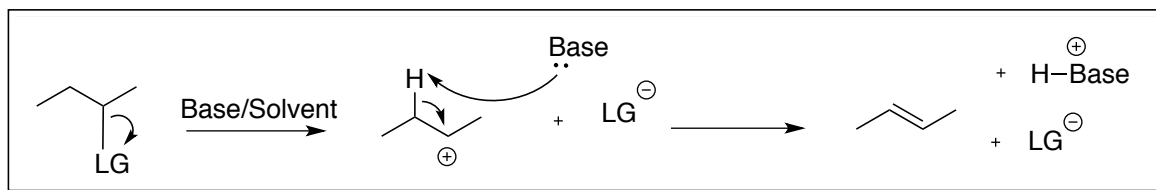


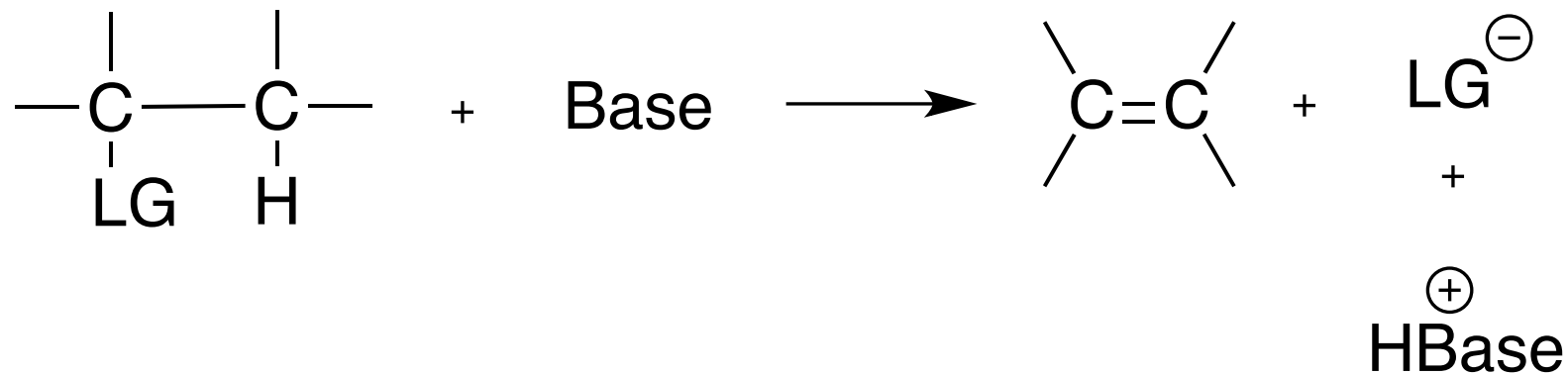
# Elimination Reactions

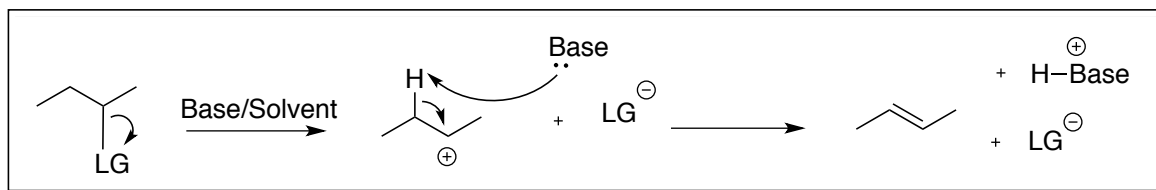
E1 Mechanism

Smith: 8.6



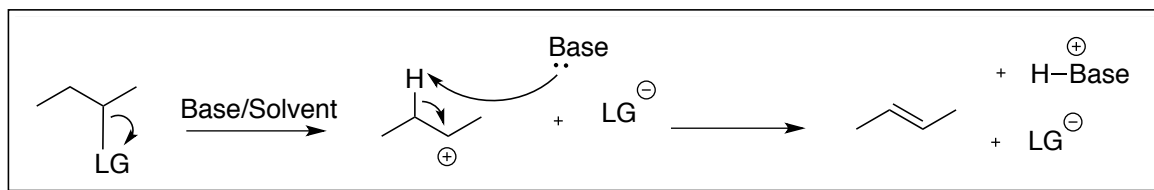
# Elimination Reactions: General features



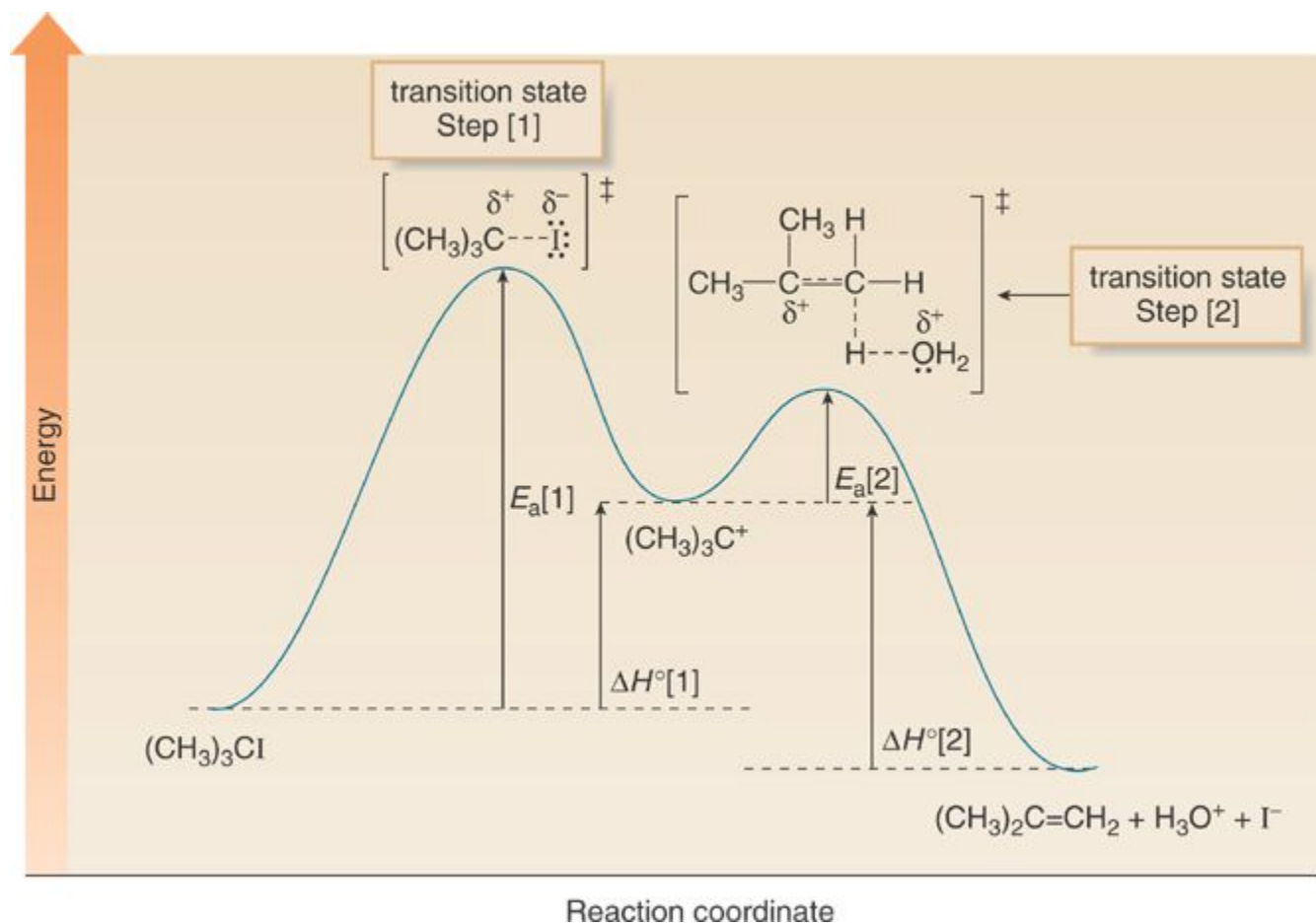


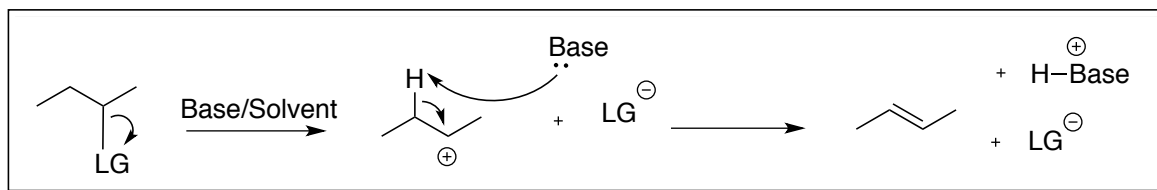
## Mechanism 1:

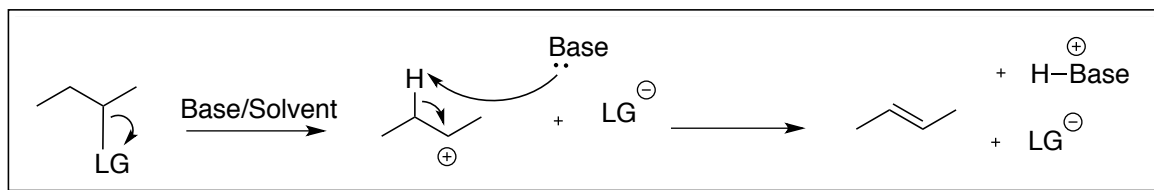
E1 Reaction:  $R = k[\text{starting material}]$



# E1: Reaction Coordinate diagram

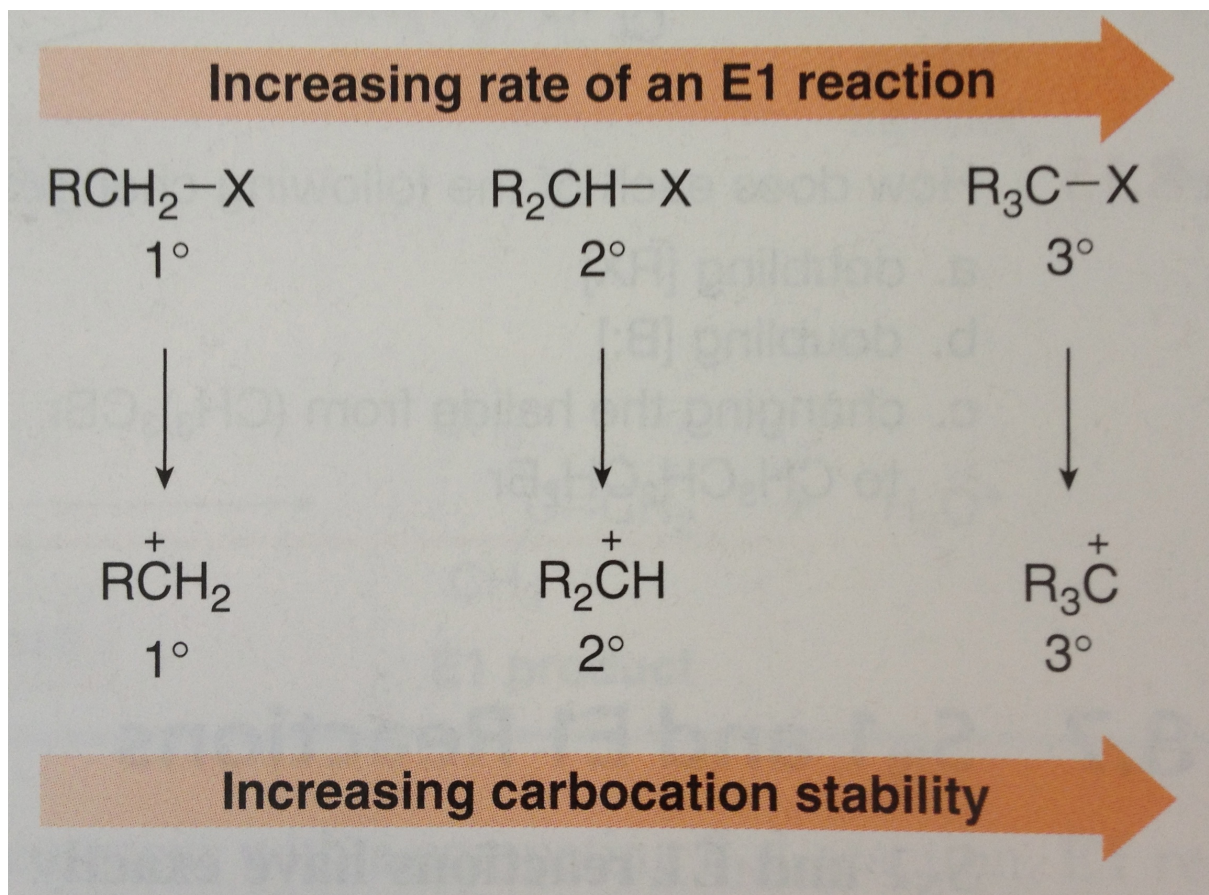


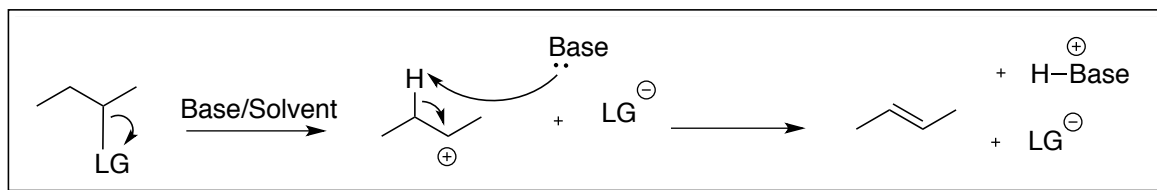




# E1 characteristics: Polar C-LG bond

- $\alpha$  Carbon: Carbocations are UNSTABLE (HIGH E)





# E1 characteristics: Leaving group (LG)

- A good leaving group is stable.
- Good leaving groups are also weak bases

**Table 7.2** Good Leaving Groups for Nucleophilic Substitution

Starting material	Leaving group	Conjugate acid	pK <sub>a</sub>
R-Cl	Cl <sup>-</sup>	HCl	-7
R-Br	Br <sup>-</sup>	HBr	-9
R-I	I <sup>-</sup>	HI	-10
R-OH <sub>2</sub> <sup>+</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>	-1.7

These molecules undergo nucleophilic substitution.

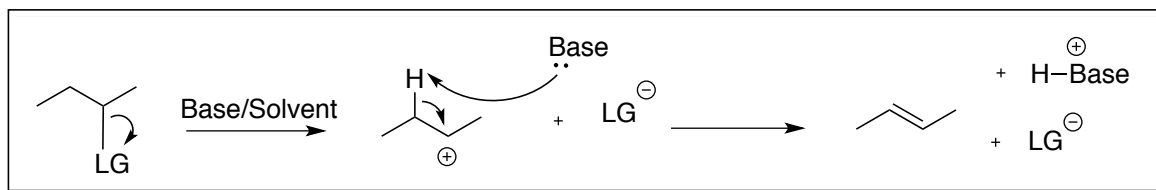
good leaving groups

**Table 7.3** Poor Leaving Groups for Nucleophilic Substitution

Starting material	Leaving group	Conjugate acid	pK <sub>a</sub>
R-F	F <sup>-</sup>	HF	3.2
R-OH	<sup>-</sup> OH	H <sub>2</sub> O	15.7
R-NH <sub>2</sub>	<sup>-</sup> NH <sub>2</sub>	NH <sub>3</sub>	38
R-H	H <sup>-</sup>	H <sub>2</sub>	35
R-R	R <sup>-</sup>	RH	50

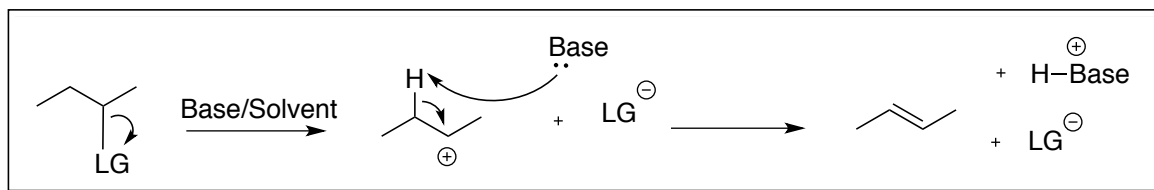
These molecules do *not* undergo nucleophilic substitution.

poor leaving groups



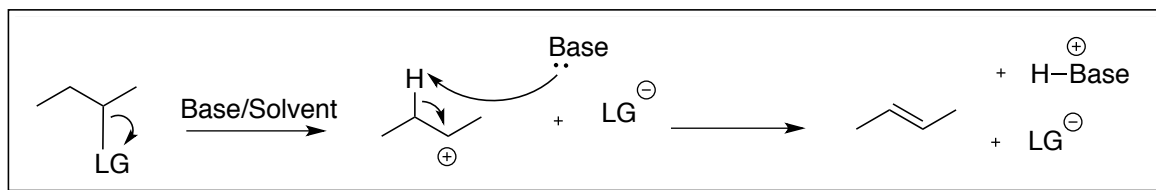
## E1 characteristics: Base and solvent

- Weaker bases favour an E1 mechanism
- Often, a solvent molecule acts as the base for the reaction
- Polar, protic solvents are best
- E.g.,

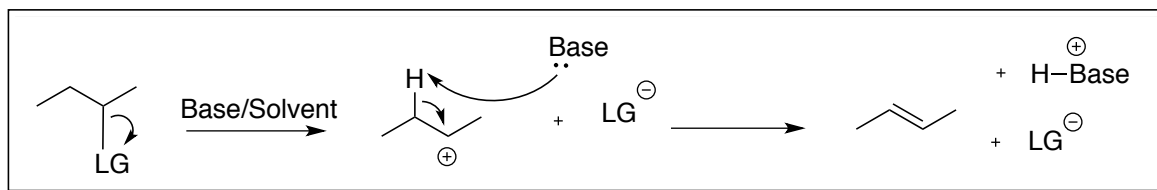


# E1 characteristics: Role of solvent

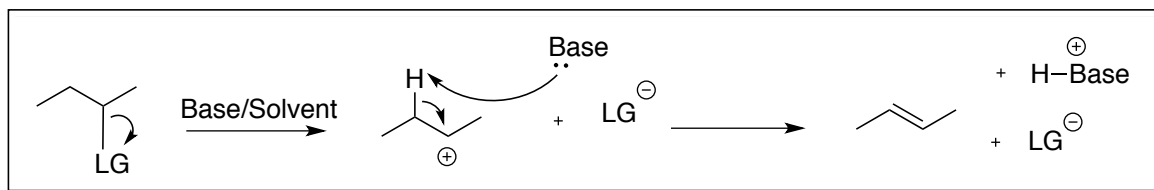
- Polar, protic solvents stabilize the developing carbocation and leaving group in the transition state (TS)
  - Lowers the TS energy of the RDS



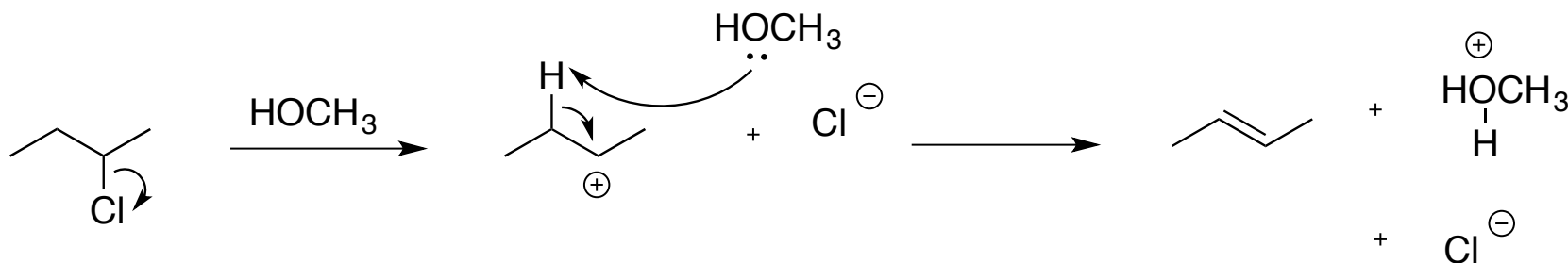
# E1 characteristics: Regiochemistry



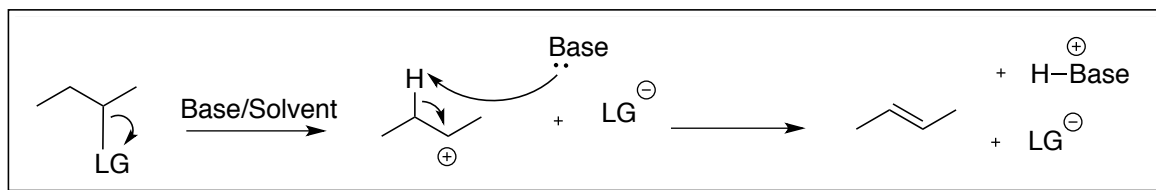
# E1 characteristics: Stereochemistry



## E1 Summary



- $\alpha$  carbon:  $3^\circ$  or resonance-stabilized  $> 2^\circ \gg 1^\circ$
- Leaving group: a weak base is best
- Base:
  - Weak bases favour E1
  - Often the solvent
- Solvent:
  - Polar, protic
  - Stabilize the TS of the RDS
- Regiochemistry: get the most substituted (stable) alkene
- Stereochemistry: get the most stable alkene



# Recall: Electrophilic Aromatic Substitution