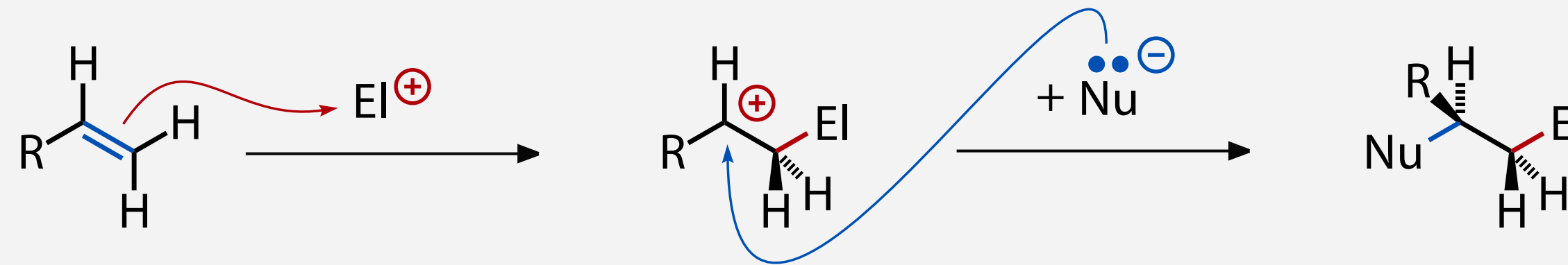


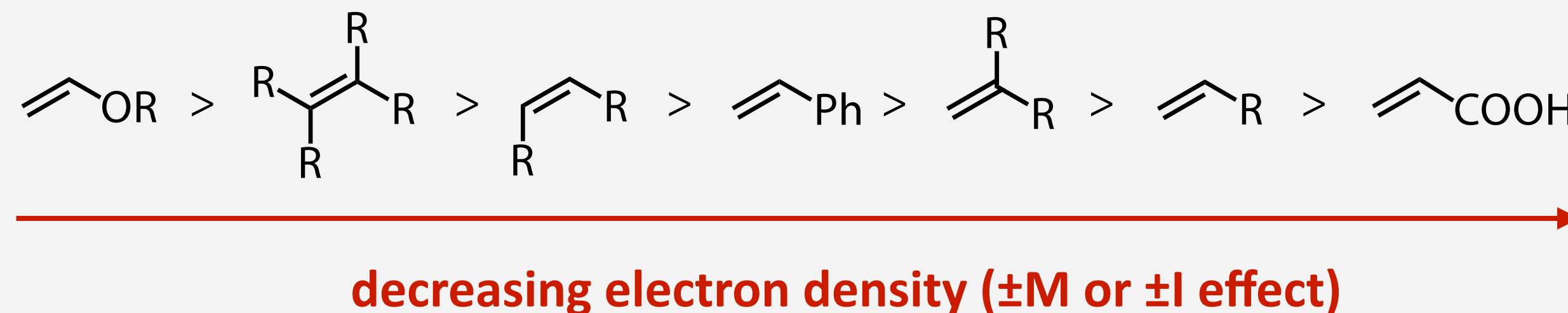
4.6 Electrophilic Additions to Multiple Bonds (A_E)

Reactions of Olefins with Electrophiles

- double bonds are (weak) nucleophiles and react with electrophiles to form carbocations
- double bonds coordinately unsaturated, carbocation intermediate can add a nucleophile

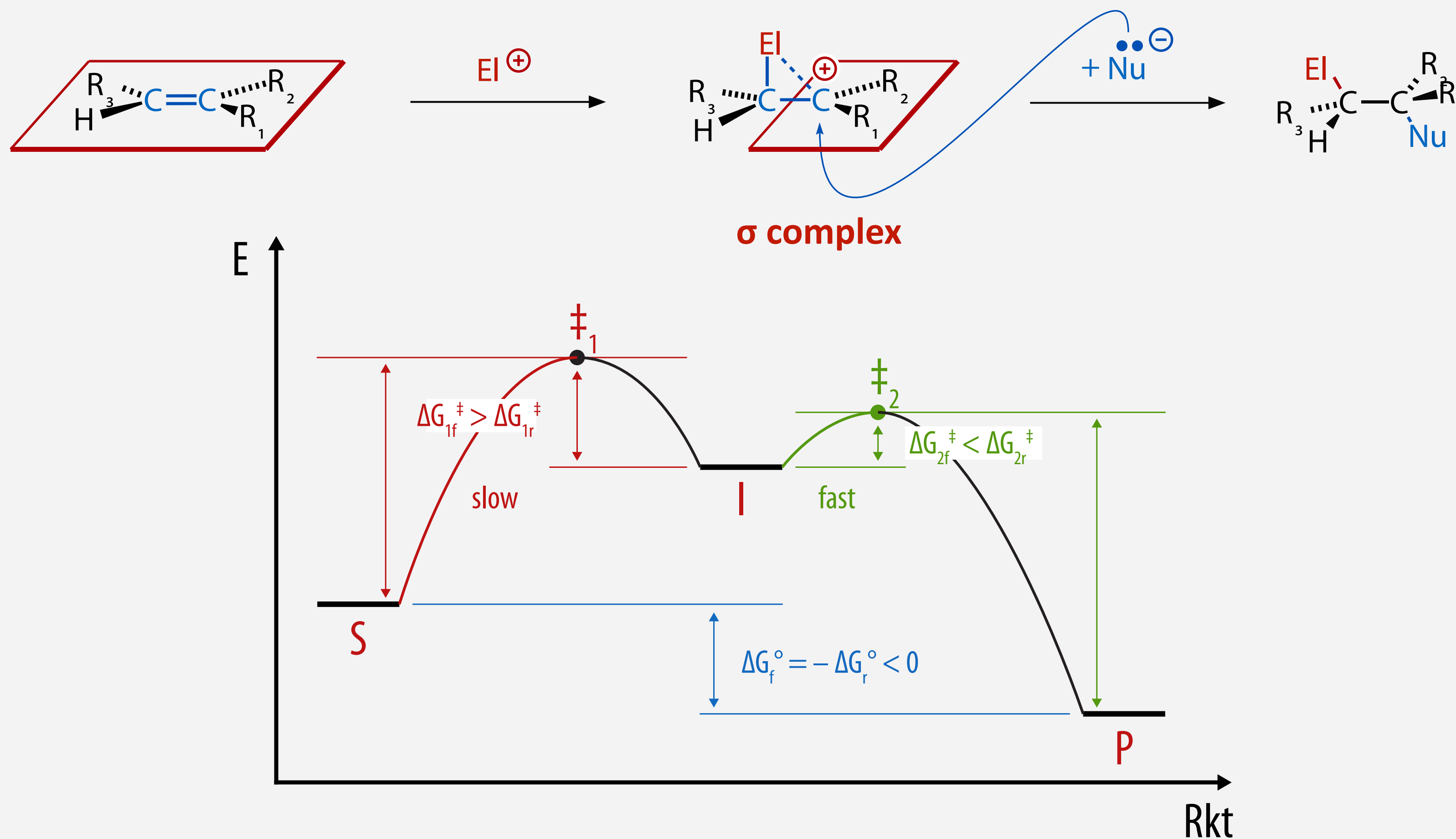


- reactivity order determined by nucleophilicity (electron density, polarizability) of the π bond



- olefins undergo addition reactions to an electrophile and a nucleophile in polar media

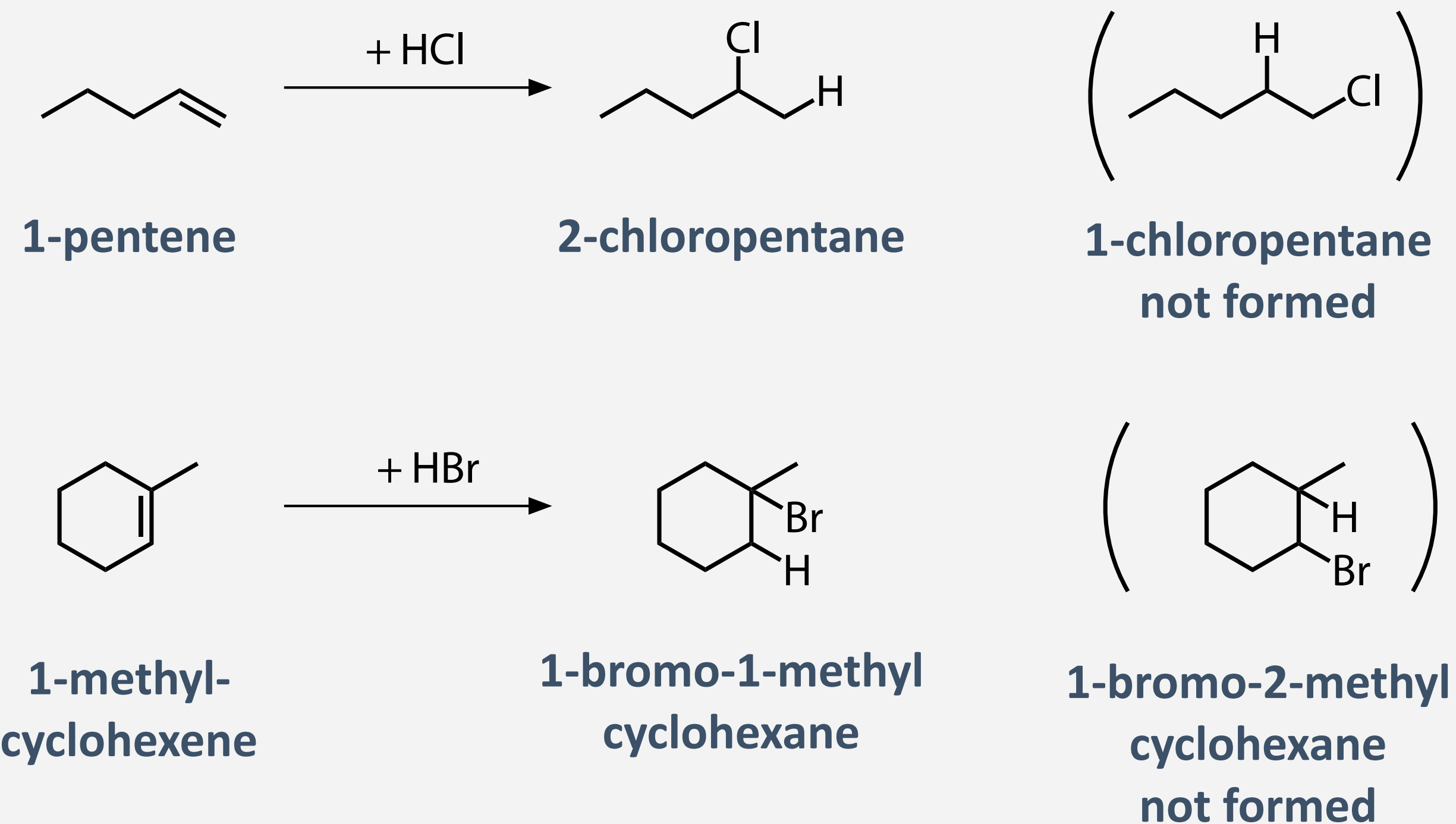
Mechanism of Electrophilic Additions



- electrophile adds to one side of the double bond, creating carbocationic intermediate
- nucleophilic attack is **regioselective** (for one carbon) and **diastereoselective** (backside attack)

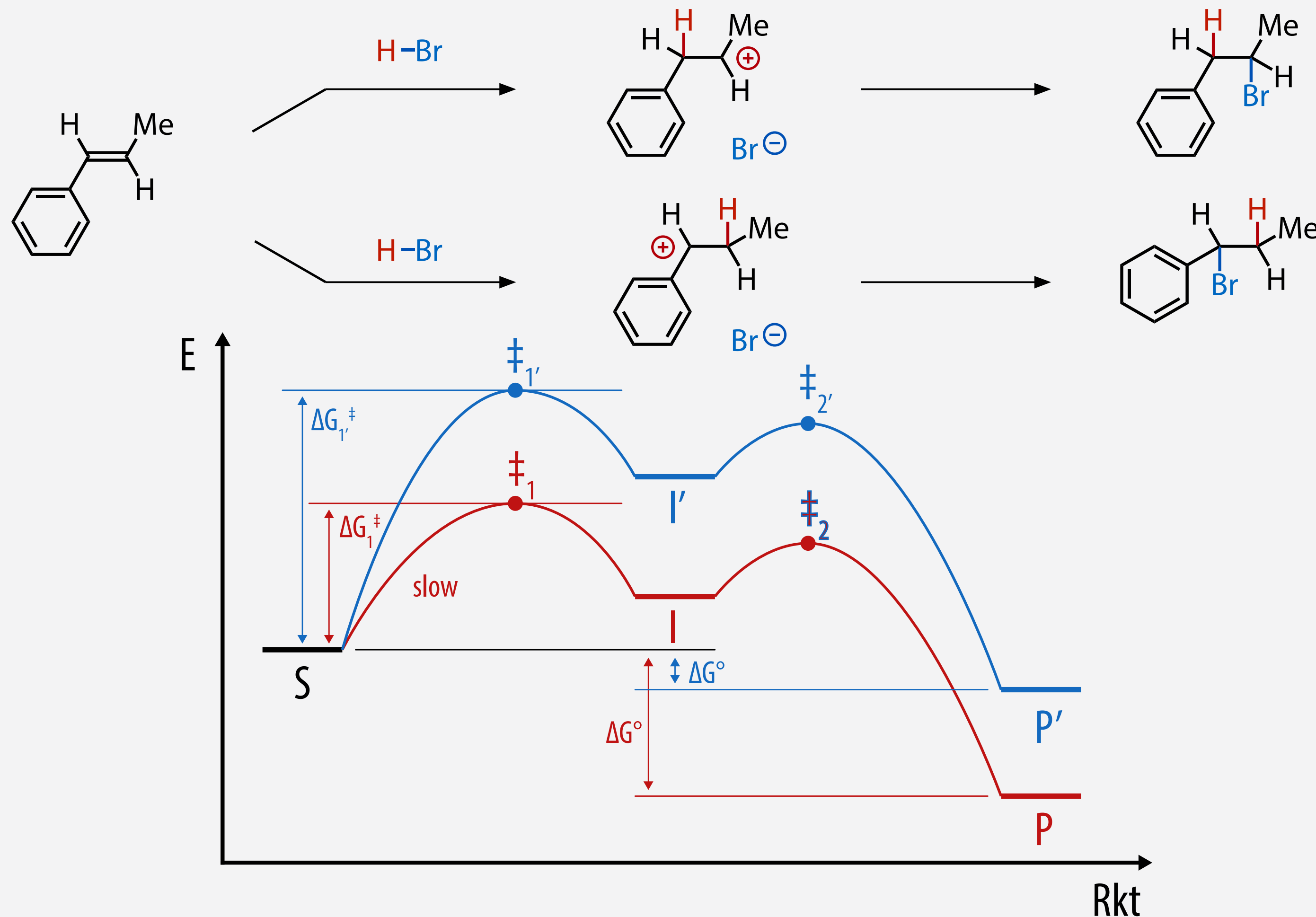
Regioselectivity of the Electrophilic Addition (Markovnikov Rule)

- not all possible constitution (position) isomers are formed in the addition of HX to an olefin
- the addition of HX to olefins is said to be “regioselective” (selective for a position isomer)



- **Markovnikov rule: hydrogen (electrophile) adds to carbon with fewer alkyl substituents, nucleophile attaches to carbon with more alkyl substituents (“the rich get richer”)**

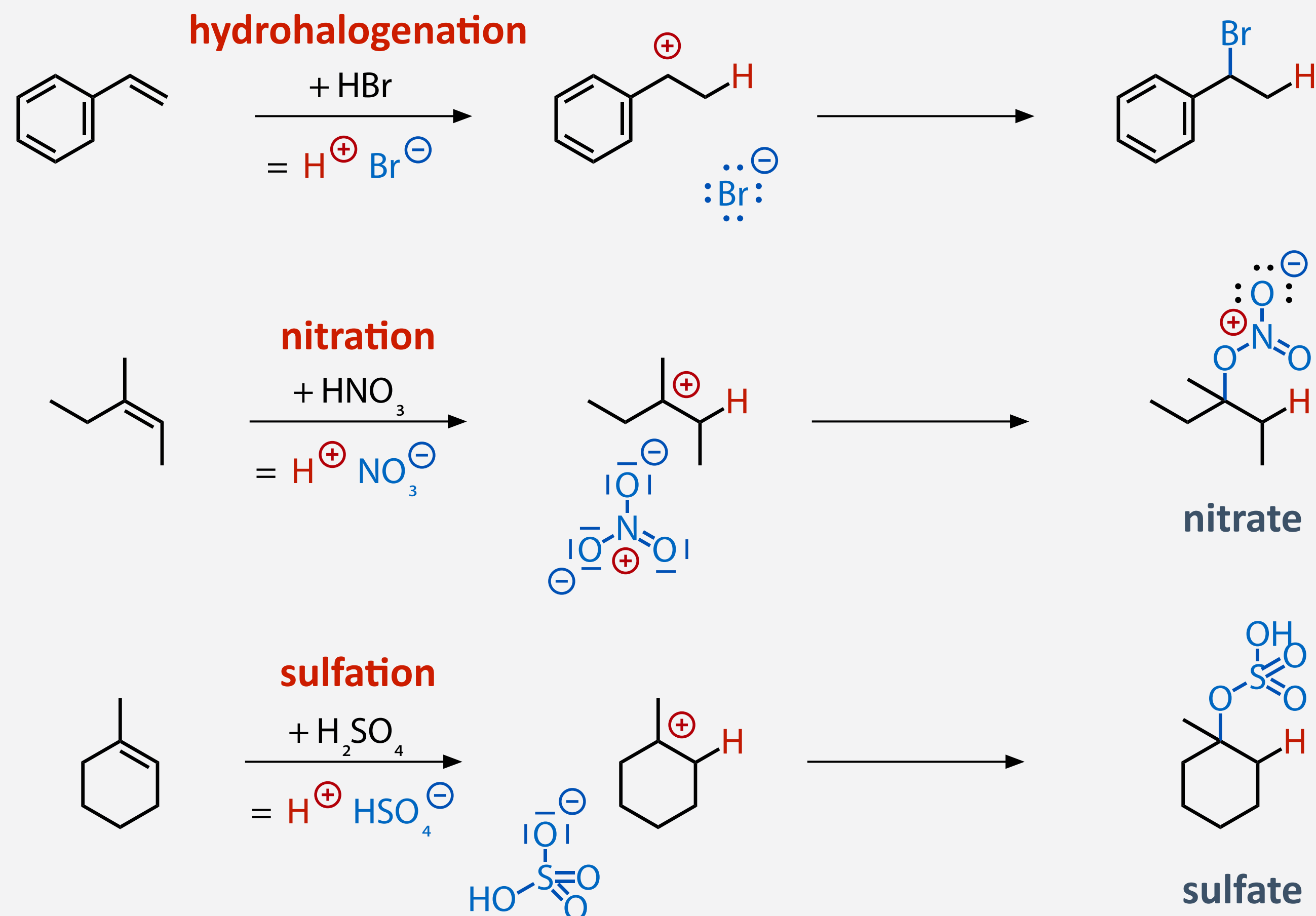
Mechanistic Explanation of the Markovnikov Rule



- **Explanation:** electrophile adds to double bond such that the better stabilized carbocationic intermediate is formed; corresponding product forms faster (Hammond)

Addition of Hydrogen Halides and Other Brønsted Acids

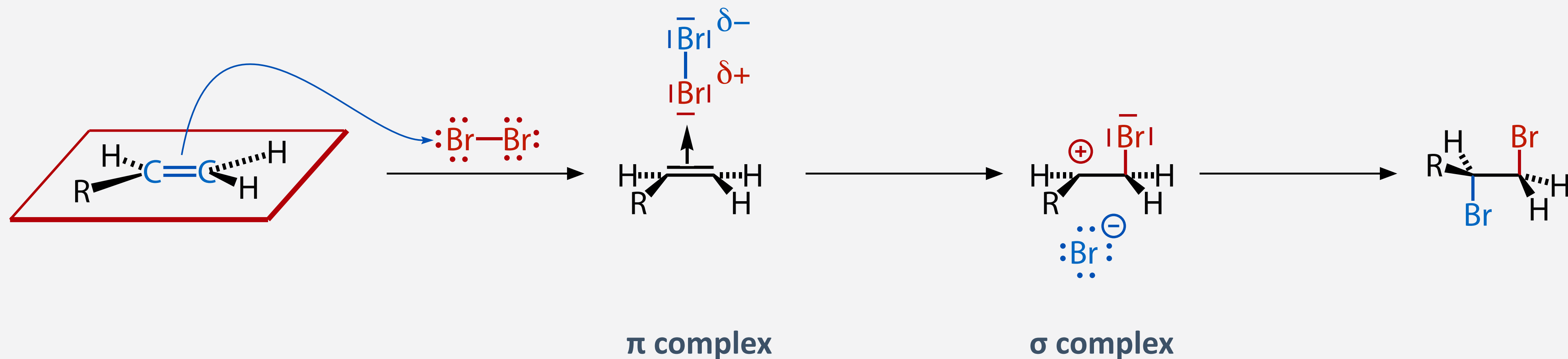
- the proton H^+ is the electrophile in the addition of Brønsted acids to double bonds



- the stronger the acid, the faster the first, and the slower the second addition step

Halogen Addition

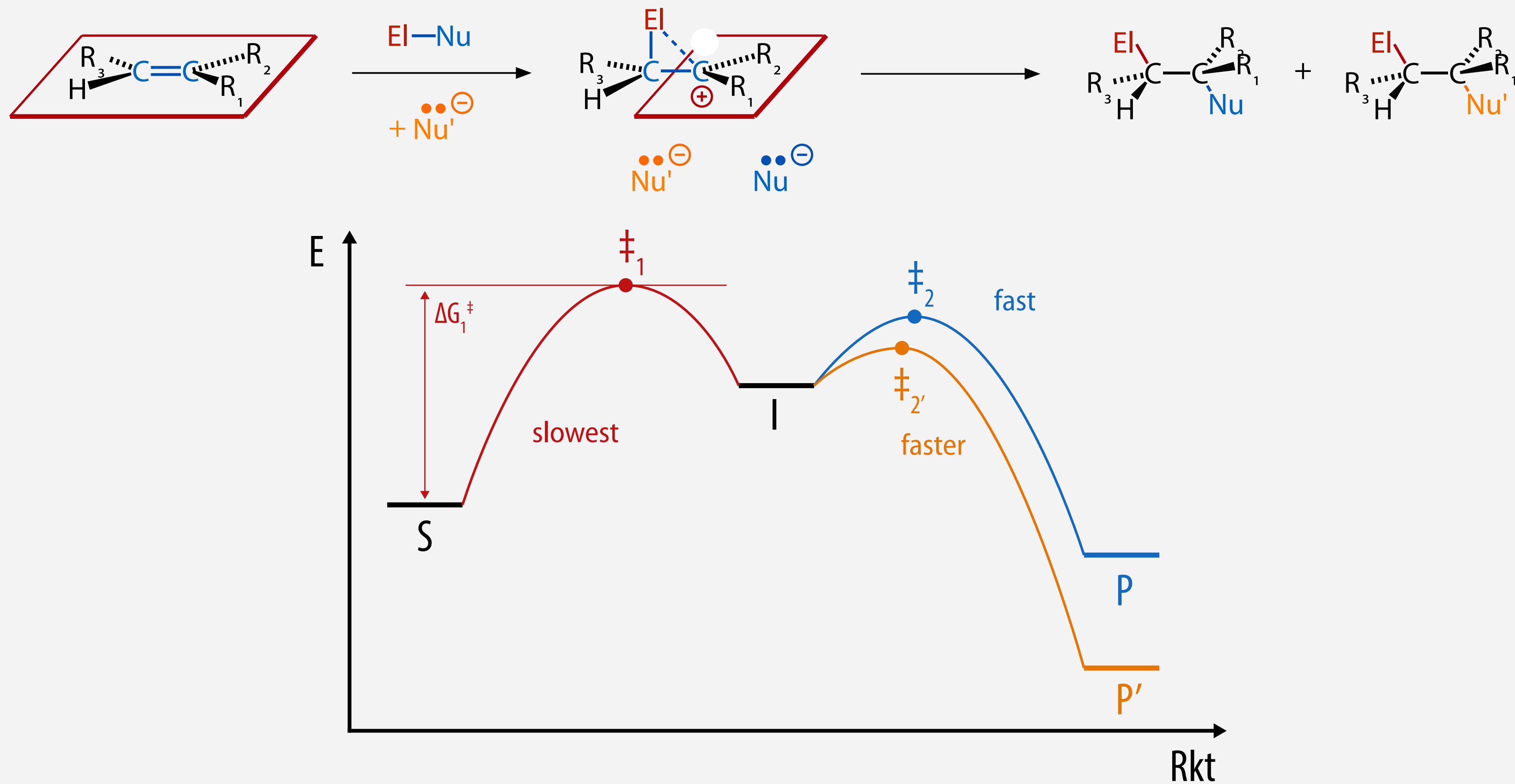
- dihalogen molecules are electrophiles (halogen atoms bind to less electronegative atoms):



- coordination of olefin to dihalogen molecule in the π complex enhances polarization
- reactivity iodine > bromine > chlorine $\gg$ fluorine, due to decreasing polarizability
- $\text{S}_{\text{N}}2$ -like attack of π electron pair on $\text{Br}-\text{Br}$ antibonding orbital with Br^- as leaving group

Competition with Other Nucleophiles

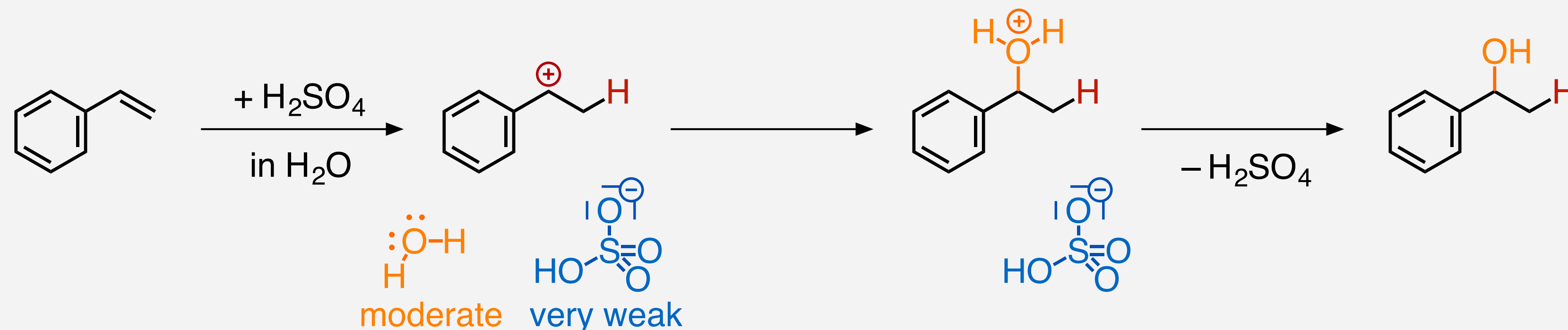
- in the second step, the nucleophile competes with other nucleophiles present in the reaction



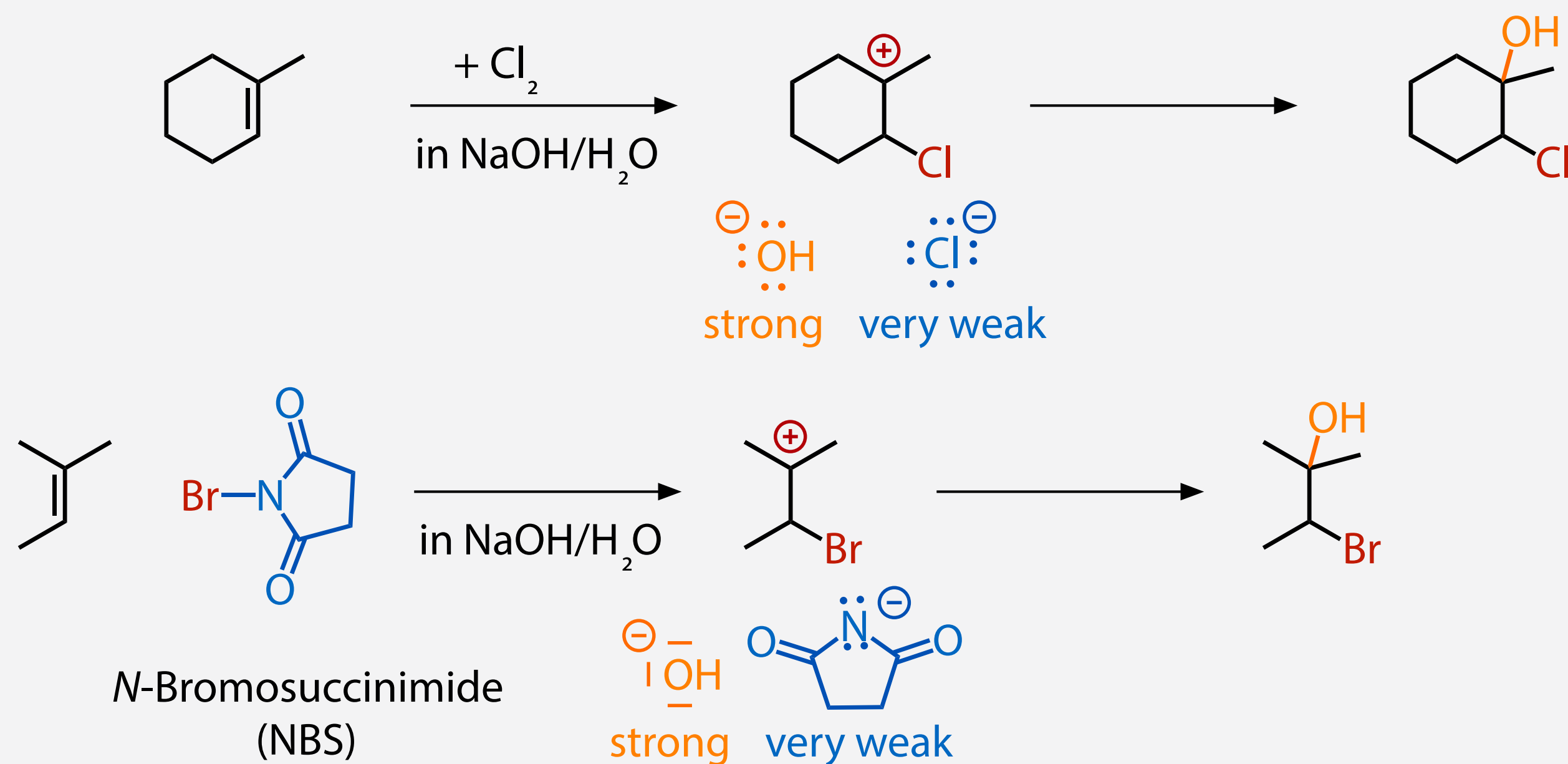
- first step remains rate-determining, but nucleophilicity determines product in second step

Hydration and Halohydrin Formation

- strong acids in aqueous media result in water addition (hydration)

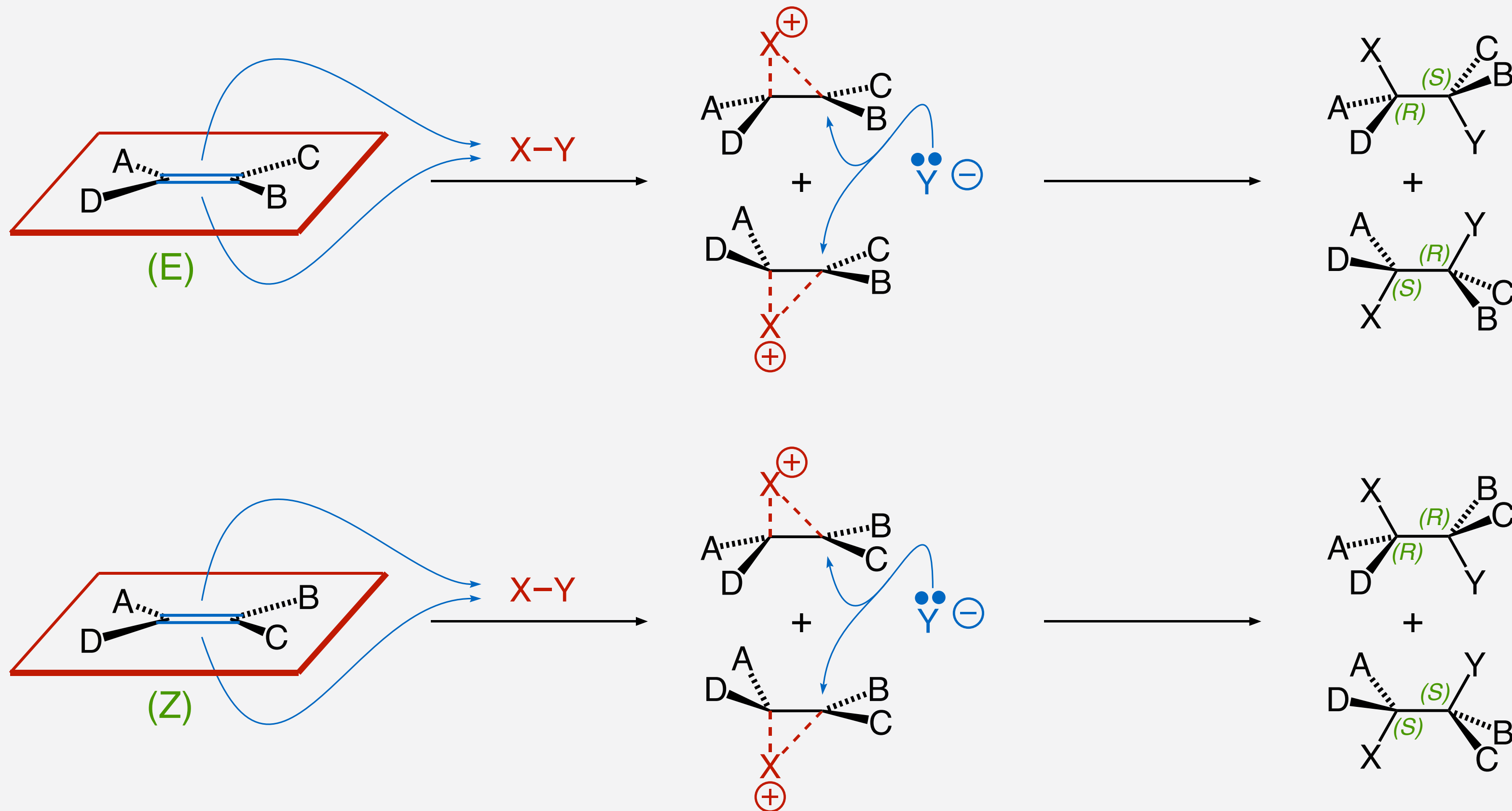


- halogenation in alkaline aqueous media results in hydroxyhalogen (halohydrin) formation



Stereoselectivity of Electrophilic Additions

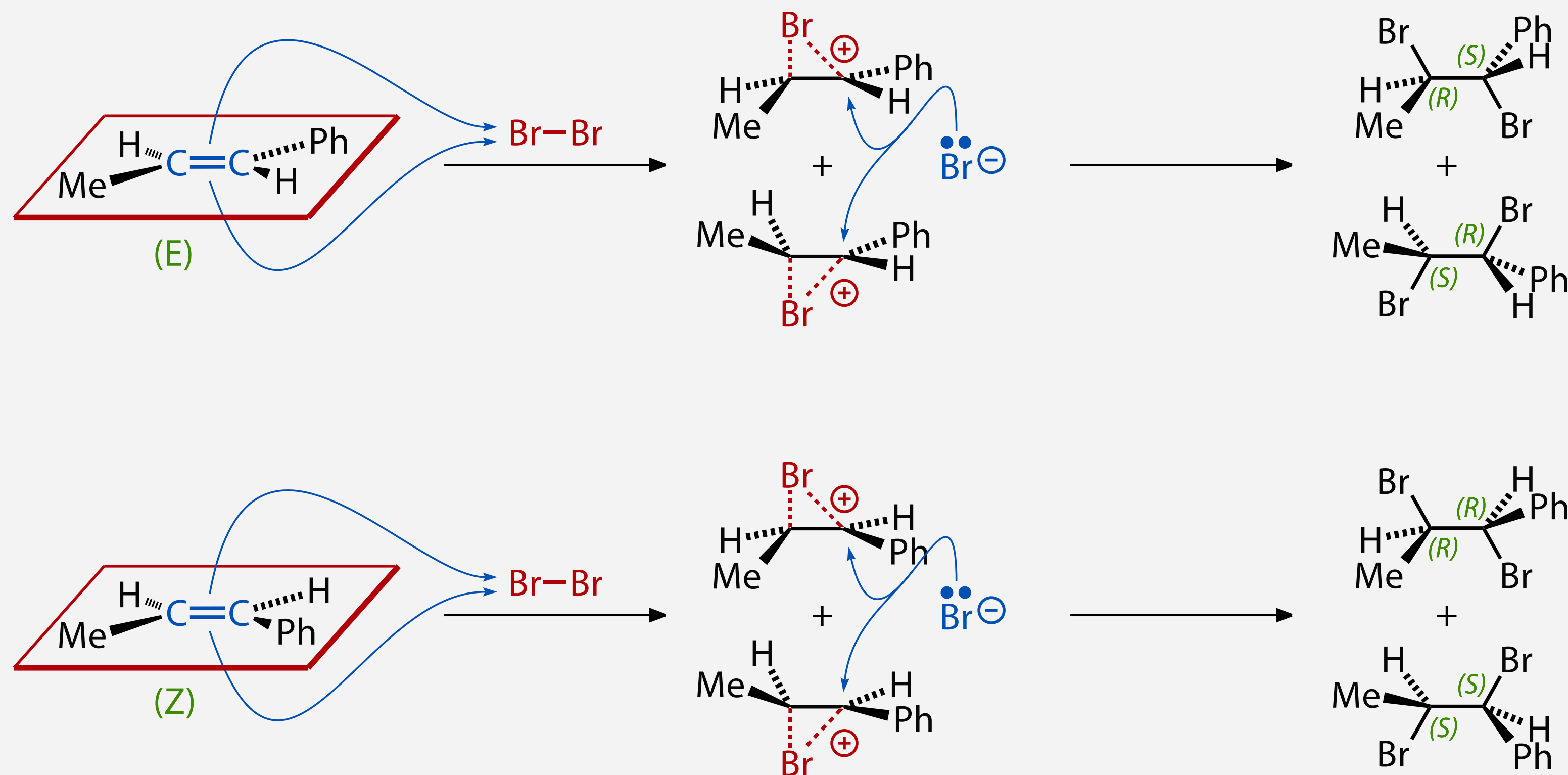
- starting material is planar, achiral: reaction with electrophile occurs from either hemisphere
- required backside attack of the nucleophile then enforces *trans* addition



- electrophilic additions are **not enantioselective** but **diastereospecific** (if two stereocenters formed)
- given *E* or *Z* configuration transformed into **one specific diastereomer** (as a **pair of enantiomers**)

Stereoselectivity of Electrophilic Additions (Example 1)

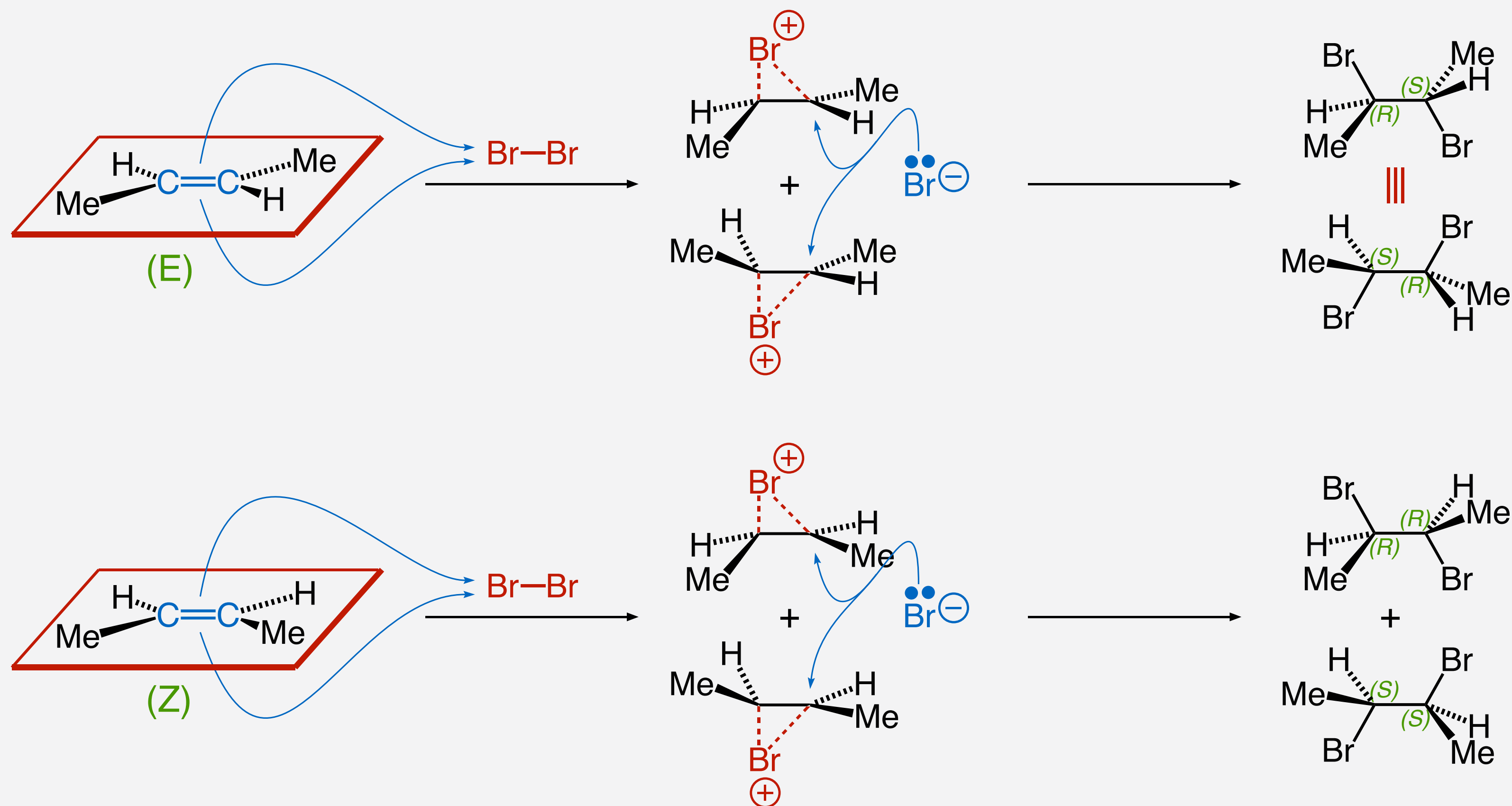
- diastereomers with two stereocenters with different substituents are formed specifically



- E* isomer results in a **racemic mixture of *RS* and *SR* diastereomers** (in this case)
- Z* isomer results in a **racemic mixture of *SS* and *RR* diastereomers** (in this case)

Stereoselectivity of Electrophilic Additions (Example 3)

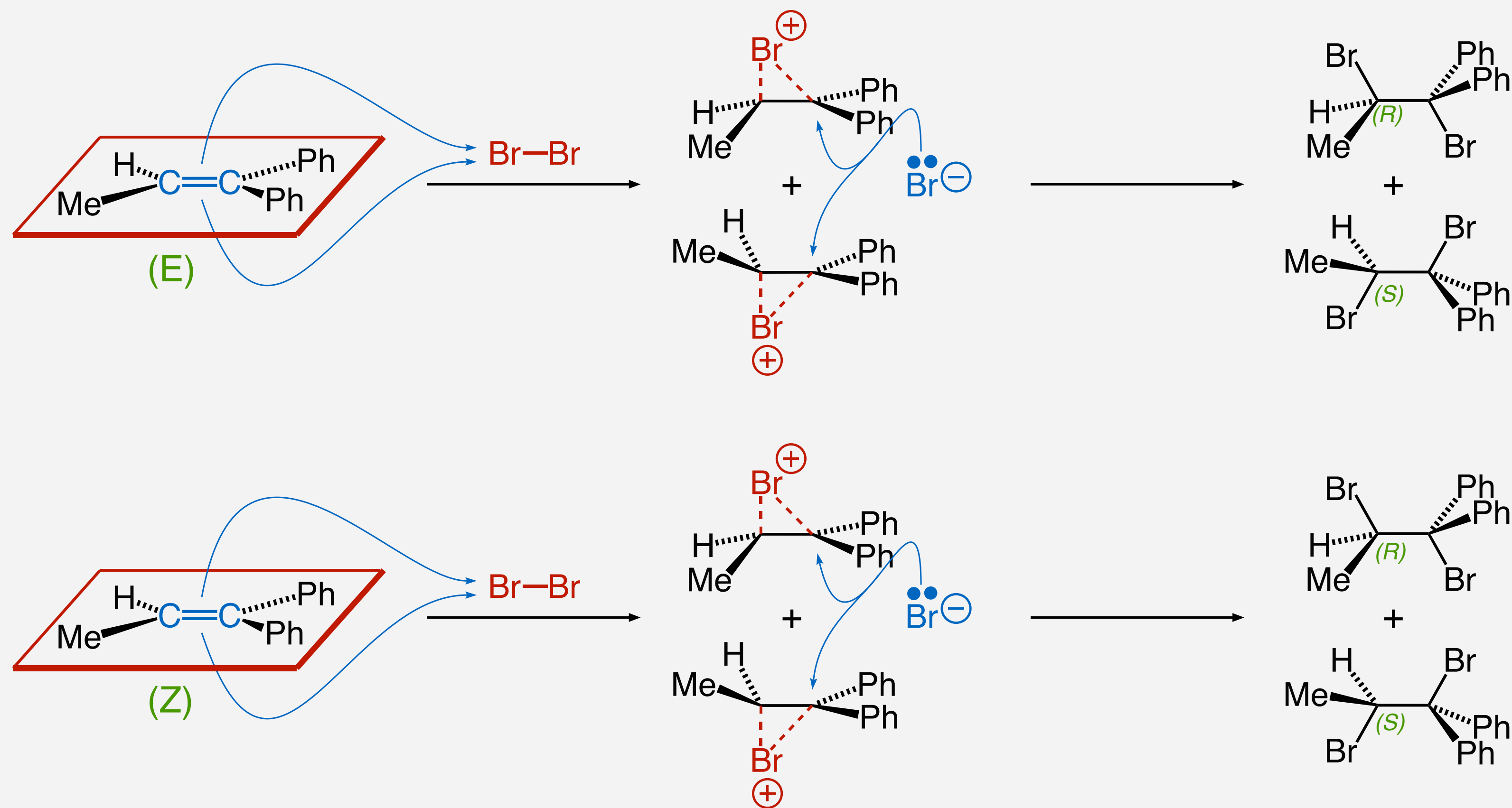
- diastereomers with two stereocenters but with identical substituents are formed specifically



- E* isomer results in a **racemic mixture of *RS* and *SR*** (“rac”) diastereomers (in this case)
- due to symmetry, *Z* isomer results in **one achiral *RS*** (“meso”) diastereomer (in this case)

Stereoselectivity of Electrophilic Additions (Example 2)

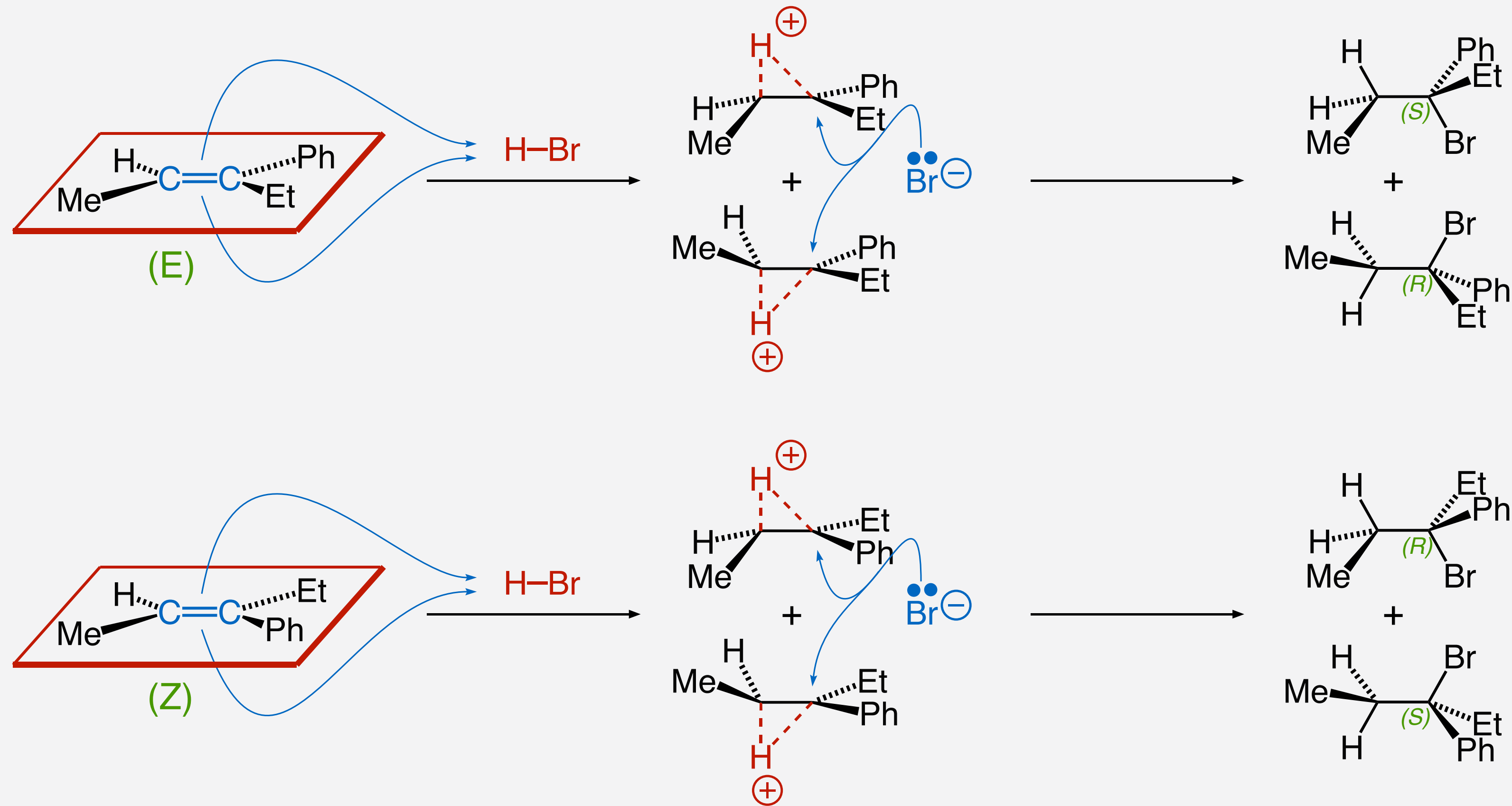
- two substituents on one alkene carbon are identical, so that carbon does not become a stereocenter



- E* isomer results in a **racemic mixture of *R* and *S* enantiomers** (in this case)
- Z* isomer results in **the same racemic mixture of *R* and *S* enantiomers** (in this case)

Stereoselectivity of Electrophilic Additions

- one of the substituents is identical with one of the added fragments on the same carbon



- E* isomer results in a **racemic mixture of *R* and *S* enantiomers** (in this case)
- Z* isomer results in **the same racemic mixture of *R* and *S* enantiomers** (in this case)

Learning Outcomes

- **double and triple bonds are weak nucleophiles, react with electrophiles**
- **first step is addition to electrophile, followed by nucleophile addition**
 - typical reactants are (strong) acids or dihalogen molecules
 - other nucleophiles compete in second step (hydration, halohydrins)
- **addition is regioselective (Markovnikov rule)**
- **addition is diastereospecific (*trans* addition)**
 - olefin with defined *E* or *Z* configuration forms one diastereomer
 - pairs of enantiomers only if different stereo centers are formed

