
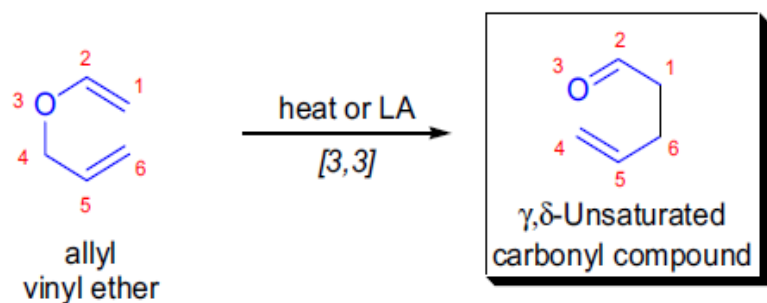
OVERMAN REARRANGEMENT

Yao Hantian

2017.4.10

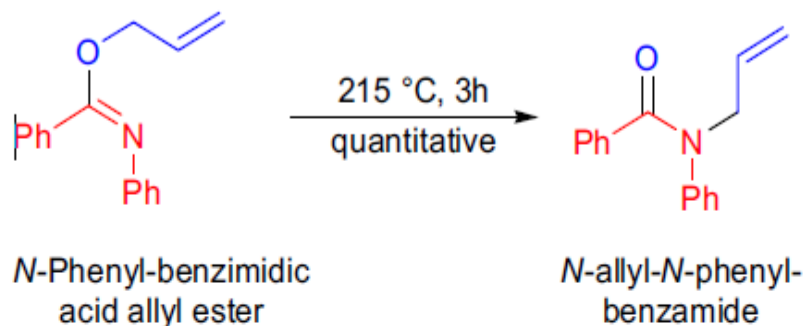
Discovery

- **Claisen rearrangement (1912).**

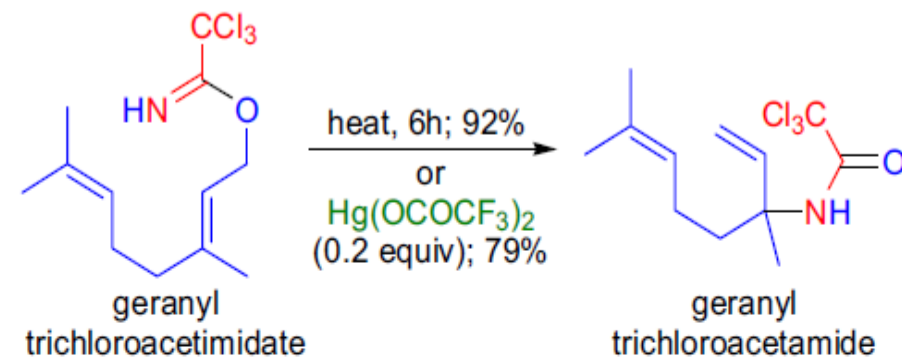


Discovery

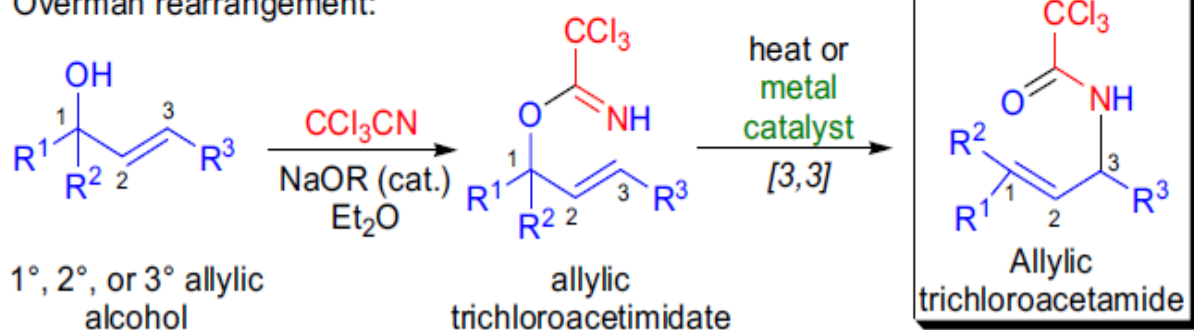
Mumm & Moller (1937):



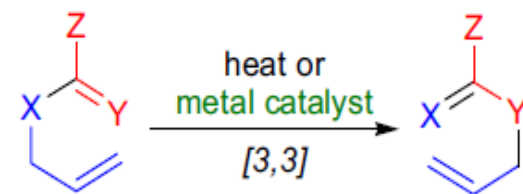
Overman (1974):



Overman rearrangement:



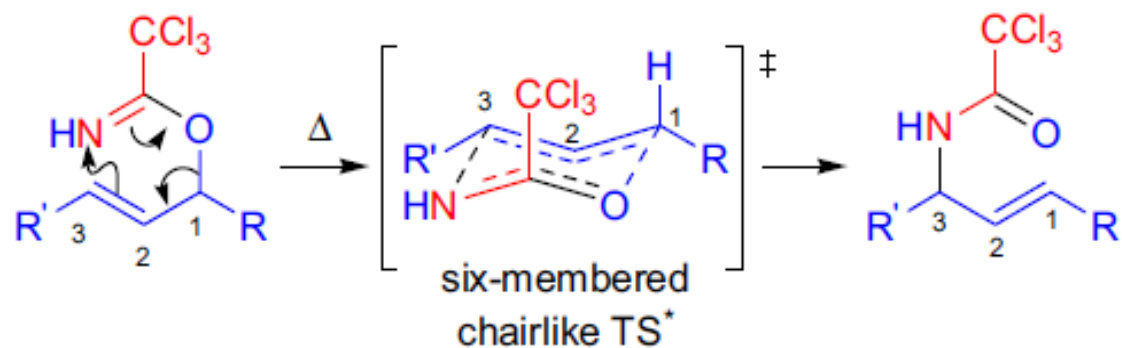
Claisen-type rearrangements:



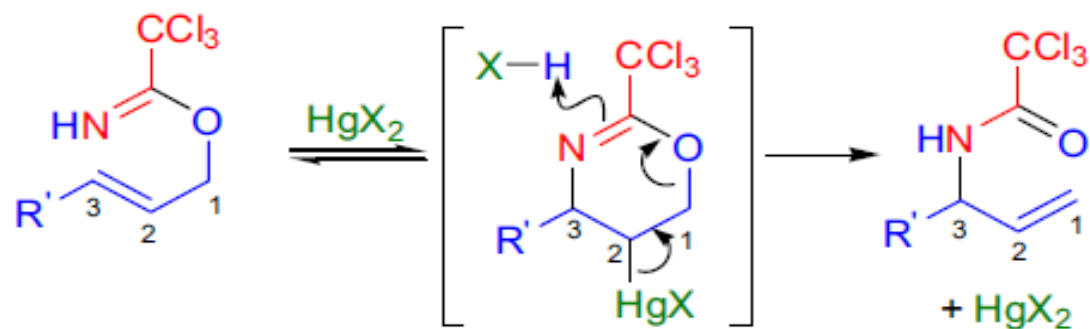
R^{1-3} = H, alkyl, aryl; metal catalyst: $\text{Hg}(\text{OCOCF}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, $\text{Pd}^{(II)}$ -salts; X = O, S, *N*-alkyl, *N*-aryl; Z = CCl_3 ; Y = NH, *N*-alkyl, *N*-aryl

Mechanism

Mechanism of the thermal rearrangement:



Mechanism of the $\text{Hg}^{(\text{II})}$ -catalyzed rearrangement:



General features

- The allylic trichloroacetimidates are easily prepared in almost quantitative yield by reacting allylic alcohols with trichloroacetonitrile in the presence of catalytic amounts of base (e.g., NaOR, KOR, DBU);
- The rearrangement is completely regiospecific, therefore no trichloroacetamide product with an unrearranged carbon skeleton is formed;
- A high level of stereoselectivity and preferentially the (*E*)-alkenes are formed;

General feature

- The metal catalysis, however, usually works well only for imidates derived from 3-substituted primary allylic alcohols and in all other cases the thermal conditions are preferred;
- The reaction is irreversible, which is the result of the significant driving force associated with the formation of the amide functionality.

Synthetic applications

