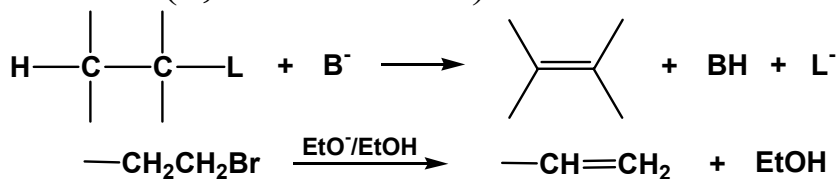
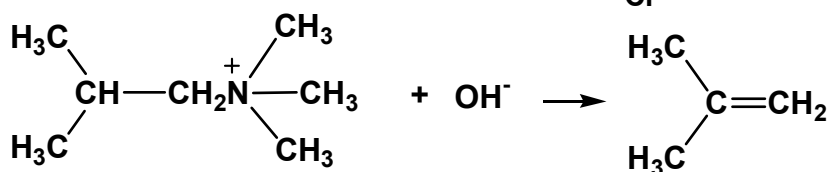
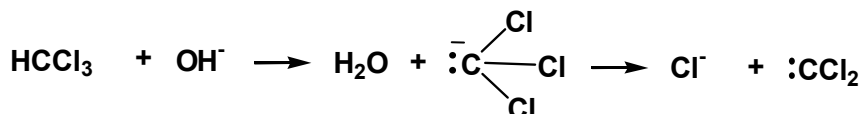
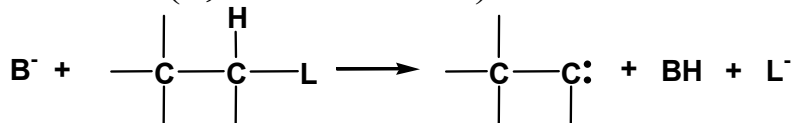


Chap 10. Elimination Reactions

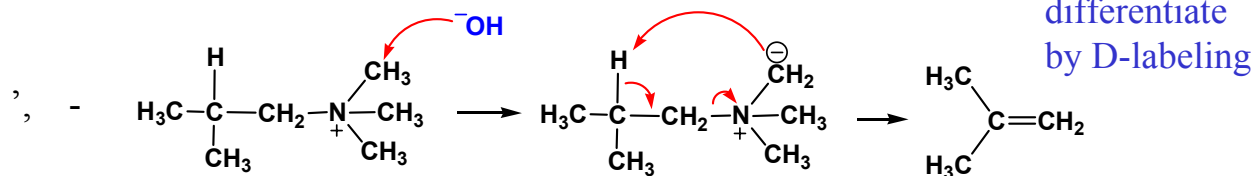
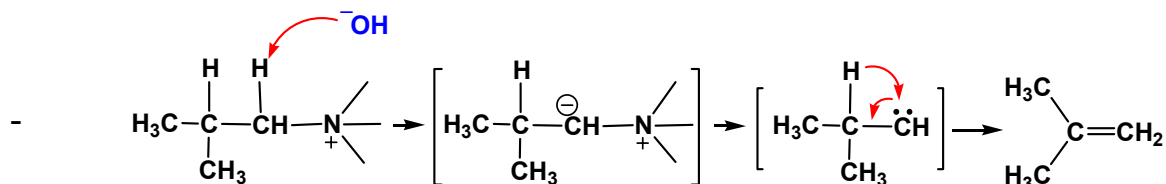
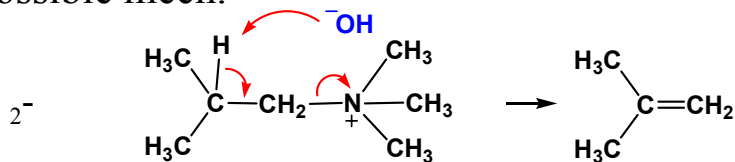
-elimination (1,2-elimination)



-elimination (1,1-elimination)



possible mech.



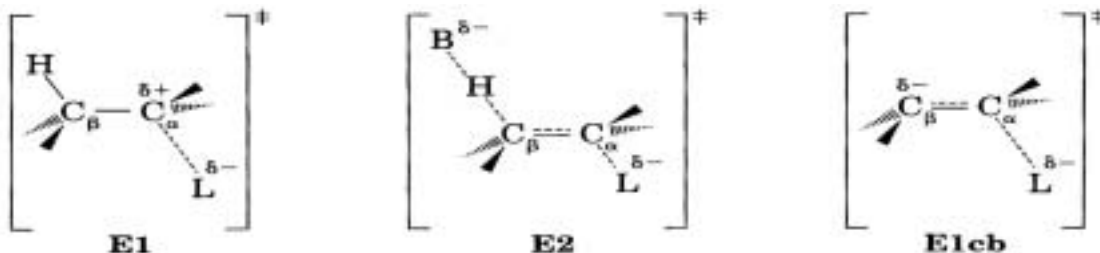
a deuterium label on β -carbon allows differentiation of the three mech.

if D appears on alkene β -elimination

if D appears on $\text{N}^+(\text{CH}_3)_3$ α -elimination

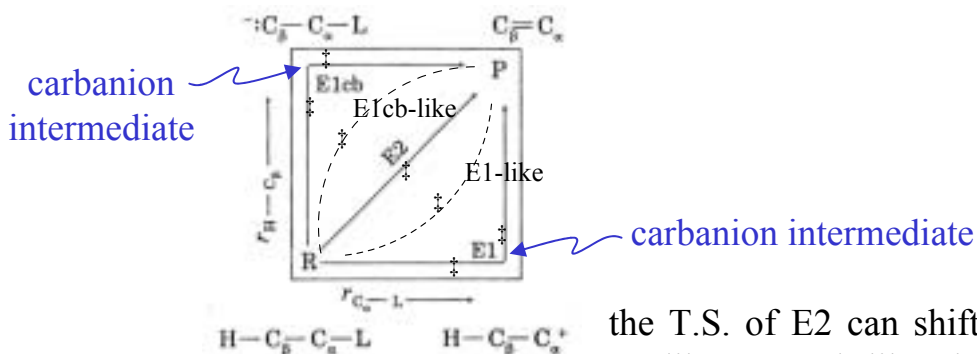
if D not on alkene, not on amine γ -elimination

1,2-elimination



differ in the timing of bond cleavage and/or the presence of intermediate

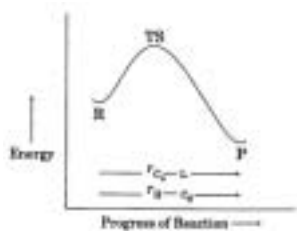
More-O'Ferrall diagram



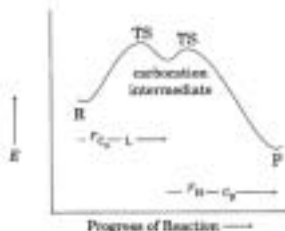
the T.S. of E2 can shift toward E1-like or E1cb-like, depending on structure & reaction medium

e.g. stronger base or poorer leaving gp \rightarrow shift to E1cb

Good LG, or high ionizing solvent \rightarrow shift to E1

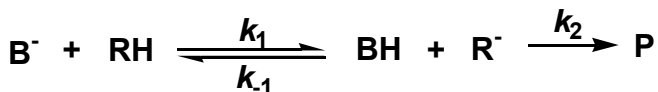


E2
second order kinetics
rate = $k[B^-][R]$



E1, first order kinetics
r.d.s. the unimolecular
ionization
rate = $k [R]$

For E1cb, an intermediate carbanion is involved



s.s.a $k_2[R^-] + k_{-1}[R^-][BH] = k_1[B^-][RH]$

$$[R^-] = \frac{k_2 \cdot k_1 [R^-][BH]}{k_{-1}[BH] + k_2}$$

$$rate = \frac{dP}{dt} = k_2[R^-] = \frac{k_2 \cdot k_1 [R^-][BH]}{k_{-1}[BH] + k_2}$$

Characteristic for substrates with acidic β -H, or poor leaving group, or having electron-withdrawing group on β -C.

E1cb(anion)

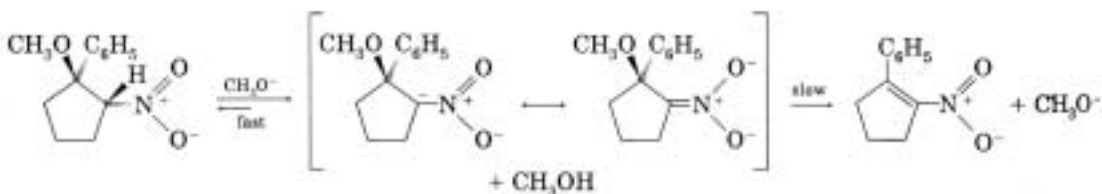
if $k_1 \gg k_{-1}$, k_2 , and $[B^-] \gg [RL]$.

Pseudo first order, all RL is in the form of carbanion

$$Rate \approx k[RL] \text{ (first order)}$$

characteristics : fast isotope exchange of C -D

$k_H/k_D \sim 1$, appreciable leaving group effect (element effect)



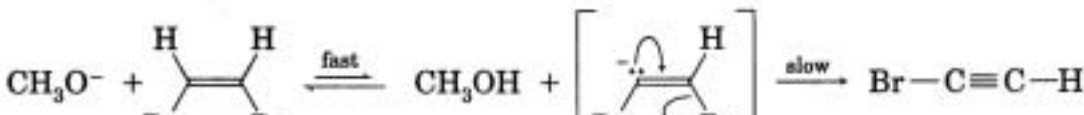
E1cb_R(reversible)

if $k_{-1} \sim k_1$, $k_{-1}[BH] \gg k_2$,

$$Rate = \frac{k_2 k_1 [RL][B^-]}{k_{-1}[BH]} = k_{obs}[B^-][RL] \text{ if BH is the solvent}$$

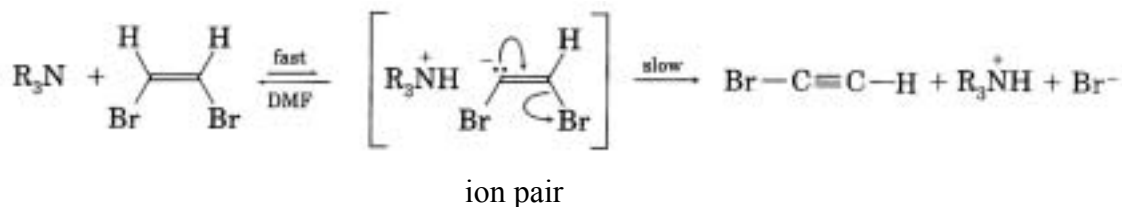
If $[B^-]/[BH]$ is kept constant using buffer, rate is independent of the concentration of base \Rightarrow specific base catalysis

characteristics : C -H exchange $k_H/k_D \sim 1$, small leaving group effect



E1cb_{ip}(ion pair)

Similar to E1cb_R, but no free anion is formed, an ion pair is formed with the protonate base as the counter cation



characteristics: $k_H/k_D \sim 1-1.2$. No β -H exchange. addition of R₃N⁺DX⁻ will not affect the rate and caused no isotope exchange.(so, diff. from E1cb_R)

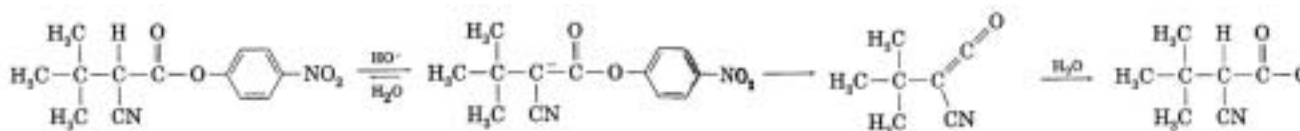
E1cb_I(irreversible)

if $k_2 \gg k_{-1}$ [BH] \gg k_1

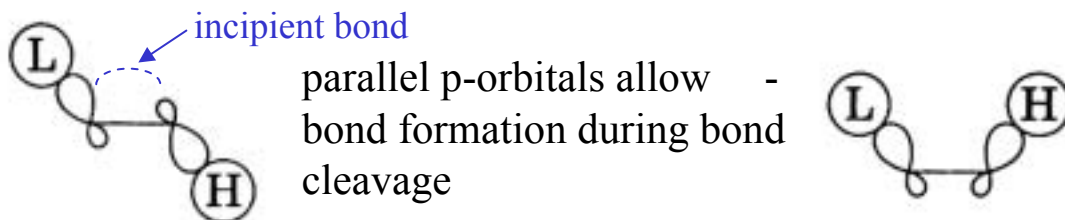
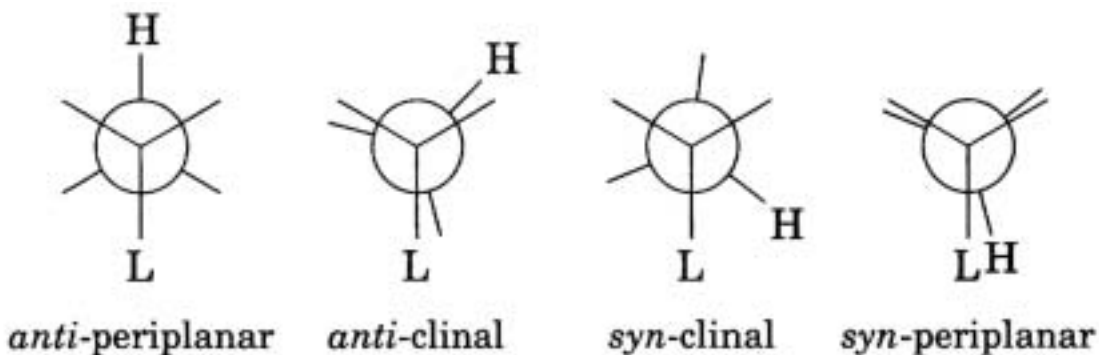
Rate $\approx k[\text{RL}][\text{B}^-]$ (second order)

characteristics : little C -H exchange

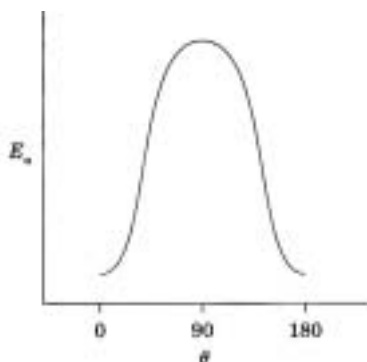
significant k_H/k_D (2~8)



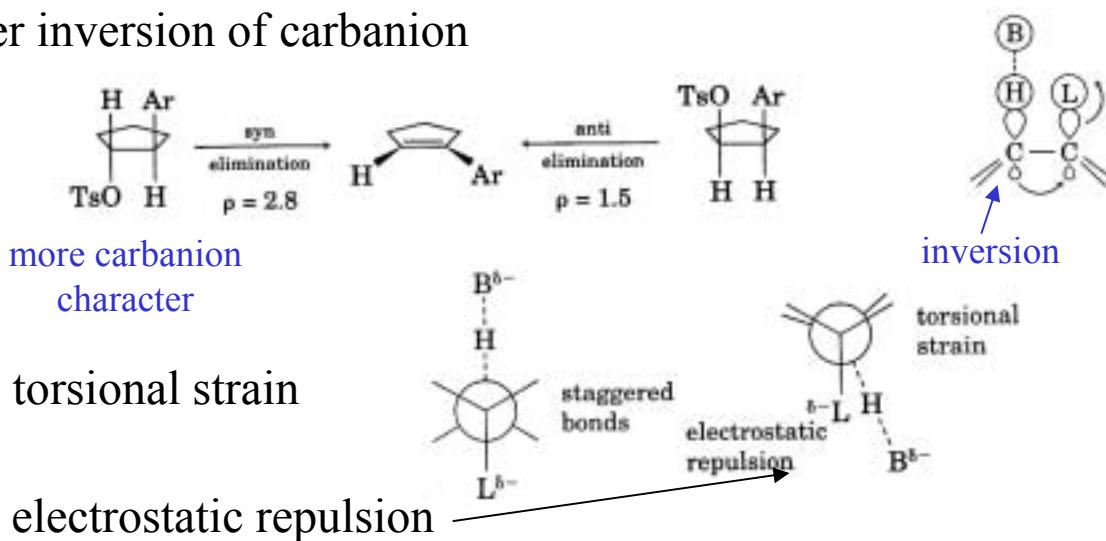
Stereochemistry of 1,2-Elimination Rxns



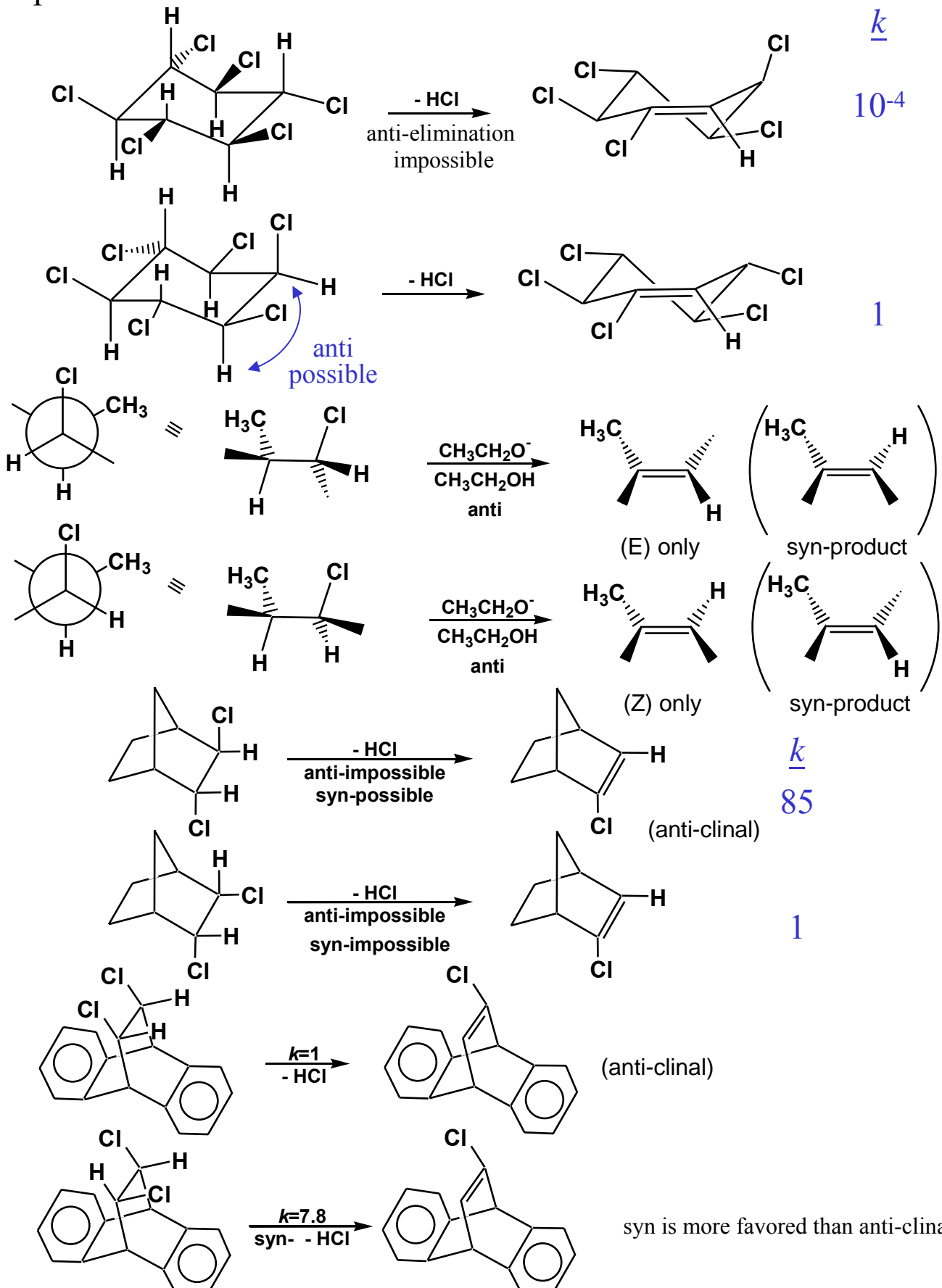
barrier to 1,2-elim.



anti-elimination is favored over syn due to (1) overlap of electron in C-H bond (HOMO) with backside of C-L bond (LUMO) if carbanion formation is extensive syn-elimination is possible after inversion of carbanion

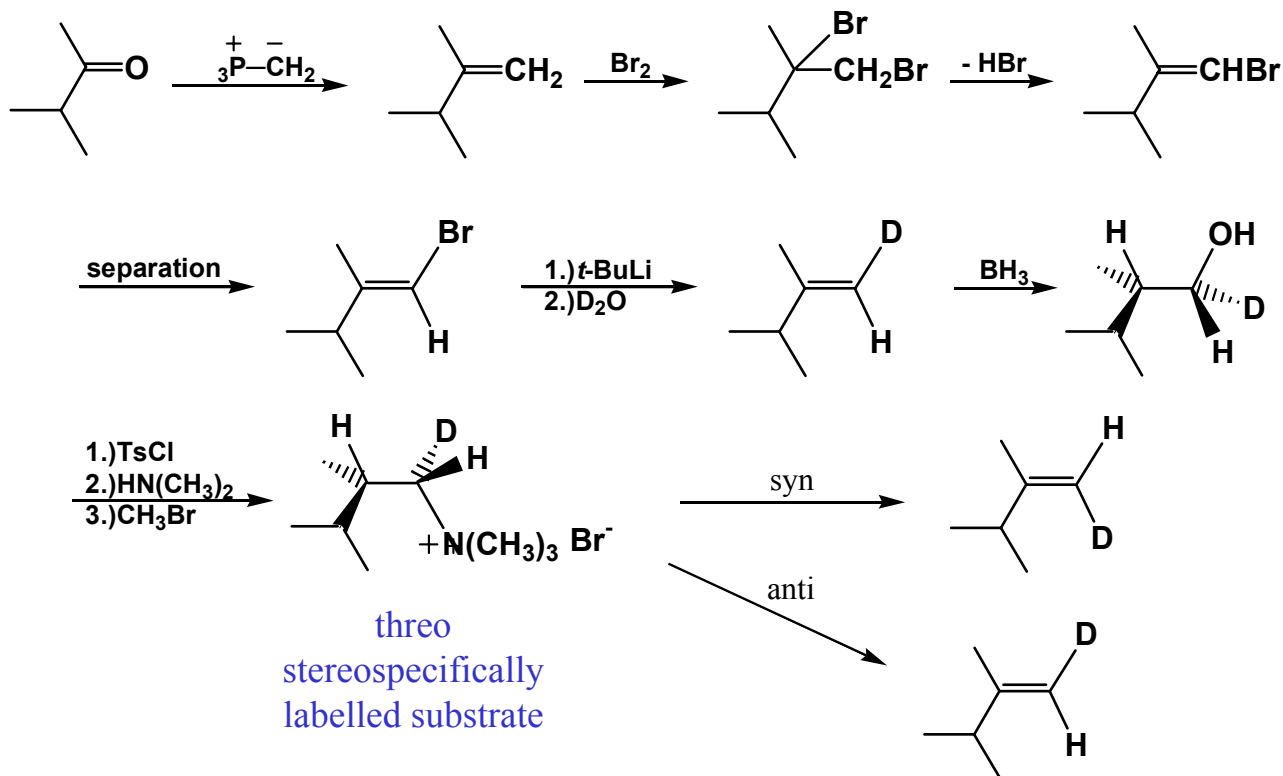
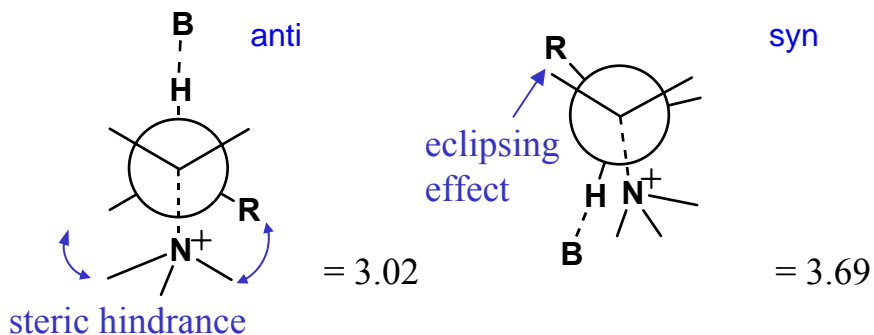
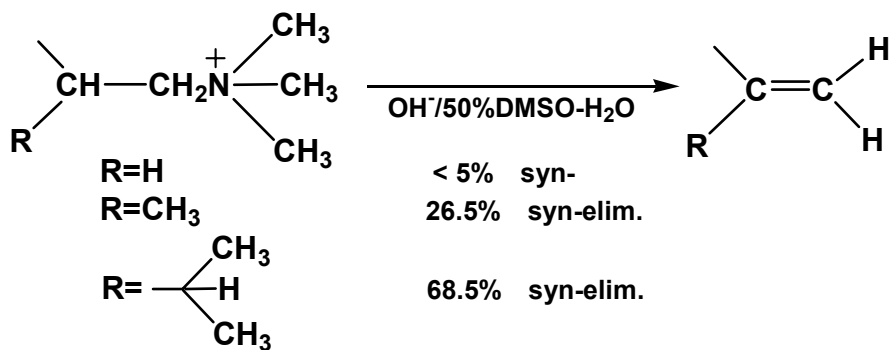


preference for anti-elimination

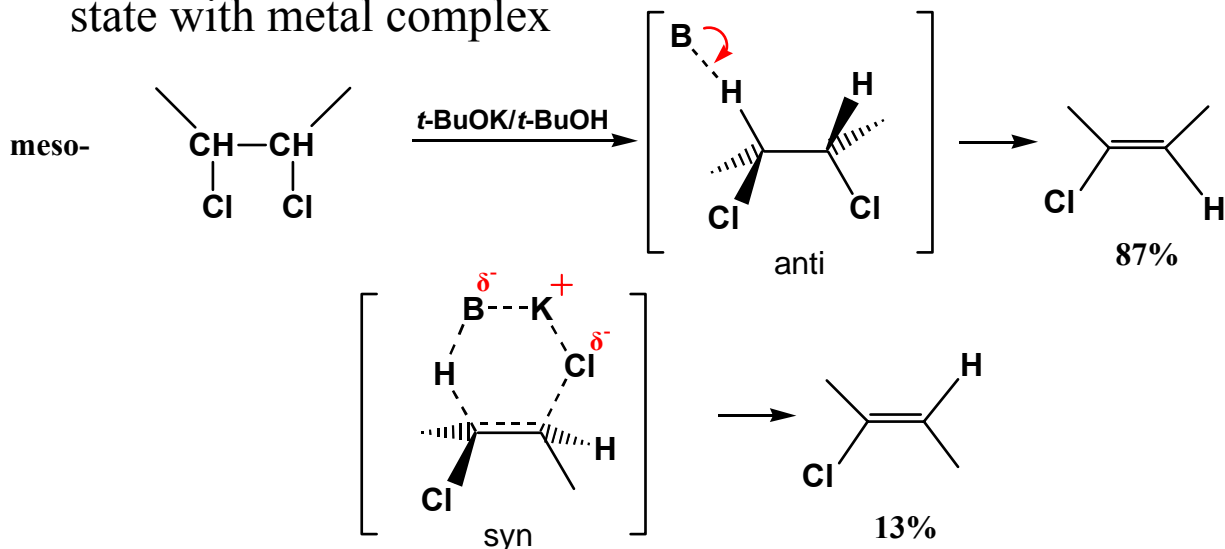


Syn-elimination can proceed in acyclic system

due to steric effect

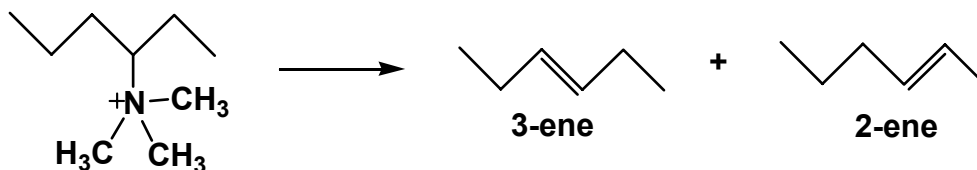


Syn-elimination can be promoted through a cyclic transition state with metal complex



In the presence of 18-crown-6, K^+ is complexed by crown ether
The 6-membered TS is suppressed, only anti-product

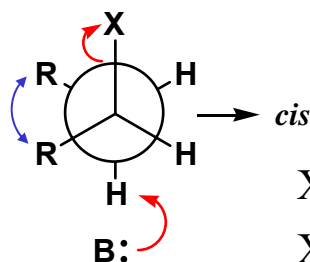
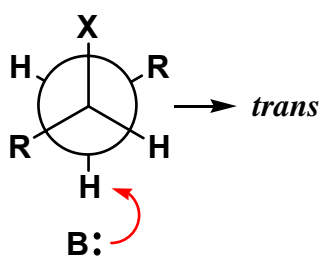
Effect of Base



Condition	Rxn prod.	Syn, %
NaOH-H ₂ O	3-ene	9.4
NaOH-DMSO	3-ene	53.0
MeOK	3-ene	20
<i>sec</i> -BuOK	3-ene	67
<i>t</i> -BuOK	3-ene	80

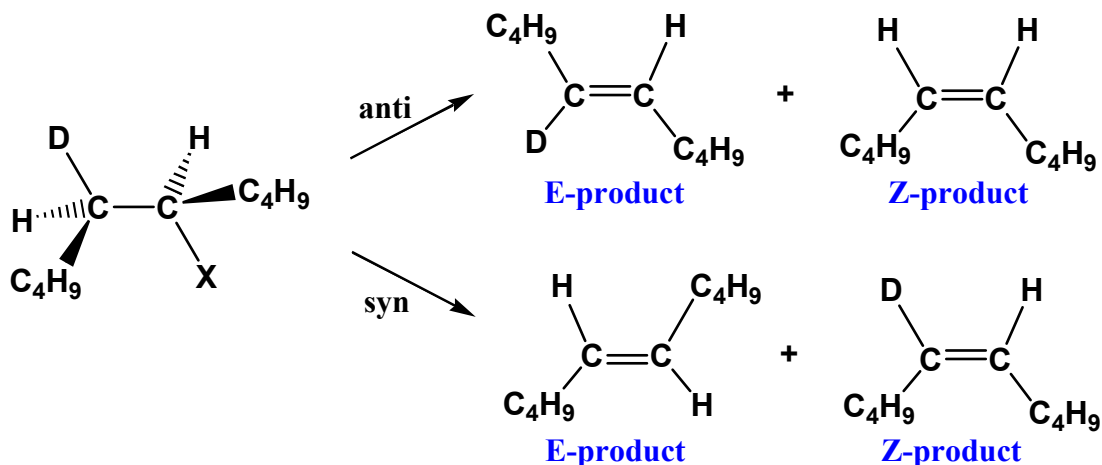
the stronger the base
the higher amt. of
Syn-elimination

cis-trans isomer



X = halide *trans*
X = OTs *cis* increase

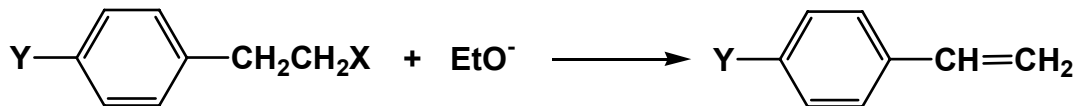
Effect of leaving gp



% syn elimination

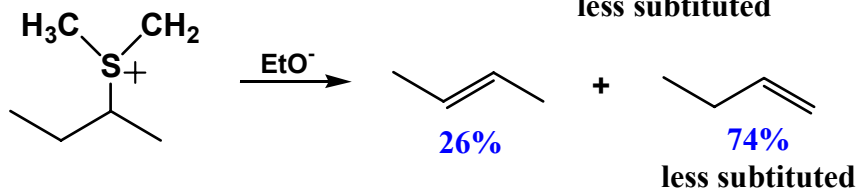
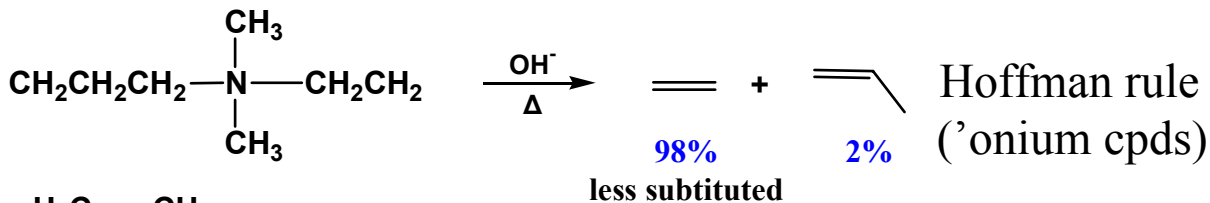
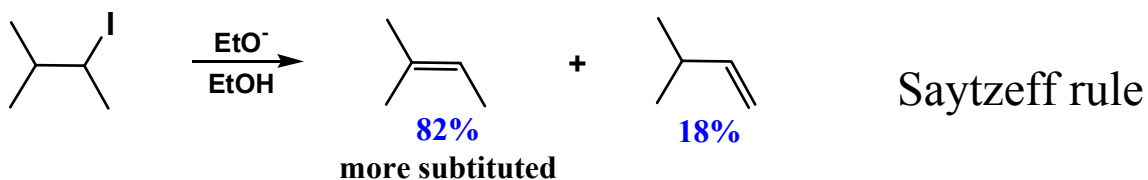
leaving gp	E product		Z product	
	DMSO	Benzene	DMSO	Benzene
Cl	6	62	7	39
OTs	4	27	4	16
⁺ N(CH ₃) ₃	93	92	76	84

better leaving gp, syn-elimination , anti-elimination favored
 polar solvent stabilize the leaving gp favor anti-elimination
 non-polar solvent favor ion-pair and complexed T.S



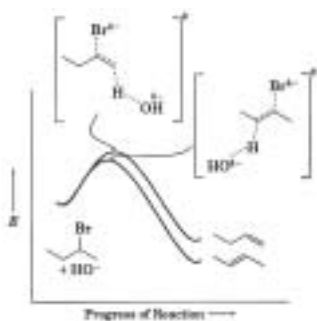
X =	Br	OTs	⁺ SMe ₂	⁺ NMe ₃	
k _H /k _D	7.11	5.67	5.07	2.98	← more than half-transferred B H C
	2.14	2.27	2.75	3.77	← more negative charge accumulation on C

Regiochemistry in 1,2-Elimination

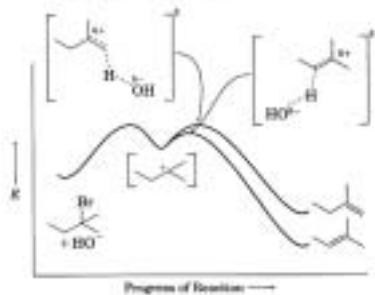


more substituted olefin is more stable,

Saytzeff rxn



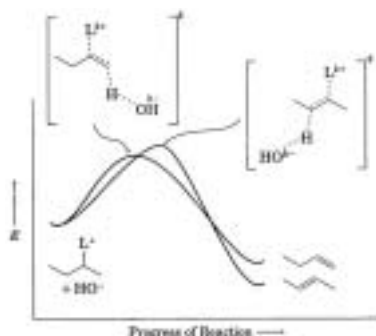
TS leading to more stable product will have lower activation energy "if" the TS has character of product i.e. E1, E2



product relative stability determine the product distribution

True for good leaving gp, eg. Br, I, OTs

Hoffman rxn

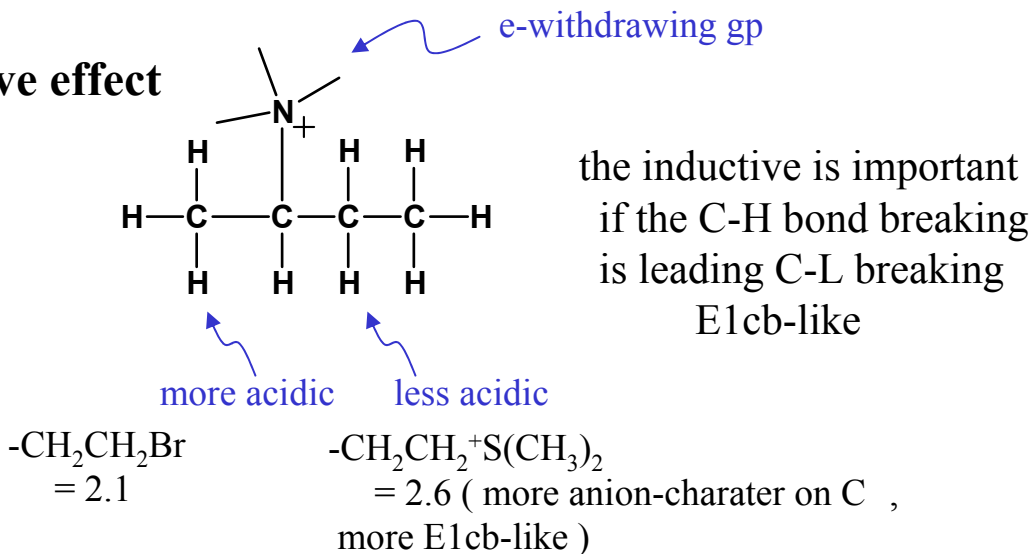


The TS more like carbanion, the stability of carbanion determine the product distribution

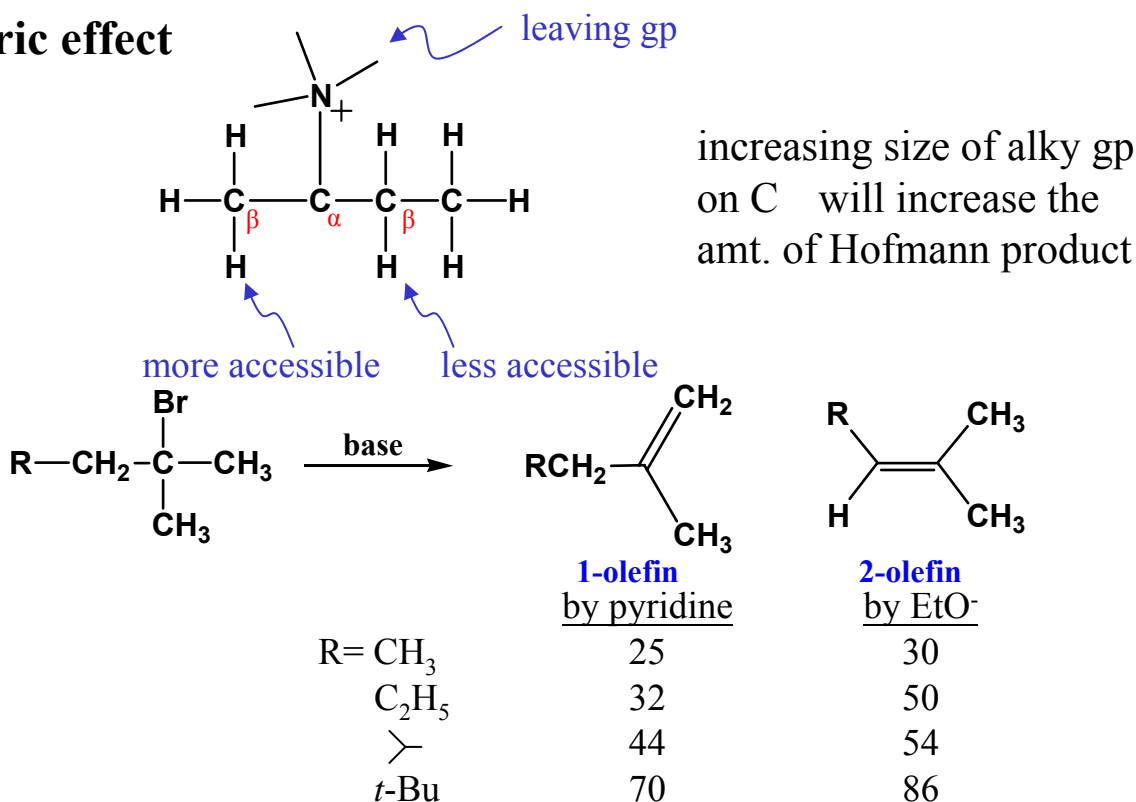
E1cb-like rxn less substituted olefin

Interpretation of Hofmann mechanism

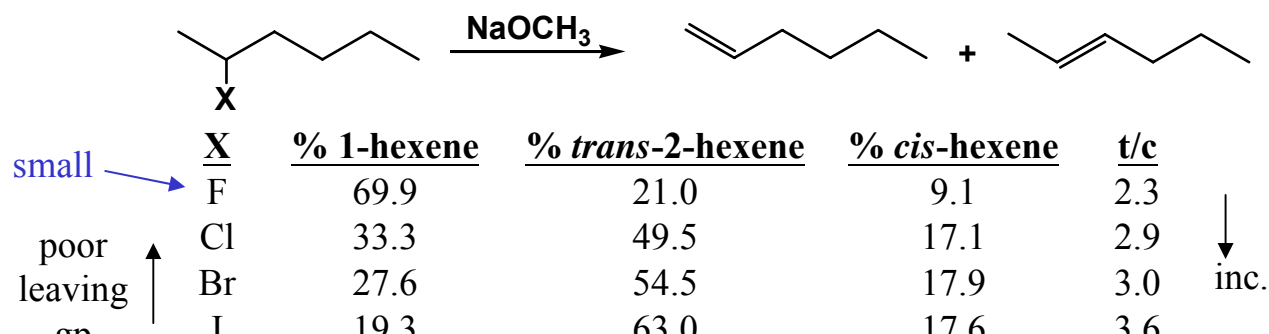
Inductive effect



Steric effect



Effect of Leaving group



Summary of Trends

The transition state structure determines the product distribution

The transition state (E1, E2, E1cb) is affected by reactant structure, solvent, base, ...

- * -aryl (or alkyl) substituent can stabilize a developing carbocation and make TS more E1-like
- * -aryl substituent can stabilize carbanion at β -carbon and make TS more E1cb-like
- *Introducing a β -alkyl gp makes the reaction more E1-like (less E1cb-like). (Shift a E1cb to more synchronous, and more E2-like, shift a E1-like more E1-like)
- *Better leaving group makes reaction more E1-like, poor leaving gp makes rxn more E1cb-like.
- *More electronegative leaving gp makes TS less carbocation character on β -carbon and more carbanion character on α -carbon atom.