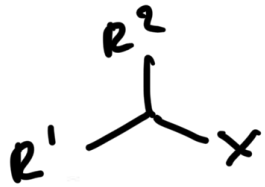
Nucleophilic substitution reactions: S_N2 vs S_N1

Effect of the nucleophile

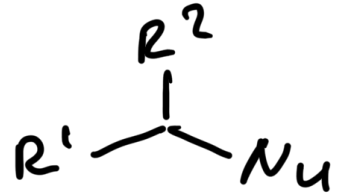
S_N2

rate = k[RX][Nu]

E_a changes with Nu



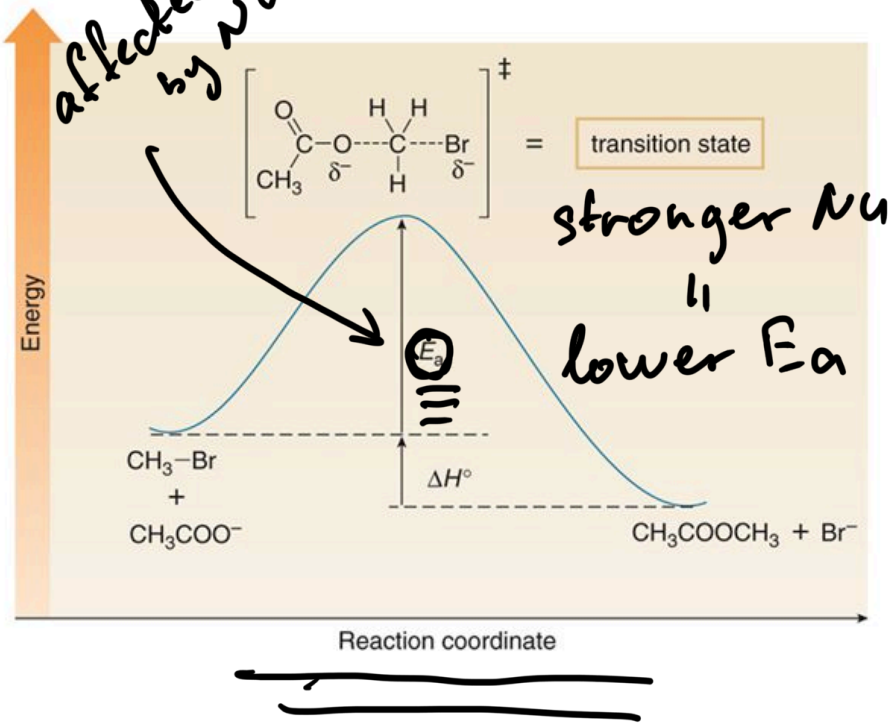
Nu



S_N1

rate = k[RX]

affected by Nu

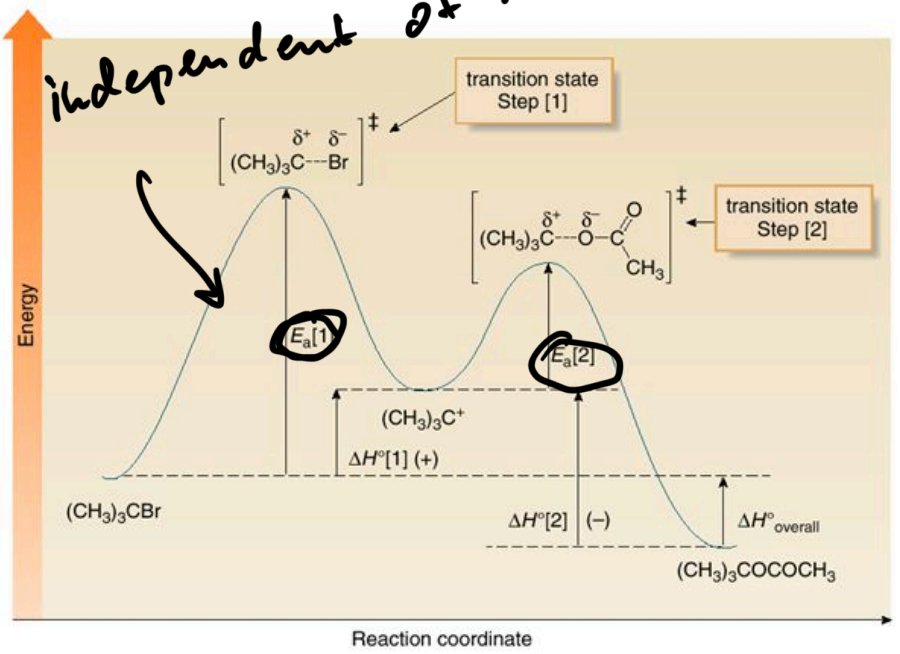


stronger Nu

⇓

lower E_a

independent of Nu



Elimination reactions: E2 vs E1

Effect of the base

E2

rate = k [RX] [B]

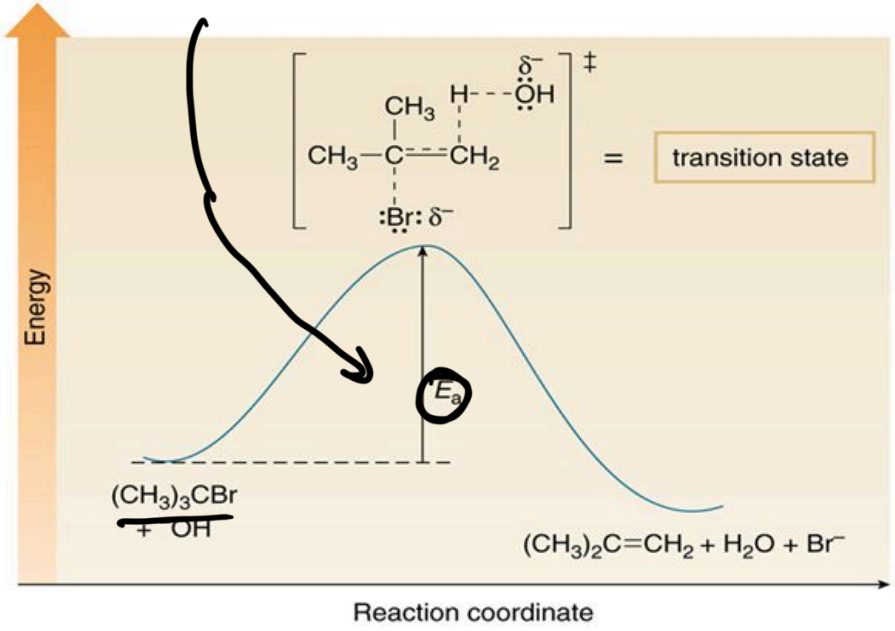
Strength of B affects E_a

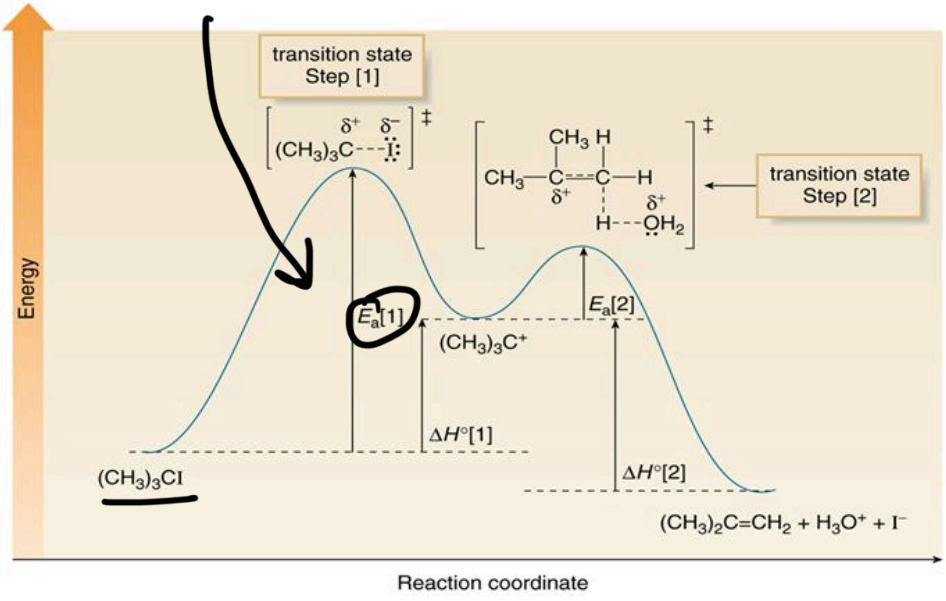
Stronger B → lower E_a

E1

rate = k [RX]

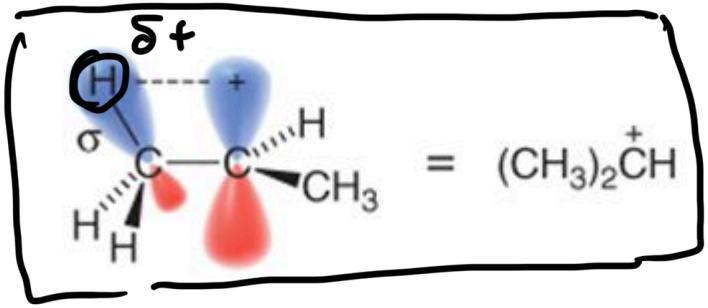
Strength of B has no effect on E_a





Elimination reactions: E1 mechanism

The second step in the E1 reaction



hyperconjugation

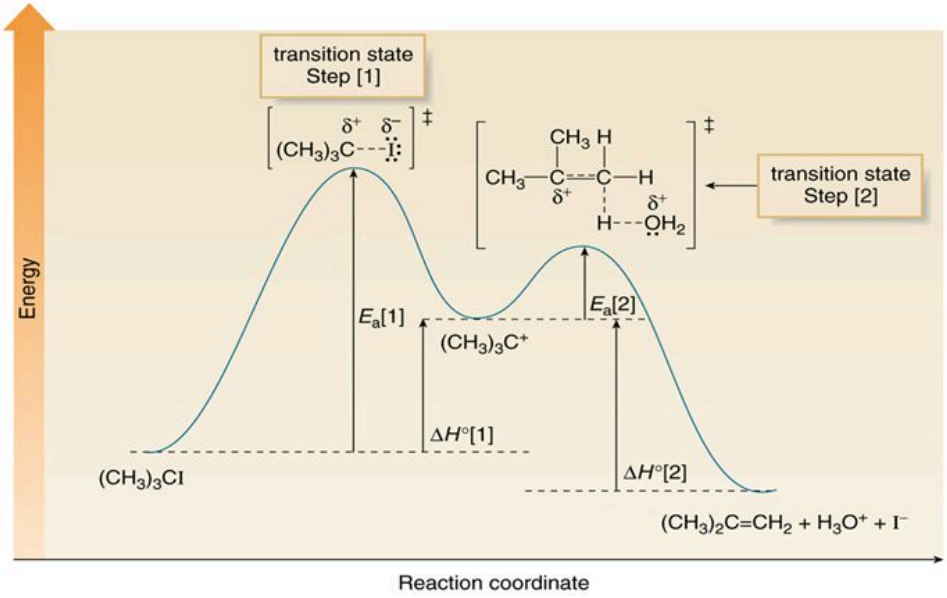
$\sigma_{C-H} \rightarrow p_C$

↓

stabilizes carbocations → distributes charge to β-hydrogens

↓

attacked by base

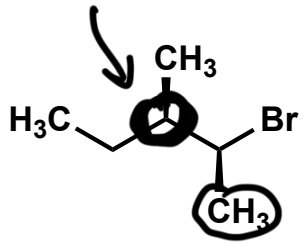


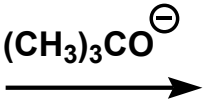
Substitution and elimination reactions: S_N2 and E2

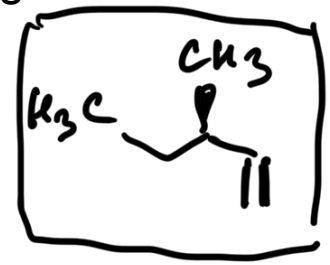
Stereochemical considerations

Substitution and elimination reactions: S_N2 and E2

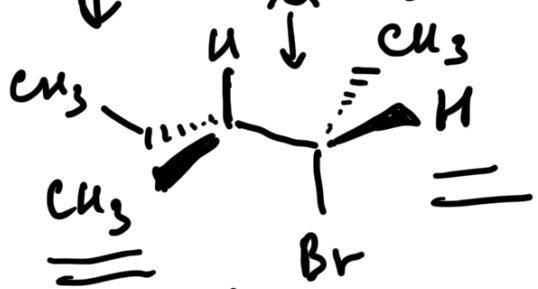
Stereochemical considerations



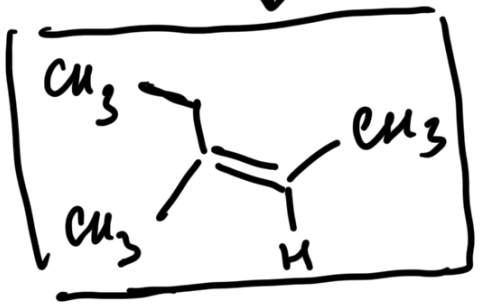


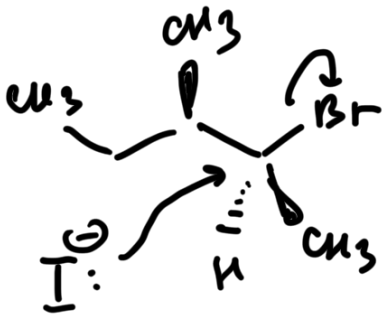


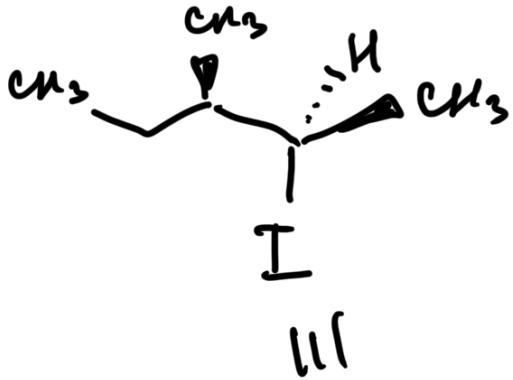
anti periplanar arrangement!

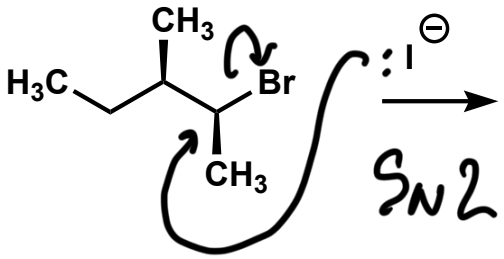


E2

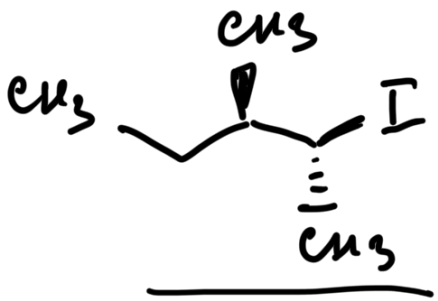






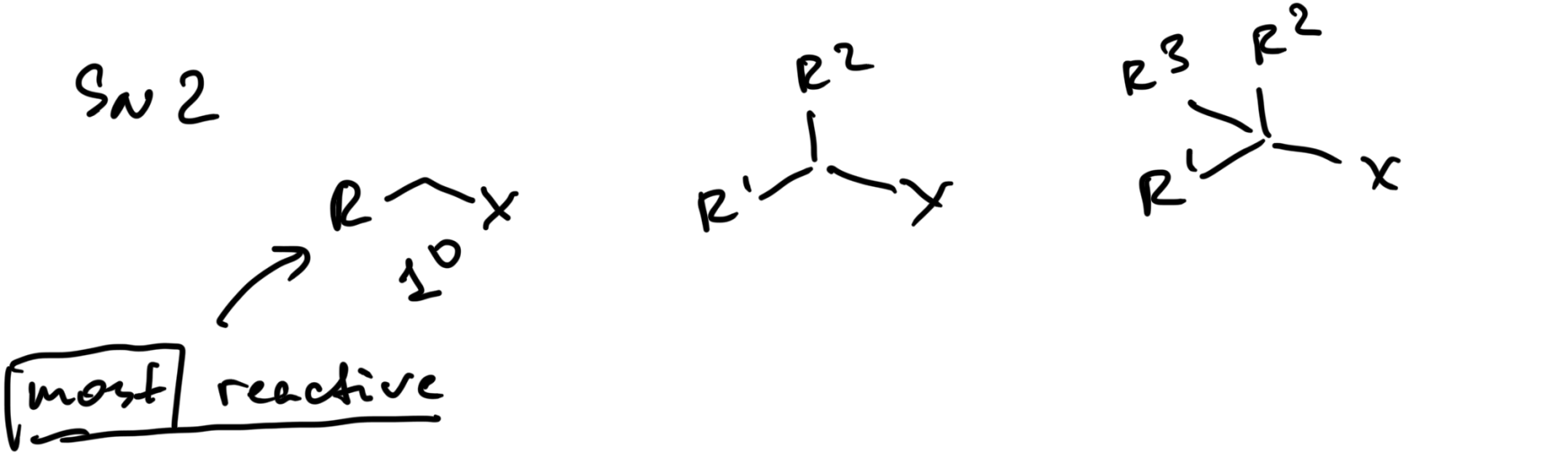


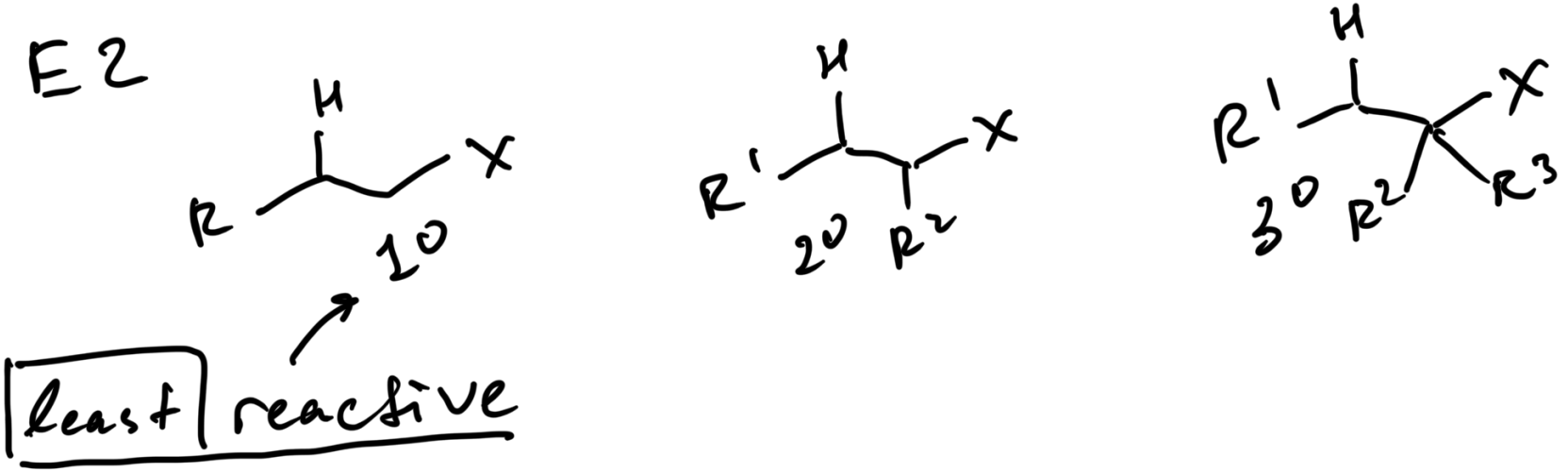
SN2



Substitution and elimination reactions: 1° alkyl halides

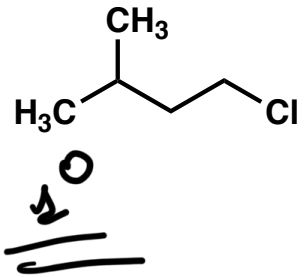
A closer look at S_N2 vs E2





Substitution and elimination reactions: rates

Can there be (almost) no reaction at all?

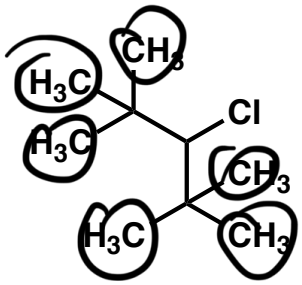


1°

H_2O

weak Nu, weak B

no reaction



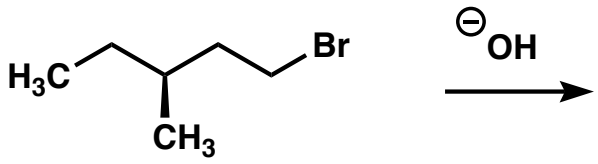
2°

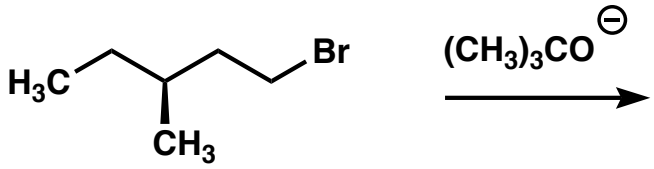
$(CH_3)_3CO^{\ominus}$

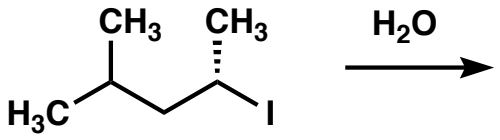
no reaction

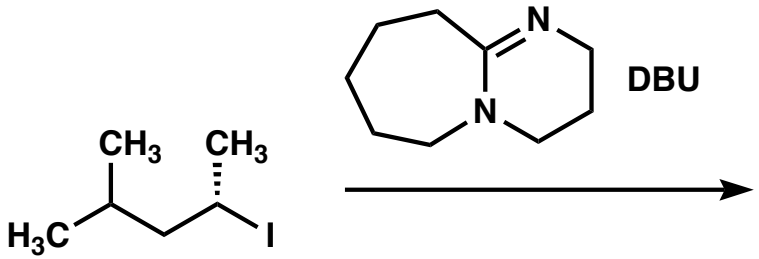
no β-hydrogens!

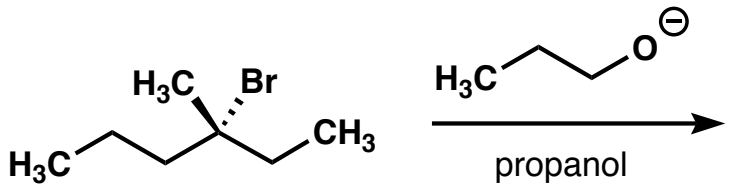
strong, bulky B

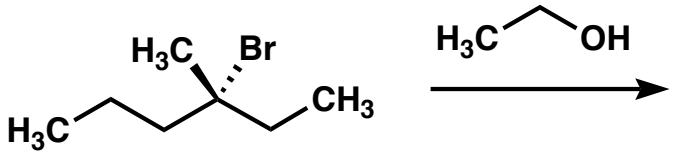

H3C
Br
CH3
⊖OH


H3C
Br
CH3
(CH3)3CO⊖


CH3
CH3
H2O
H3C
I


N
N
DBU
CH3
CH3
H3C
I


H3C
Br
CH3
H3C
H3C
O
propanol


H3C
Br
CH3
H3C
H3C
OH