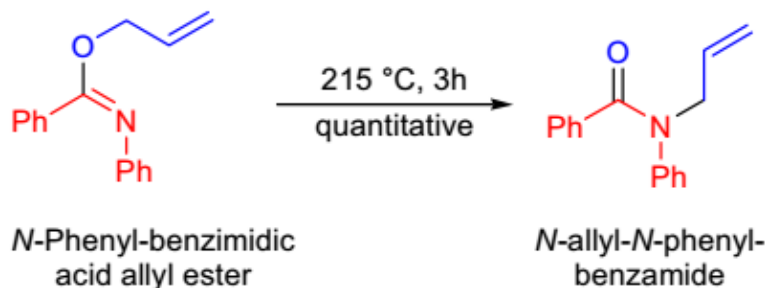


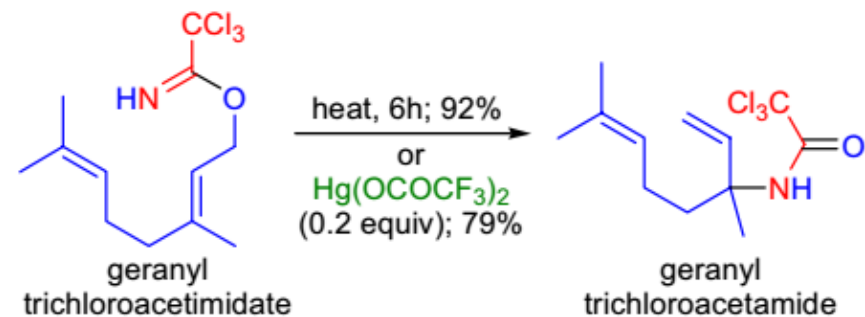
OVERMAN
REARRANGEMENT

Discovery of Overman Rearrangement

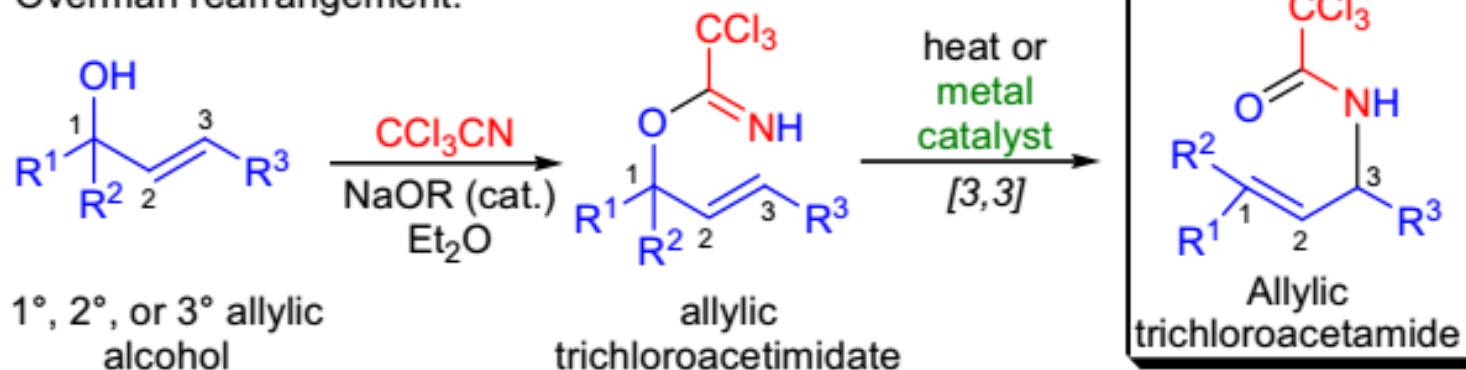
Mumm & Moller (1937):



Overman (1974):



Overman rearrangement:

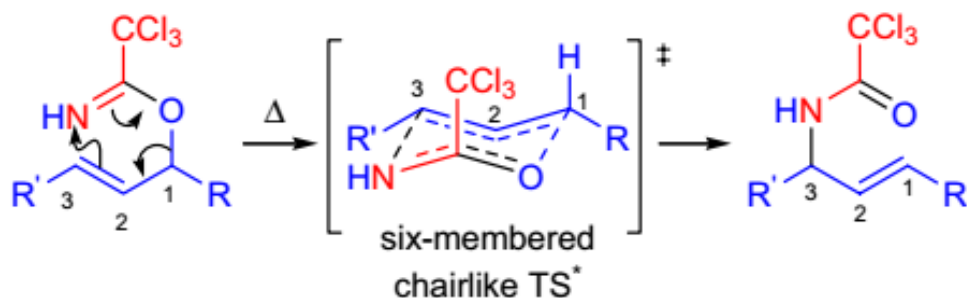


R^{1-3} = H, alkyl, aryl; metal catalyst: $\text{Hg}(\text{OCOCF}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, $\text{Pd}^{(\text{II})}$ -salts;

The 1,3-transposition of alcohol and amine functionalities via the [3,3]-sigmatropic rearrangement of allylic trichloroacetimidates is known as the Overman rearrangement.

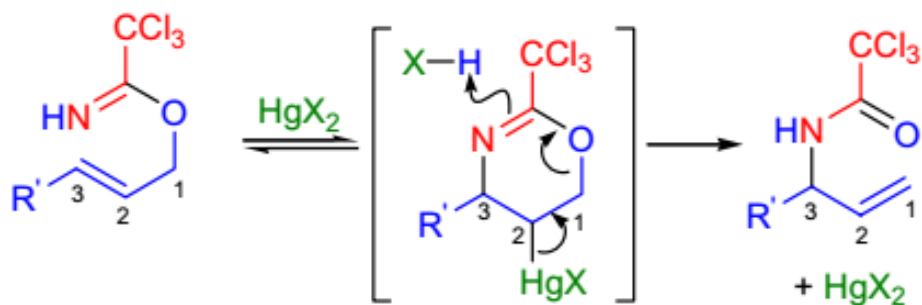
Mechanism of Overman Rearrangement

Mechanism of the thermal rearrangement:



Similarly to the mechanism of the Claisen rearrangement, the Overman rearrangement is a suprafacial, concerted, nonsynchronous [3,3]-sigmatropic rearrangement

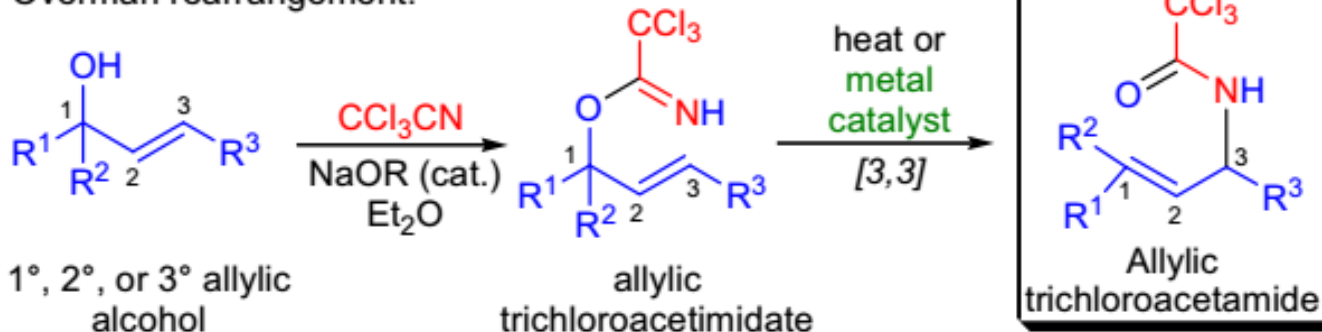
Mechanism of the Hg^(II)-catalyzed rearrangement:



The mechanism of the metal catalyzed reaction is believed to proceed via an iminomercuration deoxymercuration sequence and it is only formally a [3,3]-sigmatropic shift

Features of Overman Rearrangement

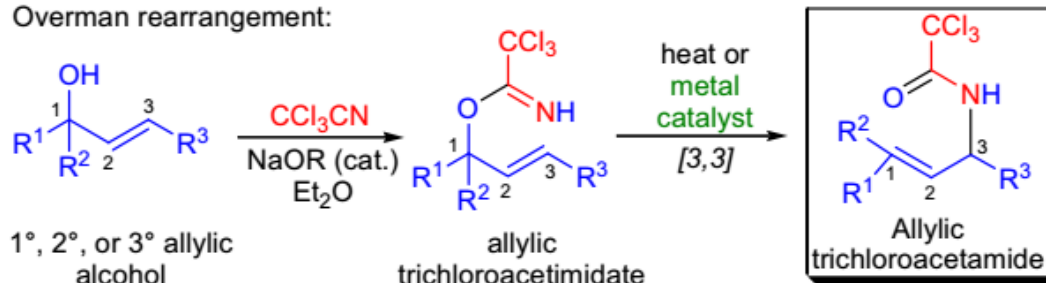
Overman rearrangement:



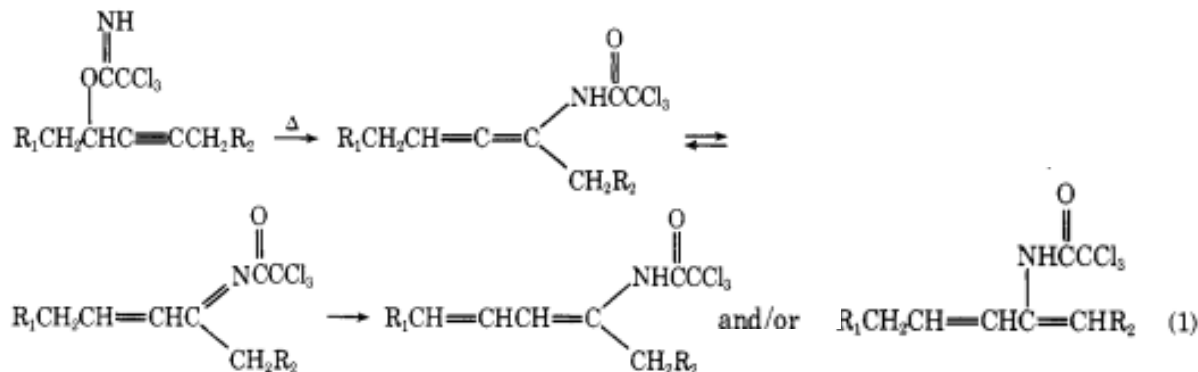
- 1) heating the crude trichloroacetimidates in a solvent (e.g., xylenes) usually between 25-140 ° C for several hours or exposure to certain metal catalysts results in a [3,3]-sigmatropic rearrangement;
- 2) the allylic trichloroacetamides can be hydrolyzed under basic conditions (3M NaOH solution at room temperature) to afford the corresponding allylic amines;
- 3) the rearrangement of trichloroacetimidates derived from secondary allylic alcohols proceeds with a high level of stereoselectivity and preferentially the (E)-alkenes are formed;
- 4) the metal catalysts are usually Hg(II)-salts, which are used in 10-20 mol% quantities and the mercury(II)-salts can be removed from the product by flash chromatography or by complexation with pyridine or PPh₃;
- 5) 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;

Features of Overman Rearrangement

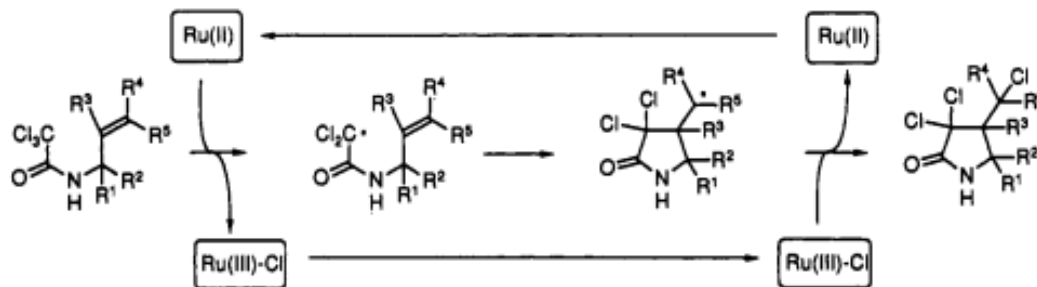
Overman rearrangement:



- 6) propargylic trichloroacetimidates rearrange to give trichloroacetamido-1,3-dienes;
 7) the trichloroacetamide functionality can be used as a radical precursor or transformed into acylureas or guanidine derivatives.



Scheme IV



Applications of Overman Rearrangement

