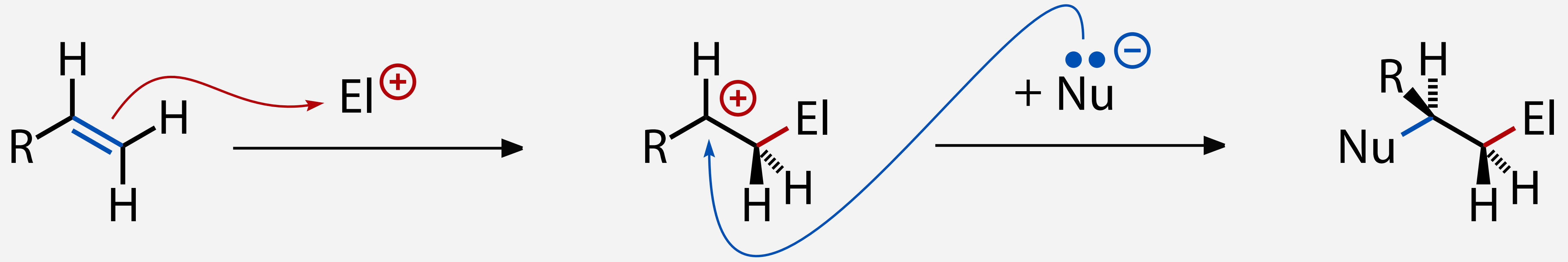
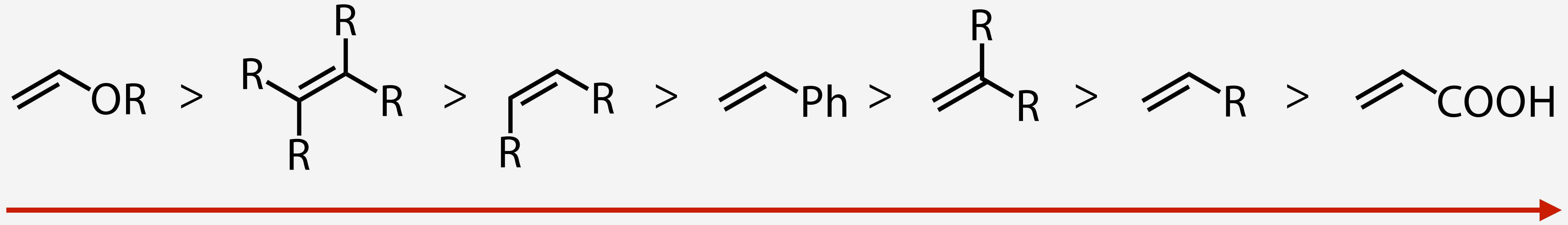
4.6 Electrophilic Additions to Multiple Bonds (A_E)

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



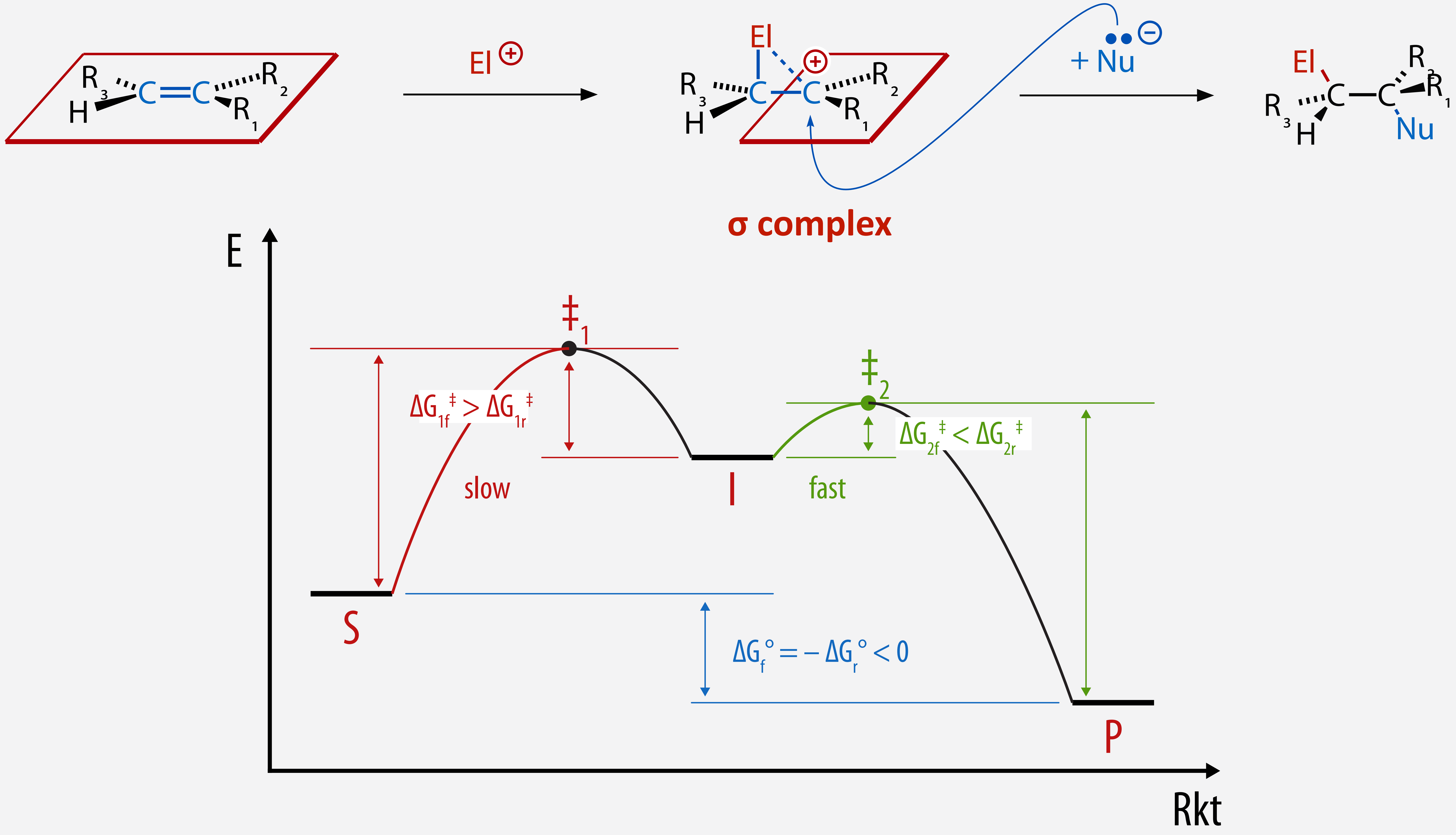
- **reactivity order determined by nucleophilicity (electron density, polarizability) of the π bond**



decreasing electron density (±M or ±I effect)

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

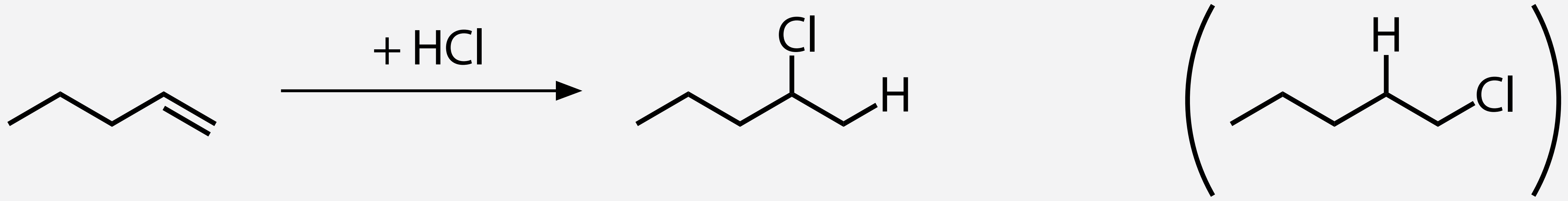
Mechanism of Electrophilic Additions



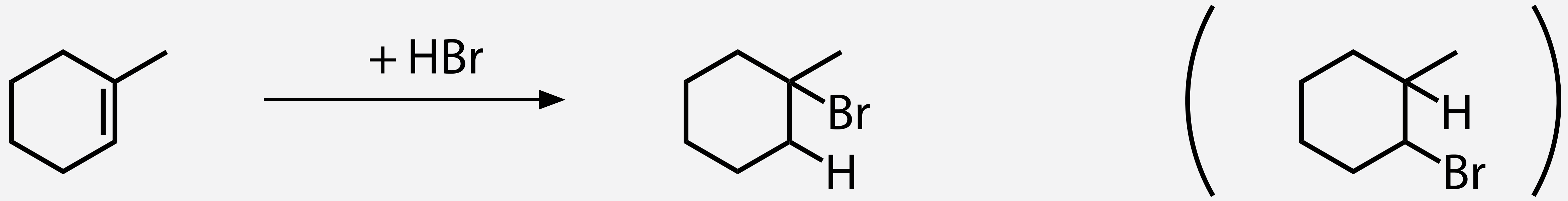
- electrophile adds to one side of the double bond, creating carbocationic intermediate
- nucleophilic attack is **regioselective** (for one carbon) and **diasteroselective** (backside attack)

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)



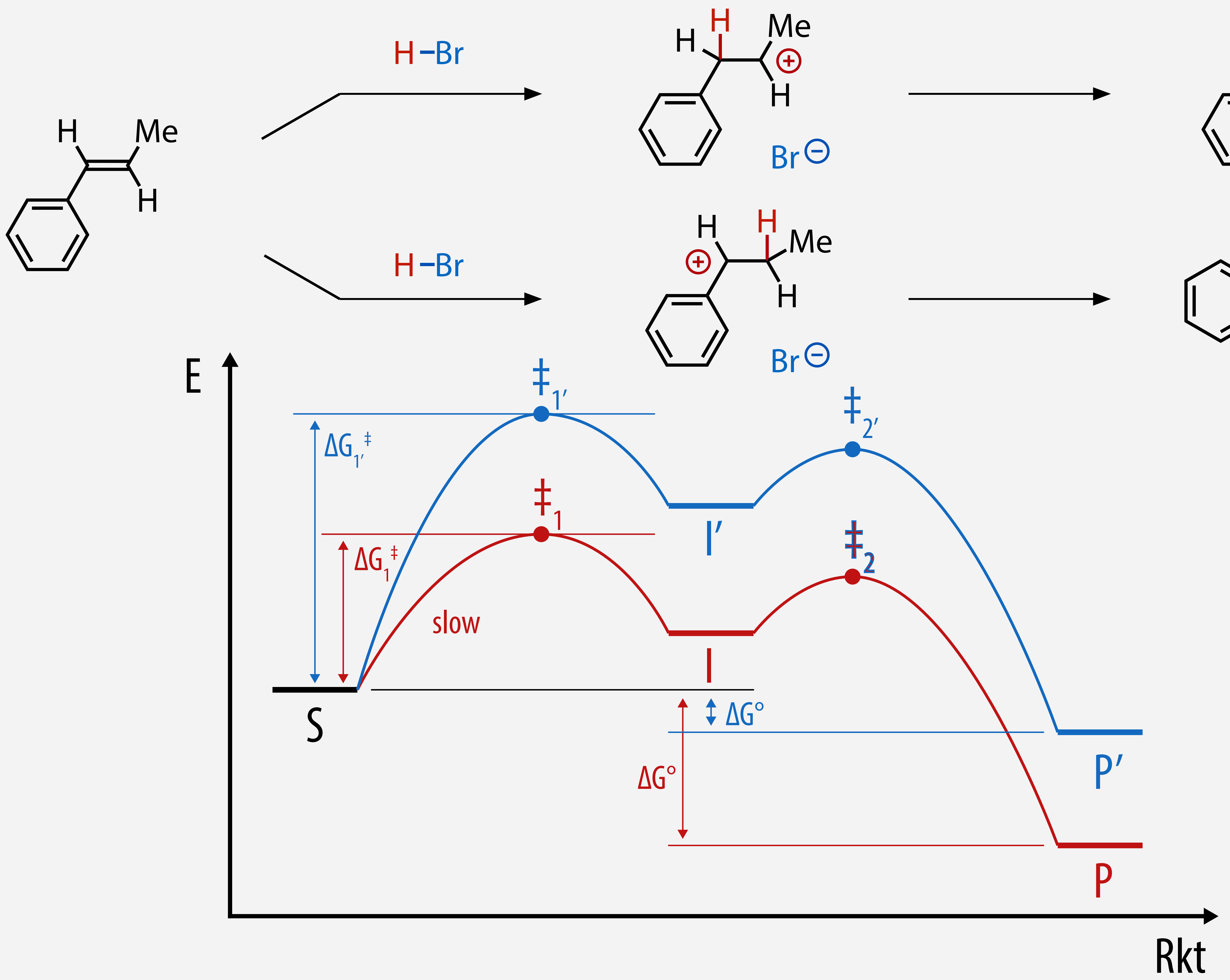
1-pentene **2-chloropentane** **1-chloropentane not formed**



1-methyl-cyclohexene **1-bromo-1-methyl cyclohexane** **1-bromo-2-methyl cyclohexane not formed**

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

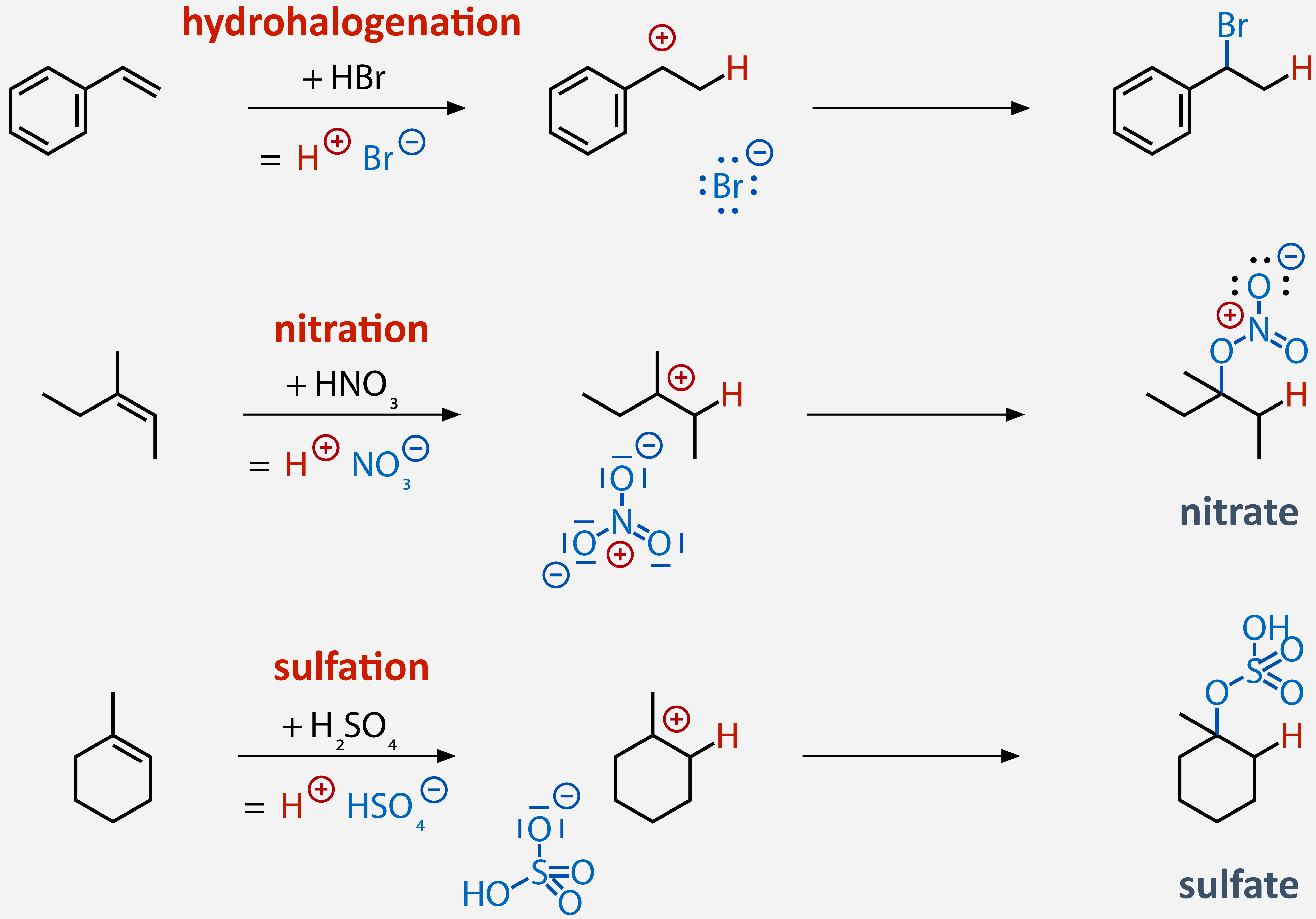
Mechanistic Explanation of the Markovnikov Rule



- **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

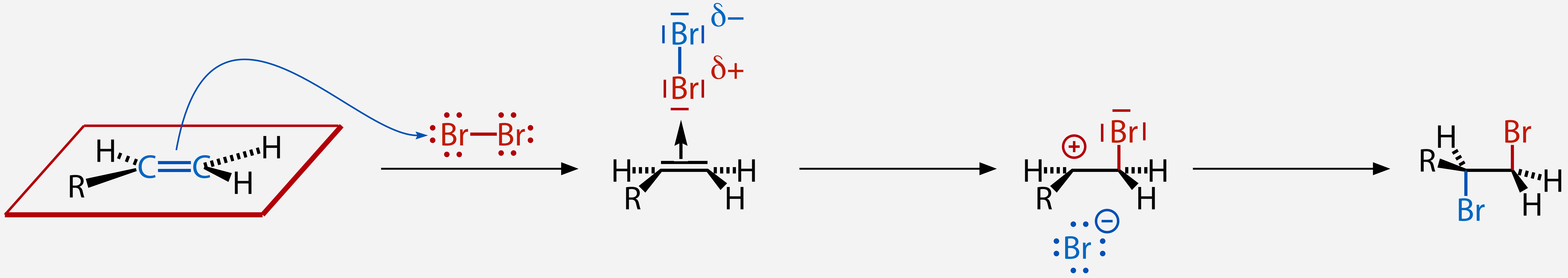
- the proton H^+ is the electrophile in the addition of Brønsted acids to double bonds



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

Halogen Addition

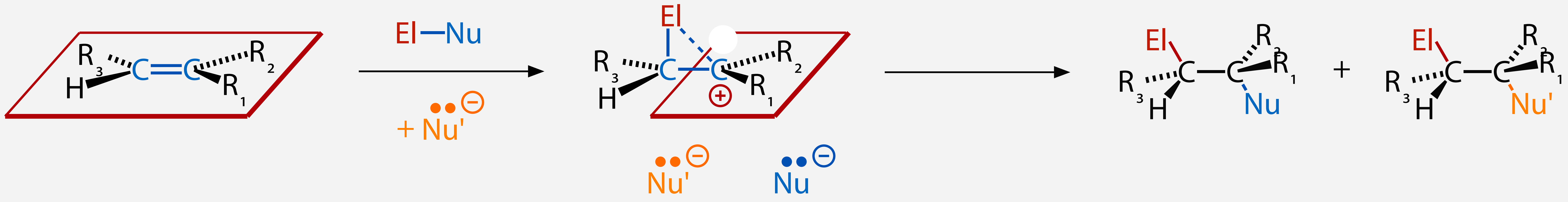
- dihalogen molecules are electrophiles (halogen atoms bind to less electronegative atoms):

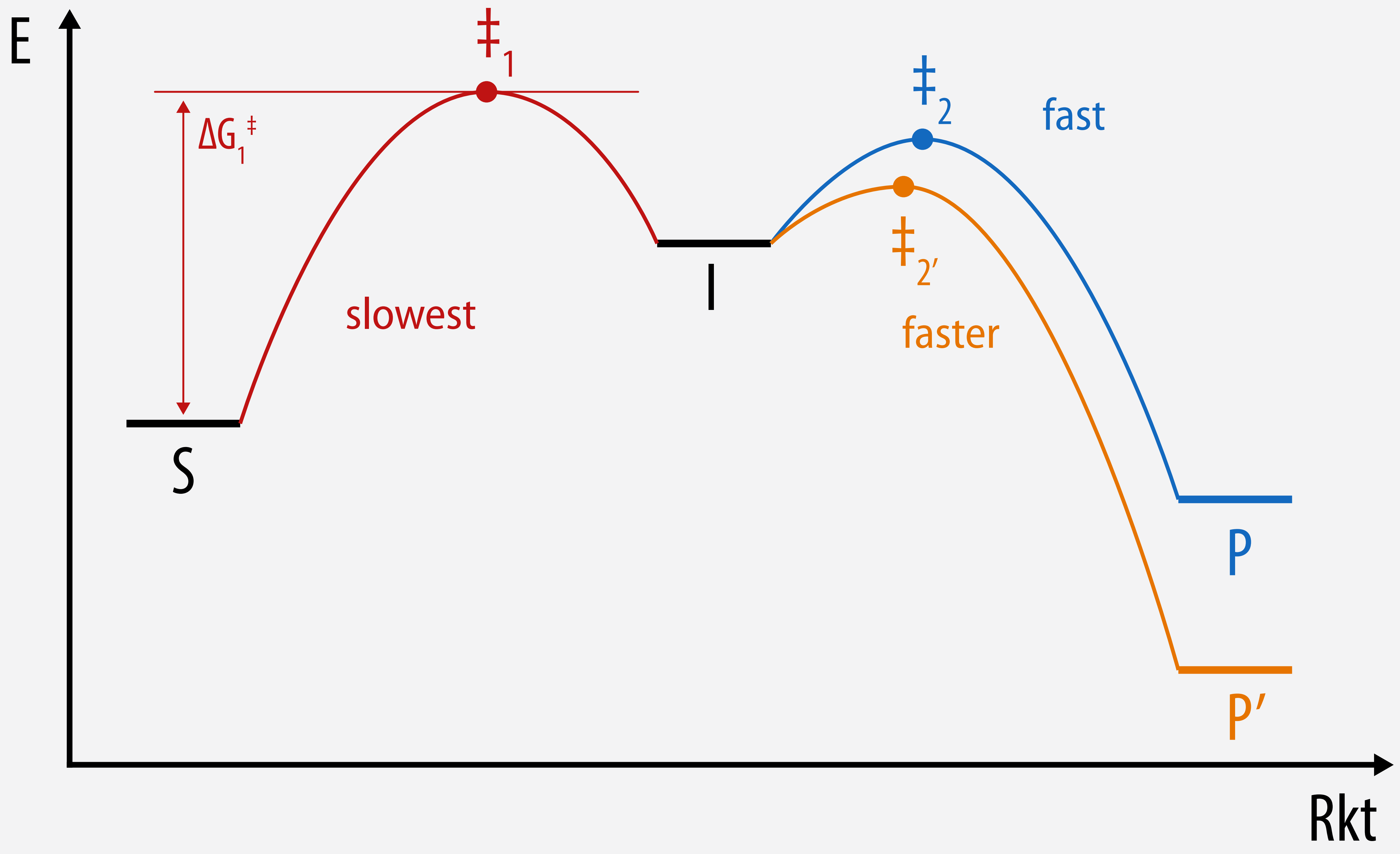


- **coordination of olefin to dihalgen molecule in the π complex enhances polarization**
- **reactivity iodine > bromine > chlorine ≫ fluorine, due to decreasing polarizability**
- **S_N2-like attack of π electron pair on Br–Br antibonding orbital with Br^- as leaving group**
- **σ complex has three-center interaction of C–Br with adjacent carbocation**
- **therefore, Br^- has to perfrom “backside attack”**

Competition with Other Nucleophiles

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

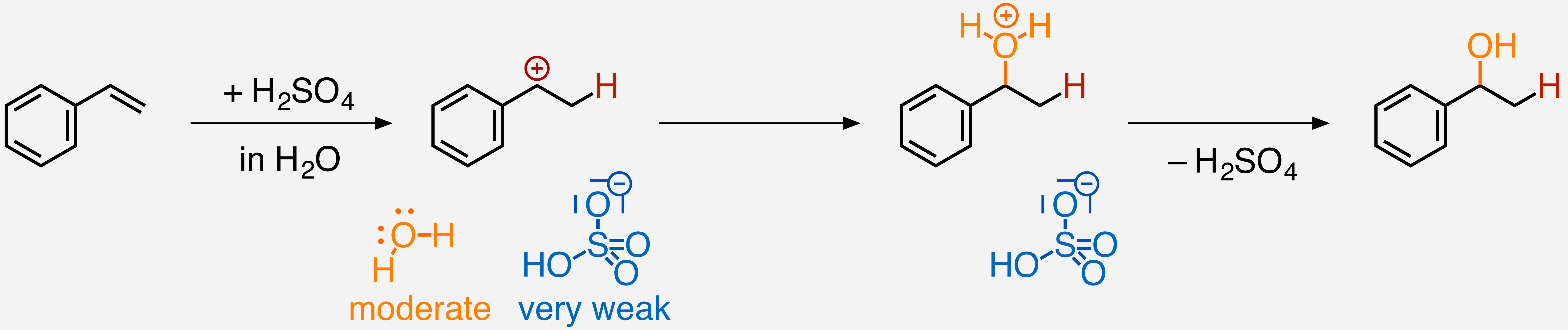




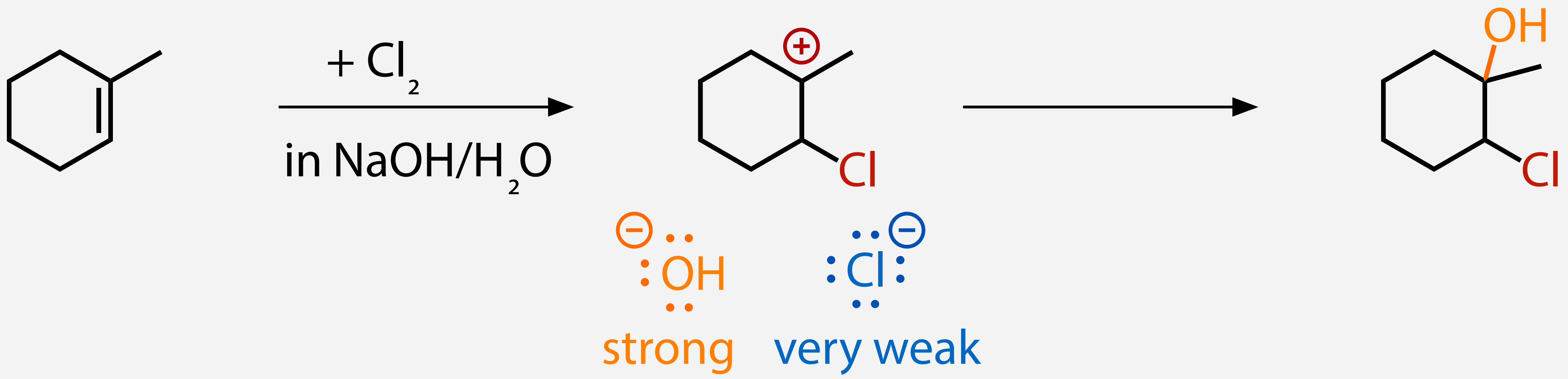
- **first step remains rate-determining, but nucleophilicity determines product in second step**

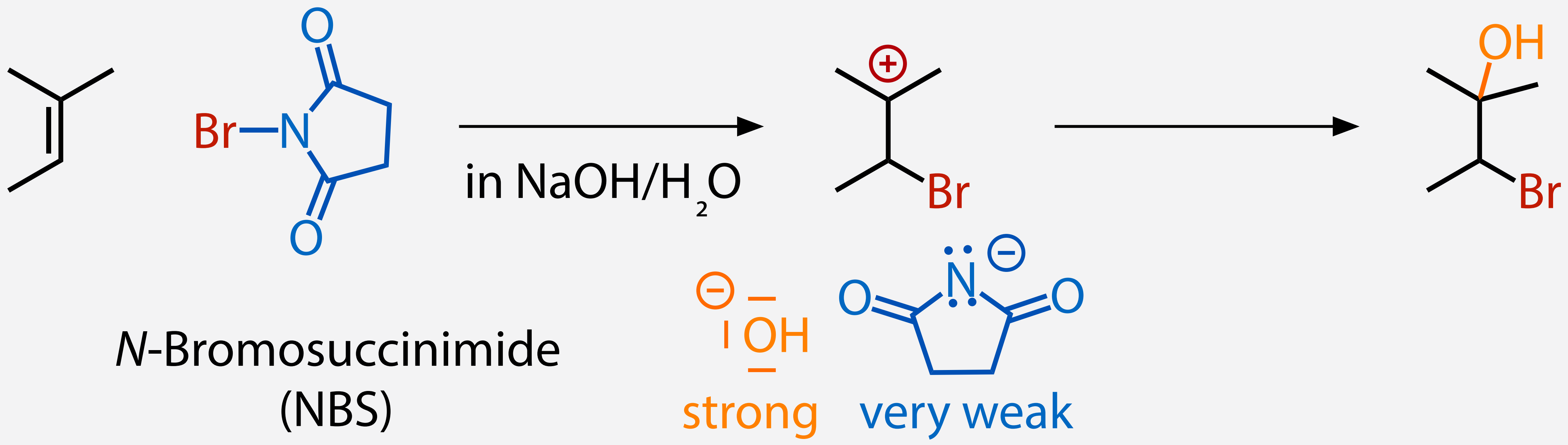
Hydration and Halohydrin Formation

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



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

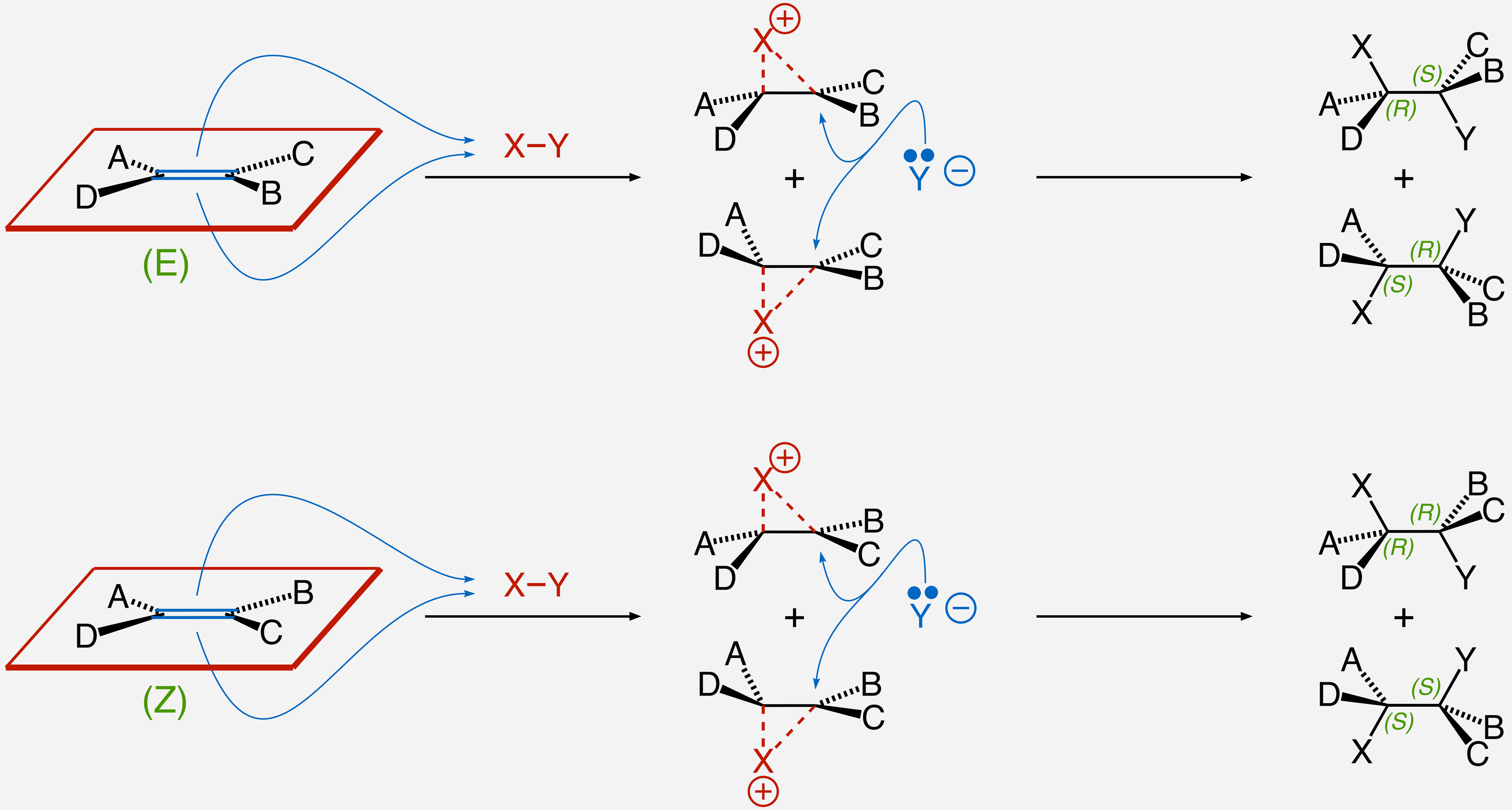




N-Bromosuccinimide
(NBS)

Stereoselectivity of Electrophilic Additions

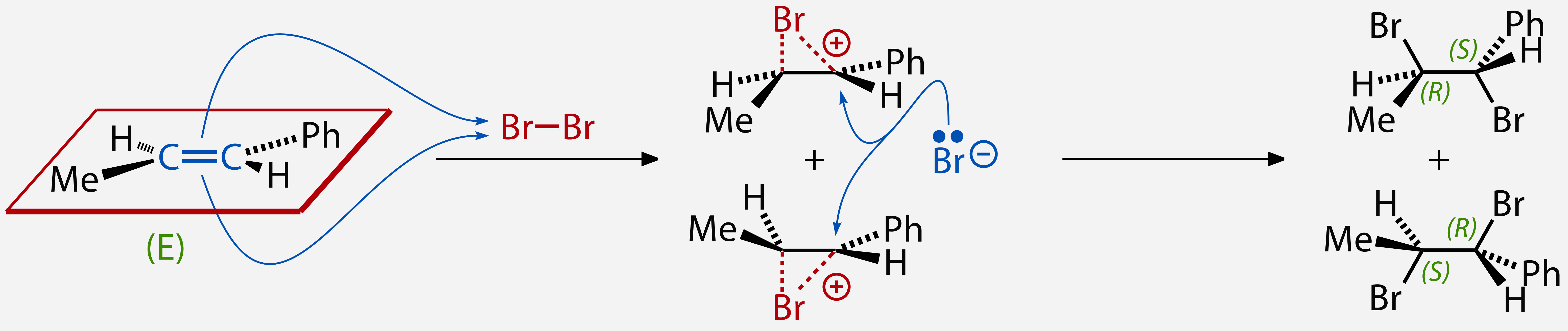
- starting material is planar, achiral: reaction with electrophile occurs from either hemisphere
- required backside attack of the nucleophile then enforces *trans* addition

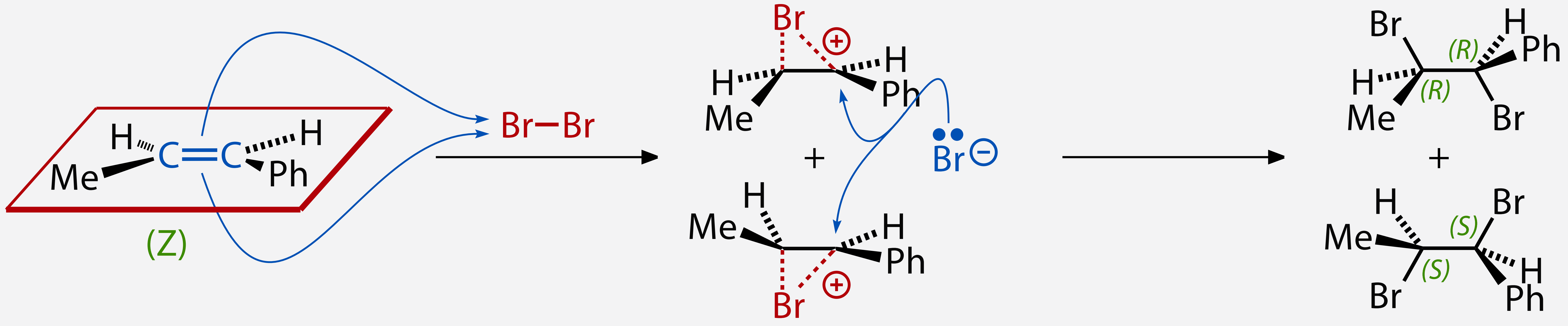


- **electrophilic additions are not enantioselective but diastereospecific (if two stereocenters formed)**
- **given *E* or *Z* configuration transformed into one specific diastereomer (as a pair of enantiomers)**

Stereoselectivity of Electrophilic Additions (Example 1)

- diastereomers with two stereocenters with different substituents are formed specifically

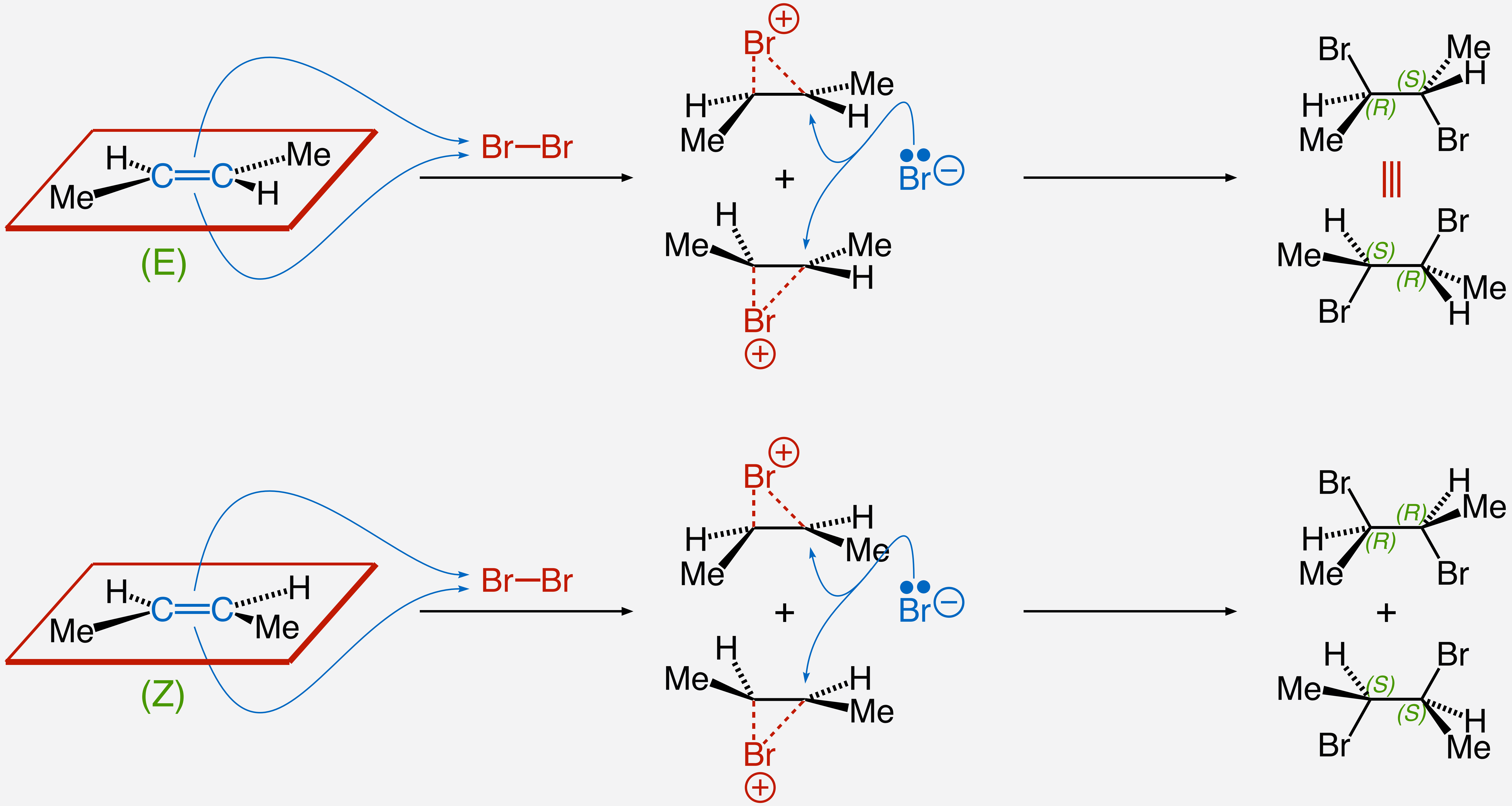




- ***E* isomer results in a racemic mixture of *RS* and *SR* diastereomers (in this case)**
- ***Z* isomer results in a racemic mixture of *SS* and *RR* diastereomers (in this case)**

Stereoselectivity of Electrophilic Additions (Example 3)

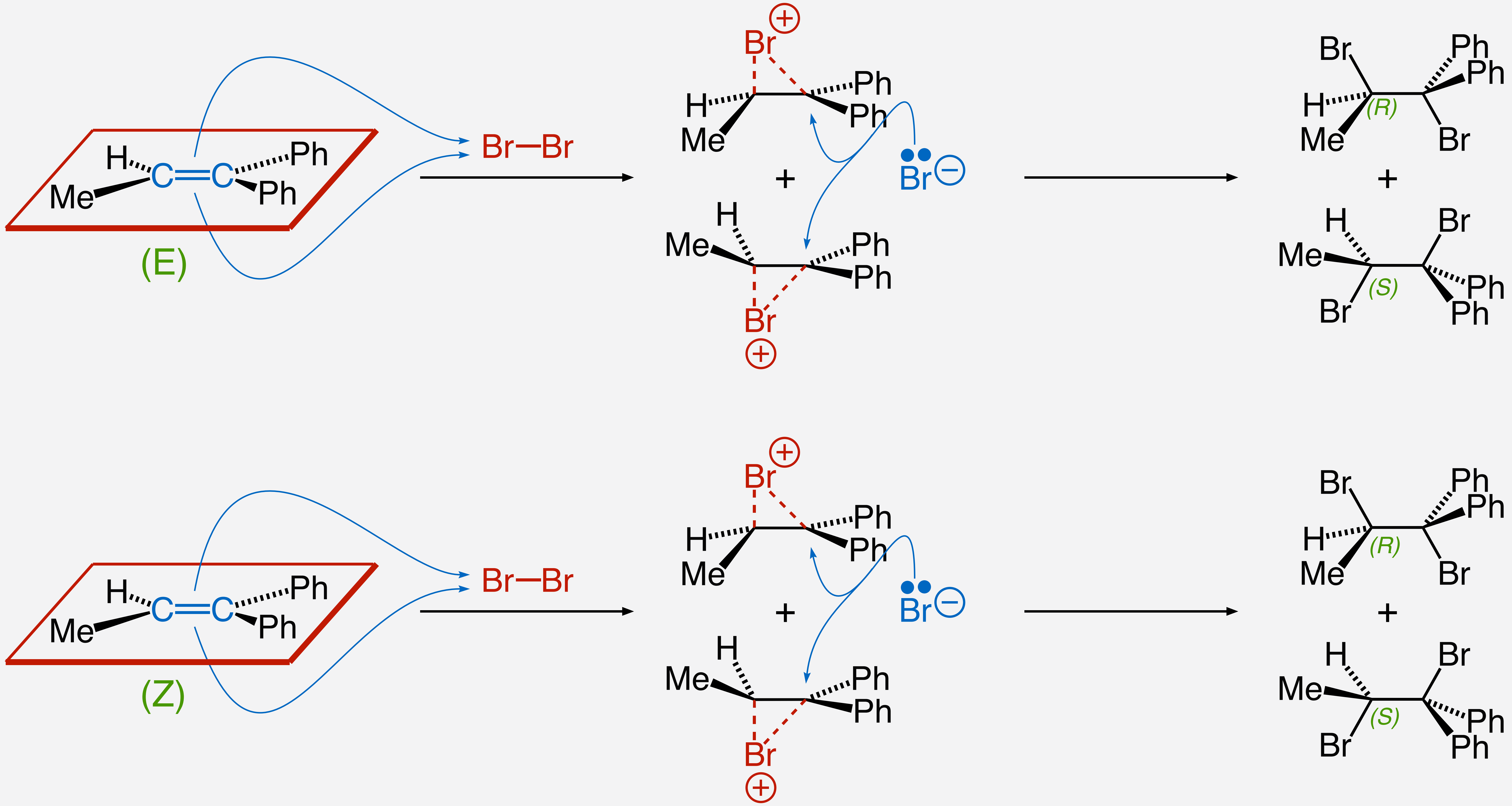
- diastereomers with two stereocenters but with identical substituents are formed specifically



- ***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)

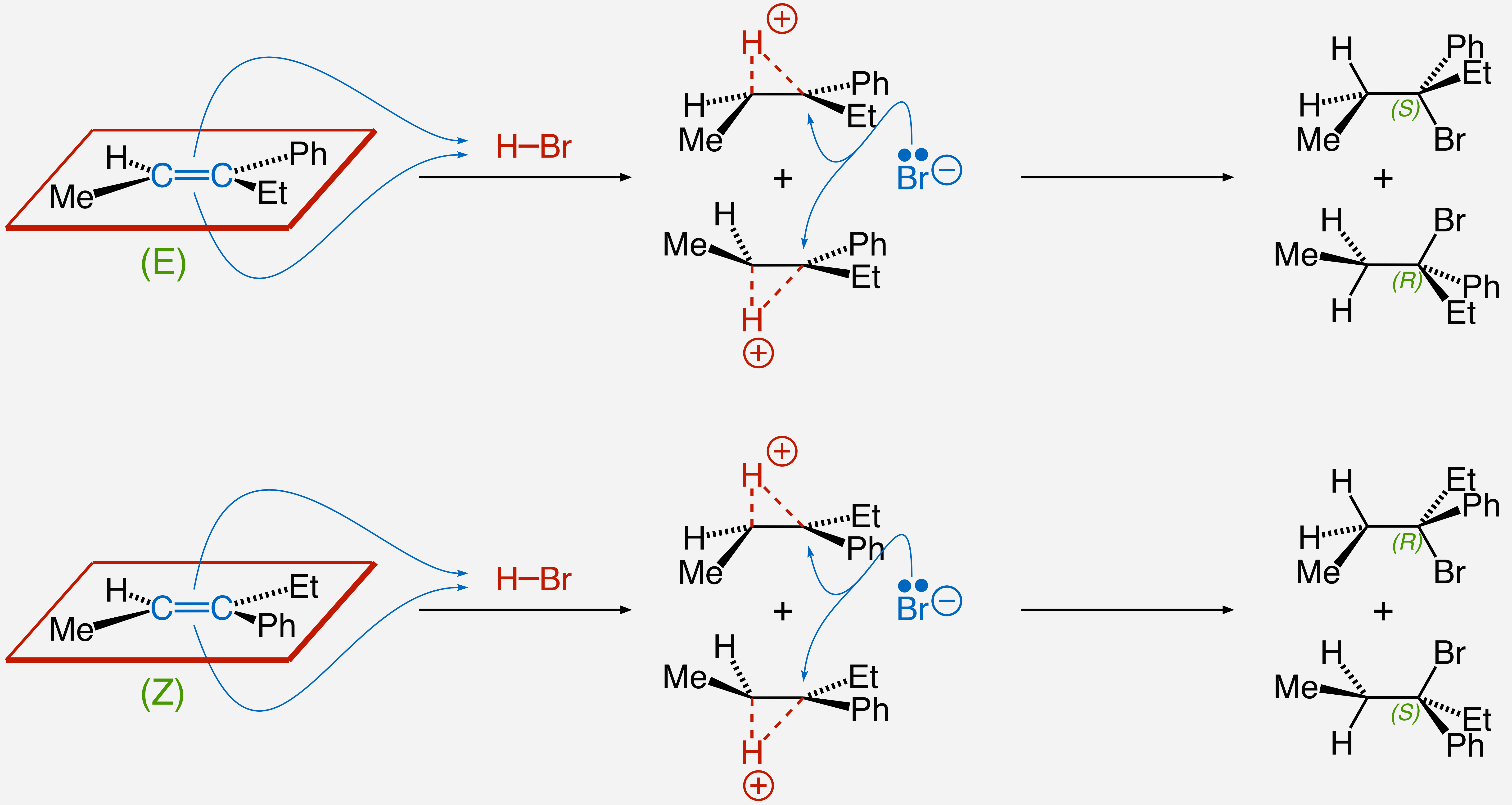
- two substituents on one alkene carbon are identical, so that carbon does not become a stereocenter



- ***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