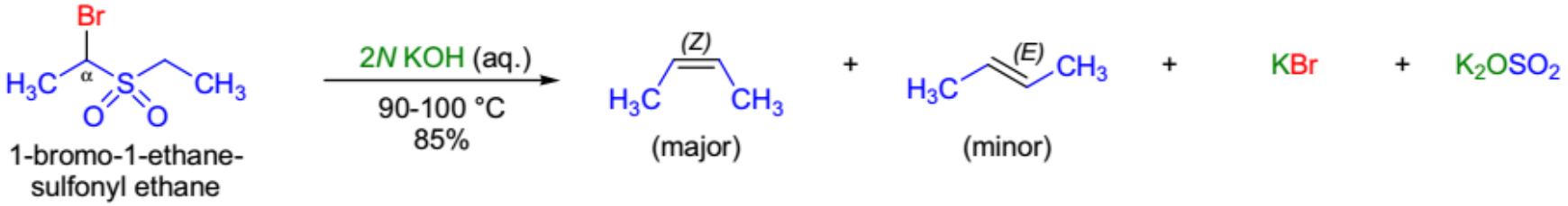
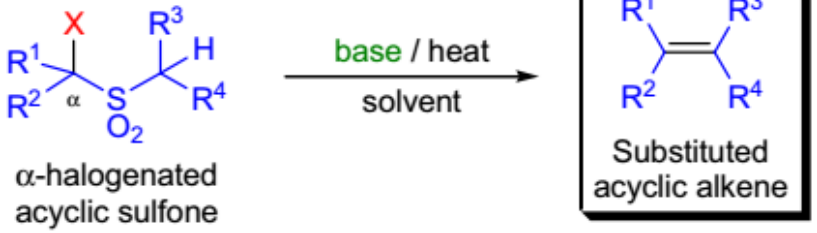
RAMBERG-BÄCKLUND REARRANGEMENT

Introduction to Ramberg-Bäcklund Rearrangement

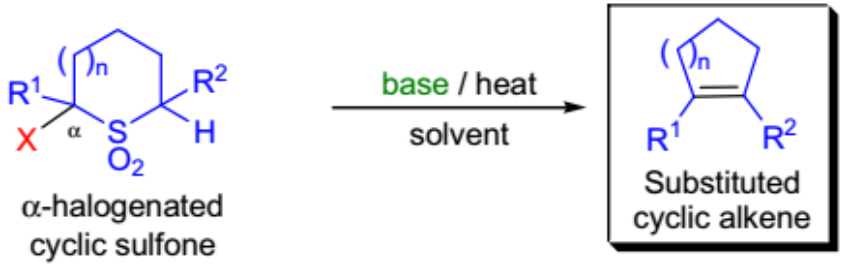
Ramberg and Bäcklund (1940):



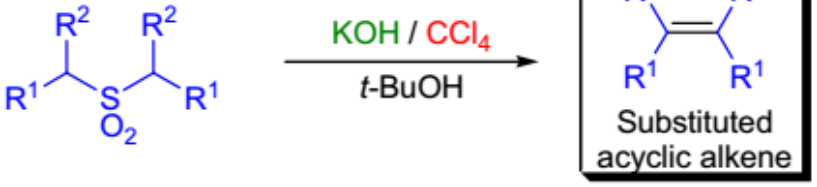
Rearrangement in acyclic systems:



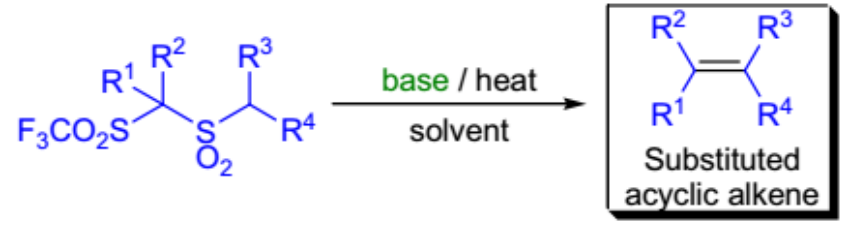
Rearrangement in cyclic systems (ring-contraction):



Meyers modification (*in situ* halogenation):



Hendrickson modification (triflinate leaving group):

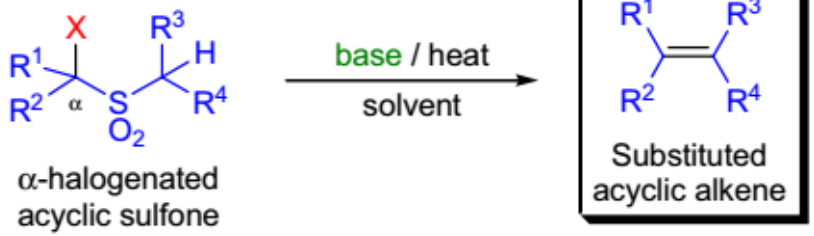


$R^{1\text{-}4}$ = H, alkyl, aryl, heteroaryl, CO_2R; n = 0-12; X = Cl, Br, I, OTs; base: KOH, NaOH, KO*t*-Bu; solvent: THF, *t*-BuOH/DCM

The base-induced rearrangement of α-halogenated sulfones via episulfone intermediates to produce alkenes is referred to as the Ramberg-Bäcklund rearrangement.

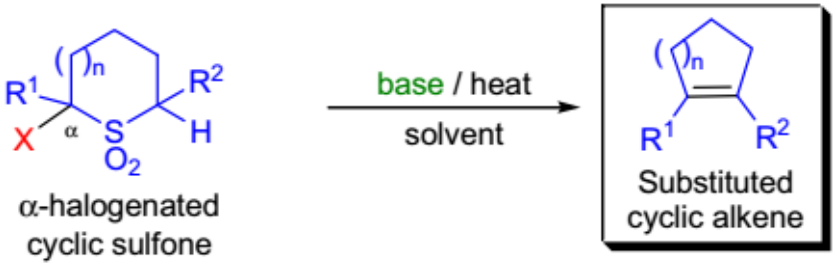
Features of Ramberg-Bäcklund Rearrangement

Rearrangement in acyclic systems:



α-halogenated acyclic sulfone

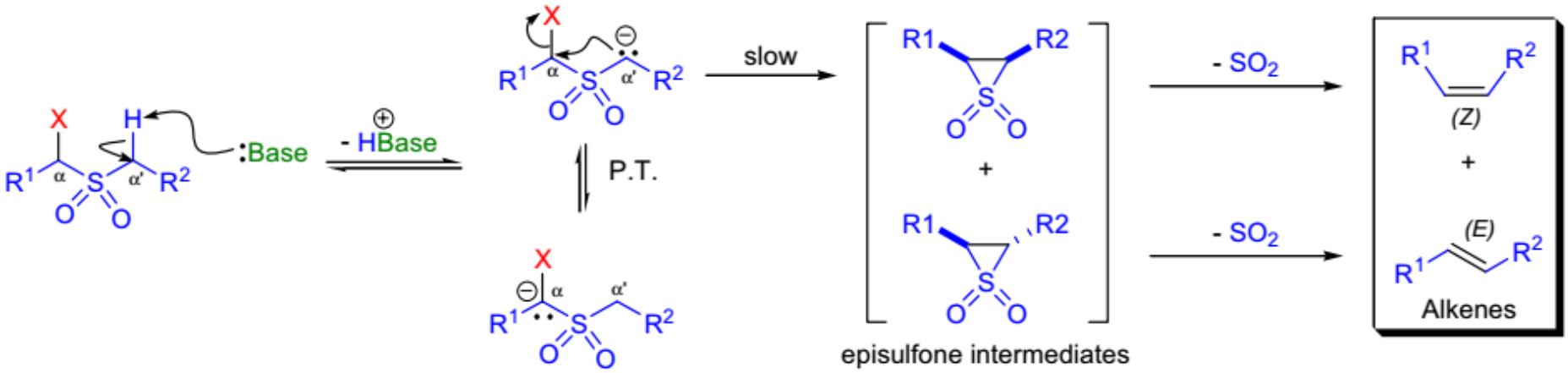
Rearrangement in cyclic systems (ring-contraction):



α-halogenated cyclic sulfone

1) the precursor halogenated sulfones can be easily prepared by the halogenation of the corresponding sulfones and the sulfones themselves are usually prepared by the oxidation of sulfides;
2) the reaction is well-suited for the preparation of 1,1- or 1,2-di, tri-, and tetrasubstituted alkenes;
3) the position of the newly formed double bond is unambiguous and under the reaction conditions no double bond migration takes place;
4) both acyclic and cyclic substrates can be used and the reaction is especially useful for the preparation of strained cycloalkenes *via* ring-contraction;
5) the stereochemical outcome of the rearrangement depends on both the base and the solvent, but the temperature is not decisive;
6) aqueous base (e.g., KOH) favors the formation of (Z)-alkenes but strong bases in aprotic solvents (e.g., KO*t*-Bu/DMSO) predominantly give rise to (*E*)-alkenes;
7) base-sensitive functional groups need to be protected

Mechanism of Ramberg-Bäcklund Rearrangement



1) deprotonation of the sulfone at the α- or α'-position, which undergoes rapid equilibration;
2) only the carbanion at the α'-position results in an intramolecular displacement reaction (SN*i* attack) on the carbon bearing the X group to give the reactive intermediate episulfones (thiirane 1,1-dioxides), which are generally formed as mixtures of *cis*- and *trans* stereoisomers (slow step);
3) the final step is the loss of SO2 either thermally or under base catalysis to give a mixture of alkene stereoisomers.

Applications