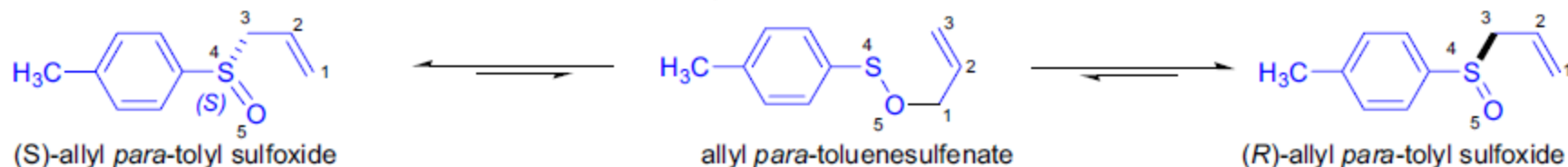


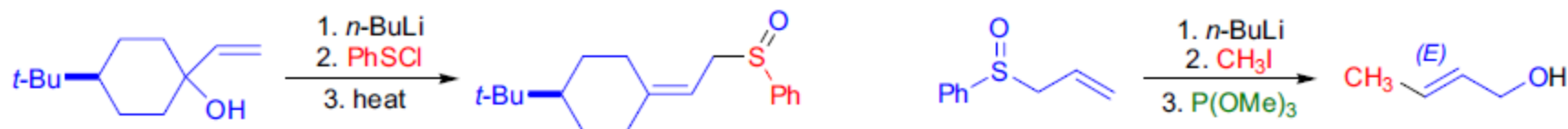
mislow-evans rearrangement



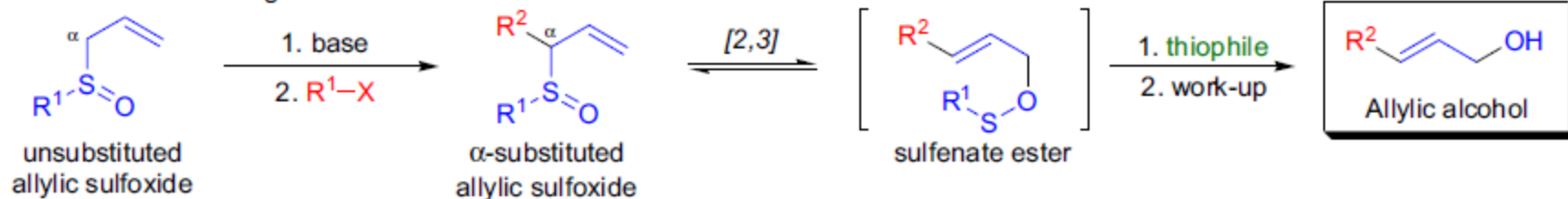
The thermal racemization of allylic sulfoxides (Mislow, 1968):



Conversion of allylic alcohols to allylic sulfoxides and allylic sulfoxides to allylic alcohols (Evans, 1971):

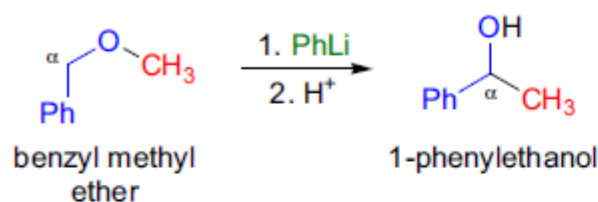


Mislow-Evans rearrangement:

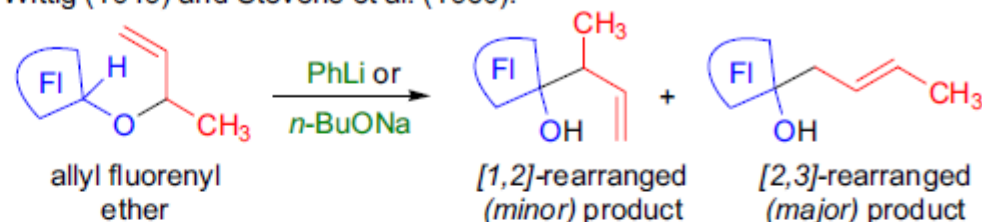


R^1 = alkyl, aryl; R^2 = alkyl, allyl, propargyl, benzyl; base: alkylolithiums, LDA; thiophile: PhSNa, P(OMe)₃, P(OEt)₃, P(NEt₂)₃, Et₂NH

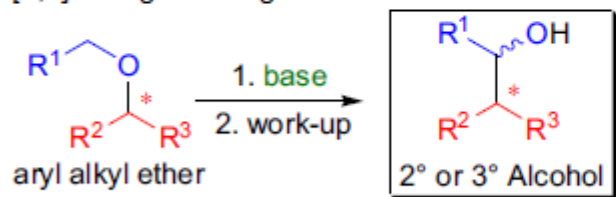
Wittig and Löhmann (1942):



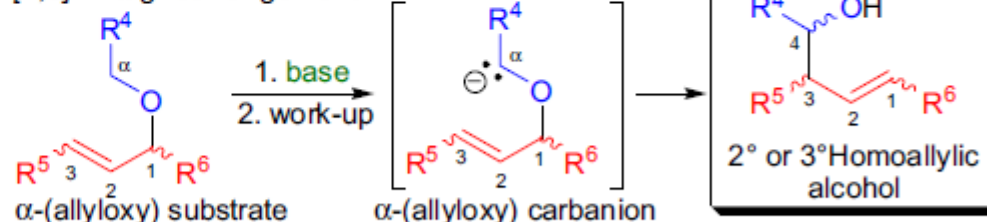
Wittig (1949) and Stevens et al. (1960):



[1,2]-Wittig rearrangement:

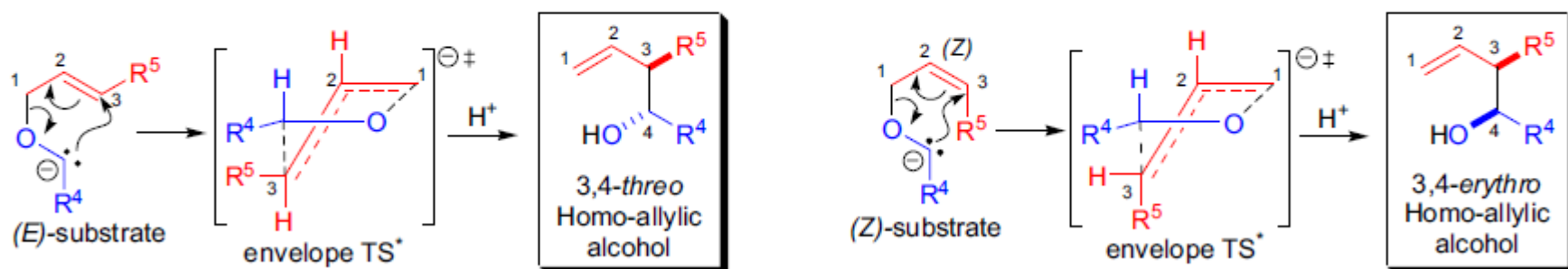


[2,3]-Wittig rearrangement:

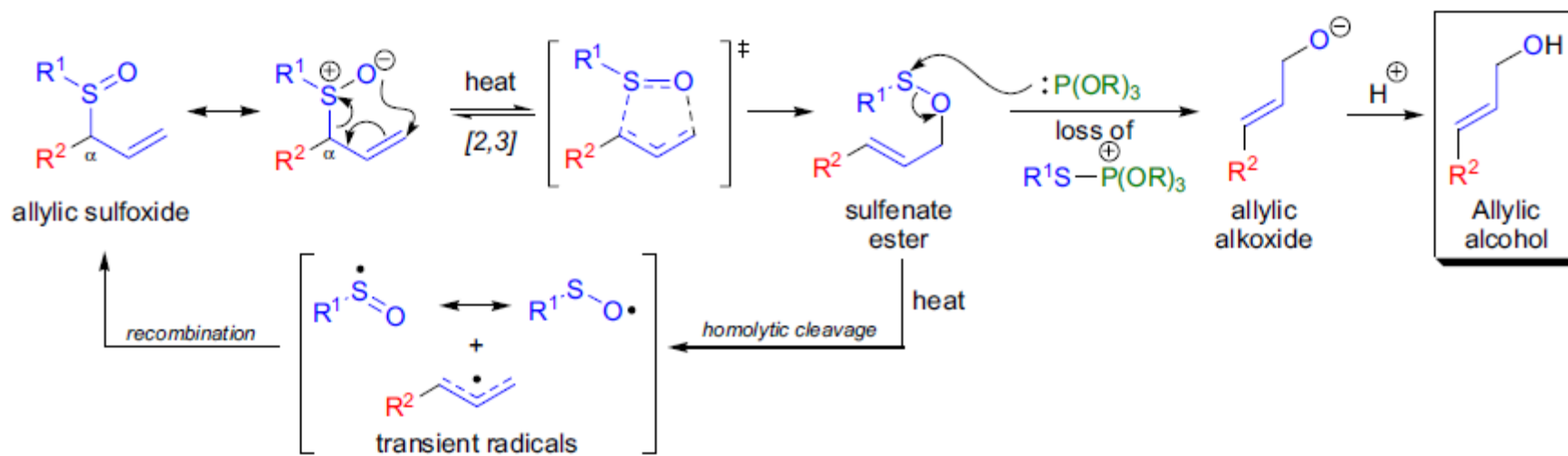


R^1 = aryl, alkenyl, alkynyl; R^{2-3} = H, alkyl; R^4 = carbanion stabilizing = aryl, alkenyl, alkynyl, COR, CN, CO₂R, CONR₂;
 when R^4 = SnR₃ (Still variant); R^{5-6} = H, alkyl; base: LDA, *n*-BuLi, PhLi, RO₂Li, NaNH₂/NH₃

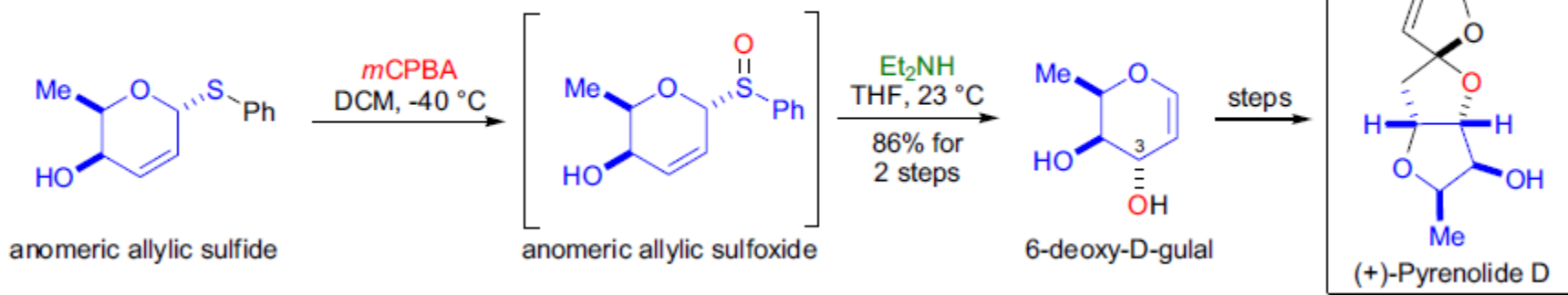
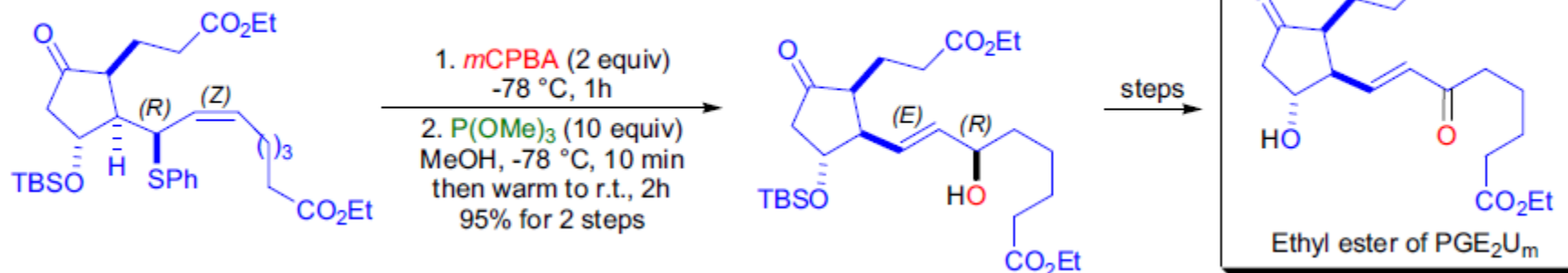
The [1,2]-Wittig rearrangement proceeds via a radical-pair dissociation-recombination mechanism, while the [2,3]-Wittig rearrangement is a concerted, thermally allowed sigmatropic process proceeding via an envelope-like transition state in which the substituents are pseudo-equatorial.



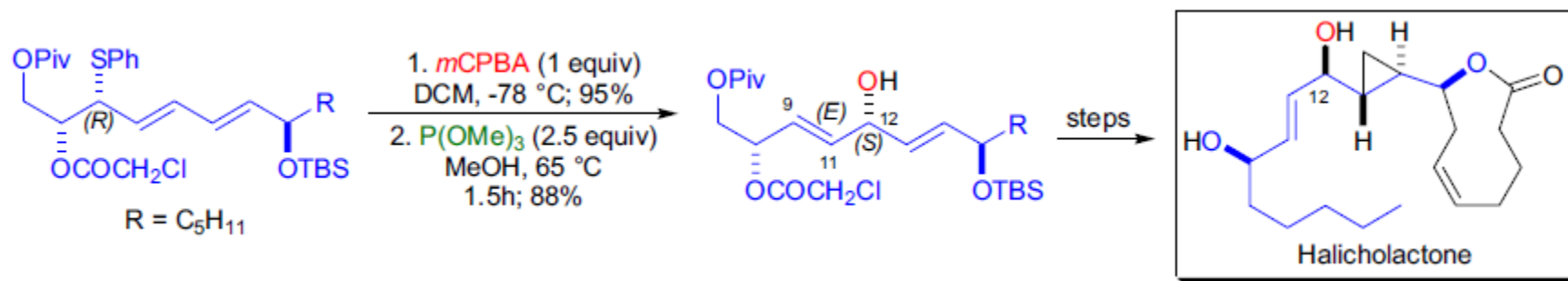
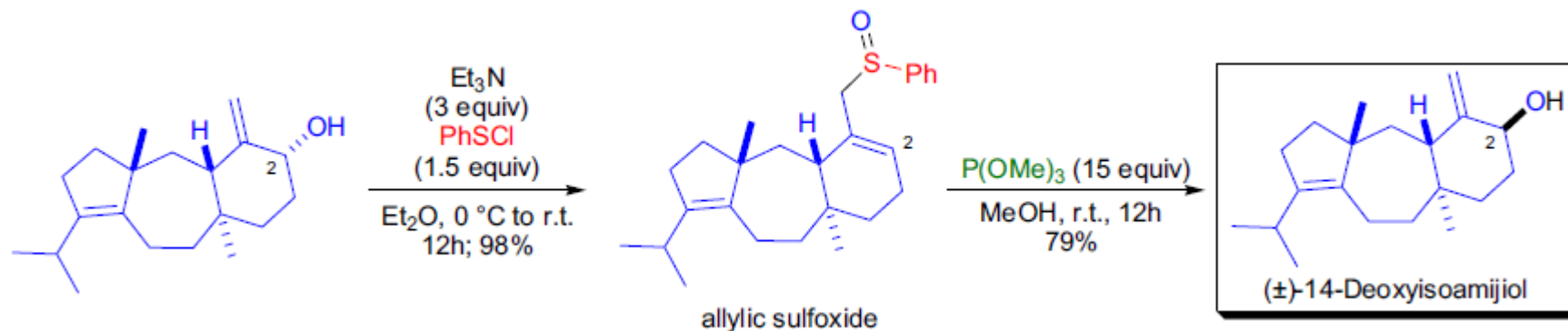
Mechanism



Synthetic Applications



Synthetic Applications





Thanks