Session 11 Worksheet

Alkenes and E1 Reactions

E and Z Designation:

Priority goes to the atom with highest atomic #

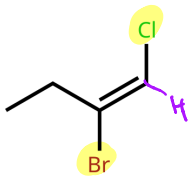
(E) configuration:

german for entgegen: "opposite"

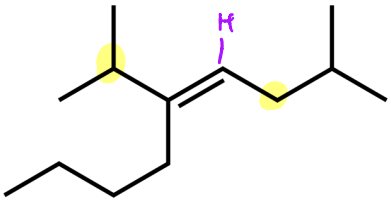
(Z) configuration:

german for zusammen: "together"

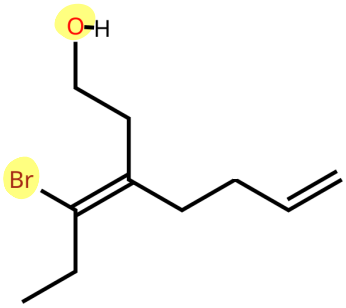
Assign Designation:



E

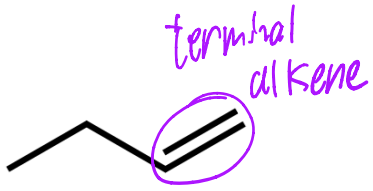


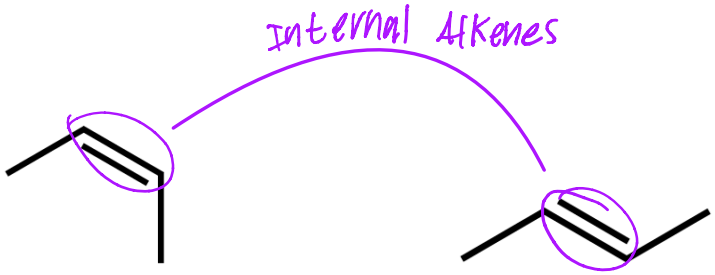
E



Z

Stability of Alkenes:

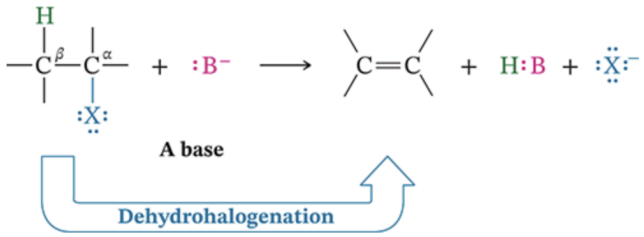




Less stable

More Stable

Dehydrohalogenation: A way of synthesizing alkenes by eliminating Hx from an alkyl halide



E2 Reactions

Elimination — [E2] — Bimolecular

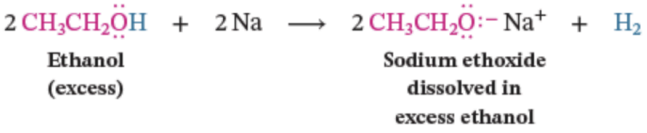
Uses a Concerted mechanism

Instead of a nucleophile, elimination uses a base, specifically a Strong base for E2

Alkoxide Base Synthesis: Typically uses an alcohol and Sodium or potassium

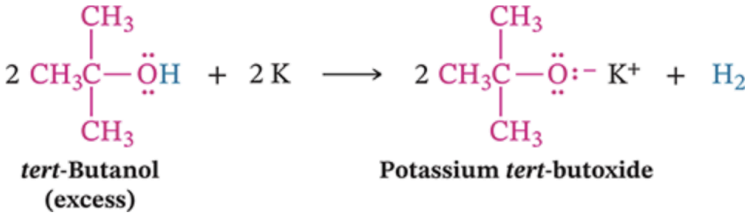
HELPFUL HINT

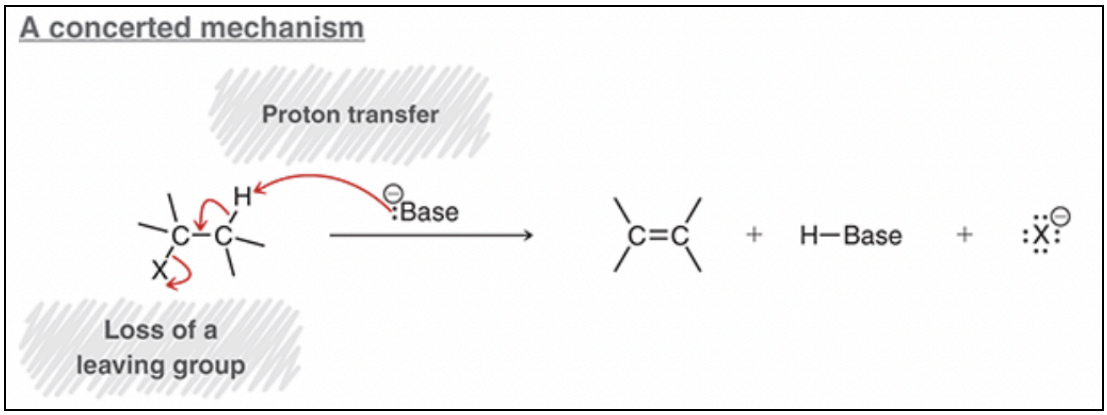
EtONa/EtOH is a common abbreviation for sodium ethoxide dissolved in ethanol.



HELPFUL HINT

***t*-BuOK/*t*-BuOH represents potassium *tert*-butoxide dissolved in *tert*-butanol.**

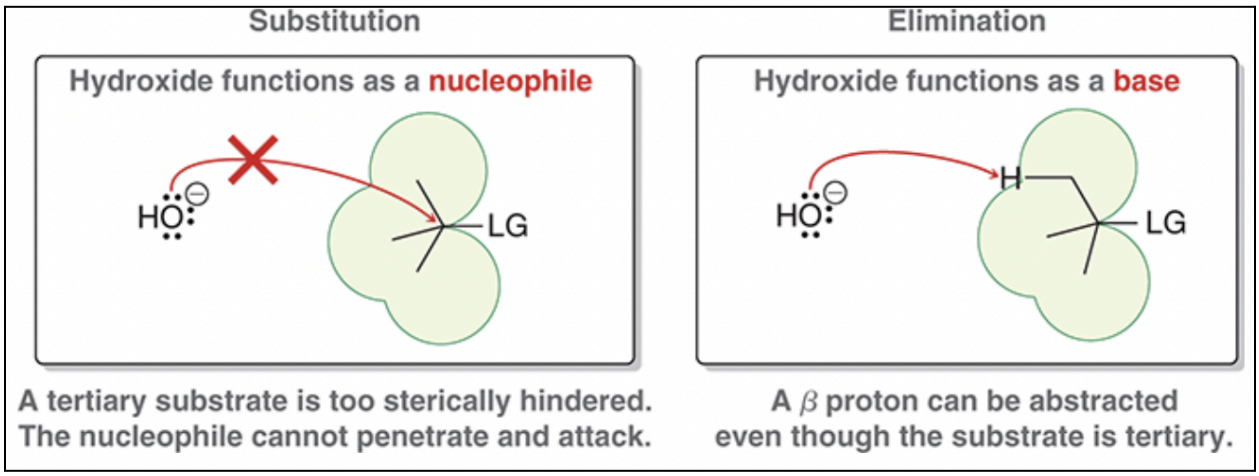




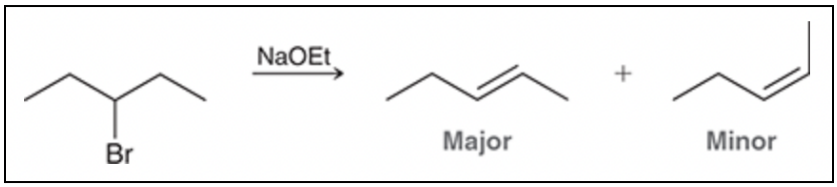
Kinetics: 2nd order

Rate = [sub][base]

E2 reacts better with 3° alkyl halides



Stereoselectivity of E2: The preference of one stereoisomer over another

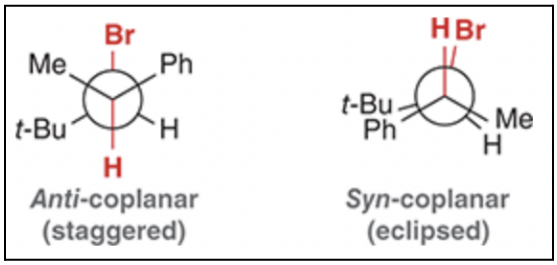


Antiperiplanar (Anti-coplanar):

H and LG are 180° apart

Synperiplanar (Syn-coplanar):

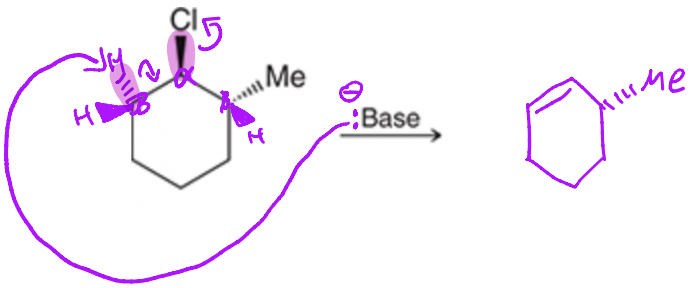
H and LG are 0° apart



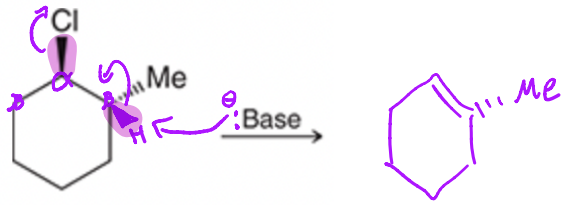
Low E High E

Example

What is observed:



What is NOT observed: (most of the time)



Types of strong bases:

$^{\ominus}OH$ (KOH)	$^{\ominus}OR$ (NaOEt)	t-buO$^{\ominus}$ (t-butOK)	DBN	DBU

Regioselectivity:

double bond in the prod. can be formed in more than one place

When a double bond can form in different regions of the compound, the reaction is

Regioselective

Zaitsev product:

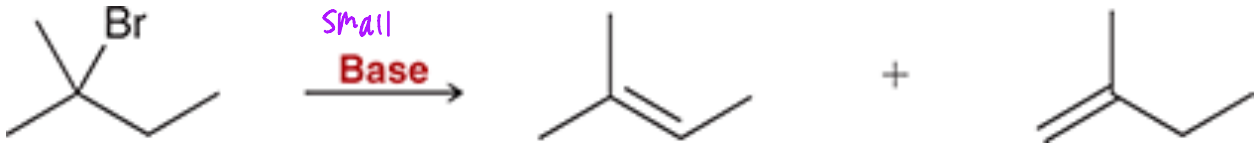
most substituted

Hoffmann product:

Least Substituted

major minor

Ex:



71 %
Zaitsev

29 %
Hofmann

The base you use determines the major/minor products

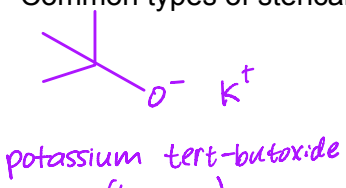
Bulky bases:

favor the Hofmann prod.

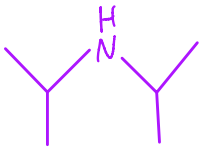
Non-bulky bases:

Favor the Zaitsev prod.

Common types of sterically hindered (bulky) bases:



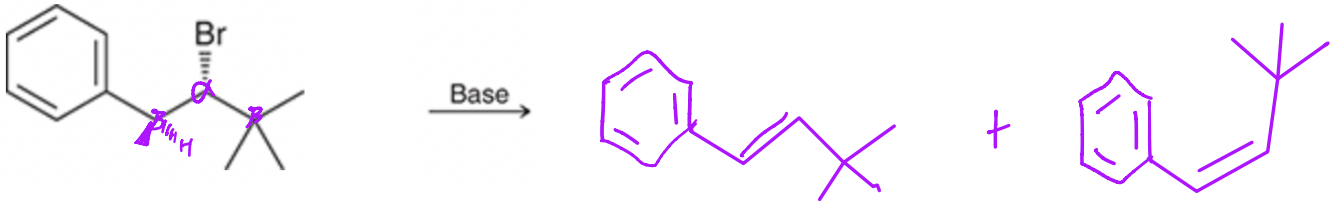
potassium tert-butoxide
(t-BuOK)



Diisopropylamine

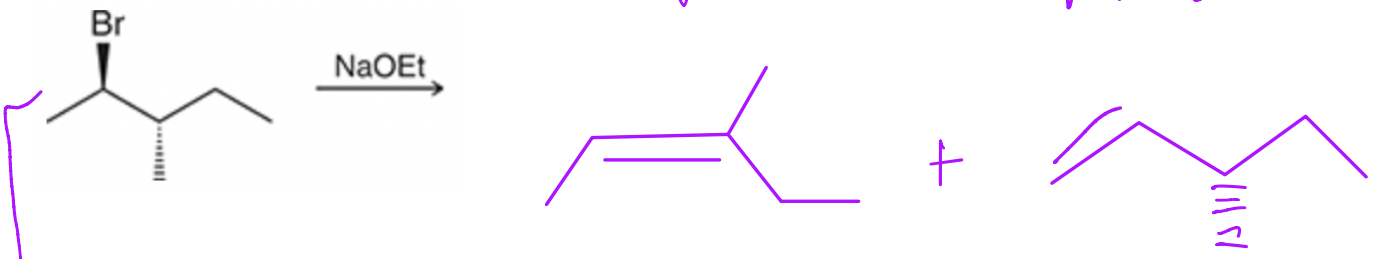
Tri-ethyl amine

Practice: Determine the major/minor products of the following E2 reaction:



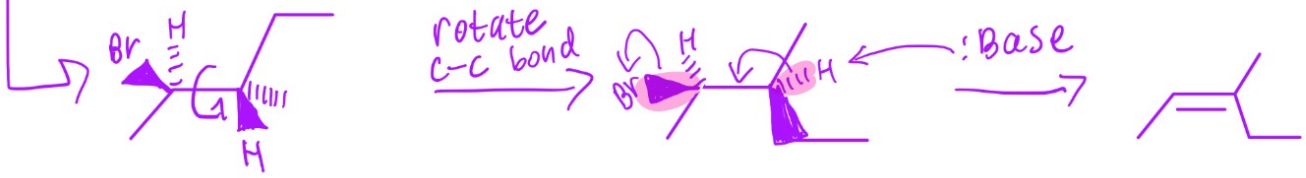
major

minor

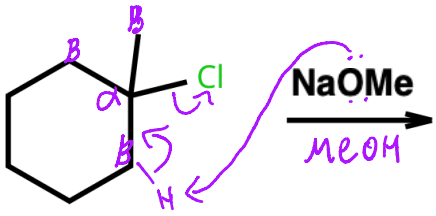


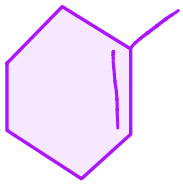
major

minor

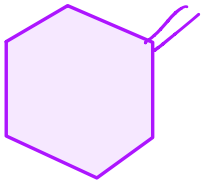


H and LG are now anti-coplanar, and E2 can begin





or

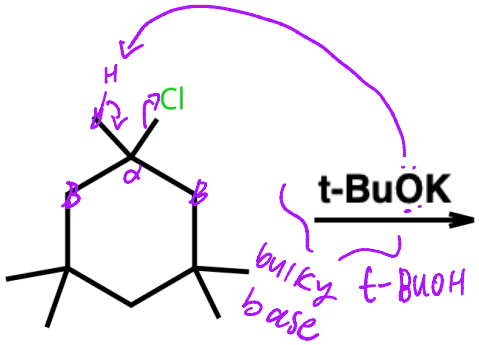


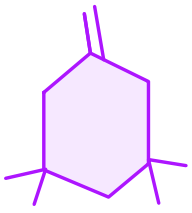
major

Zaitsev

minor

Hofmann





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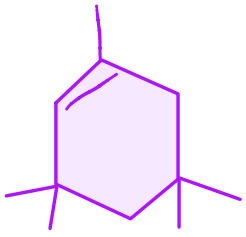


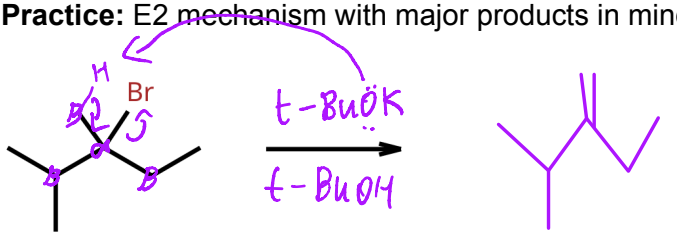
major

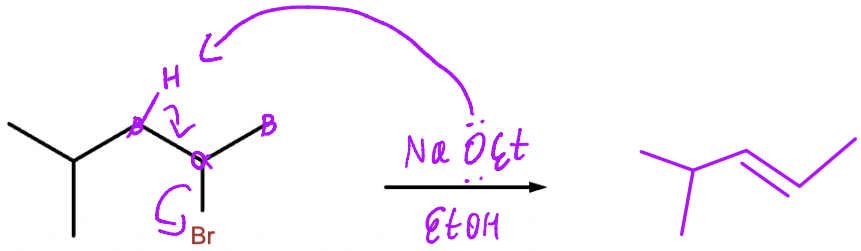
Hofmann

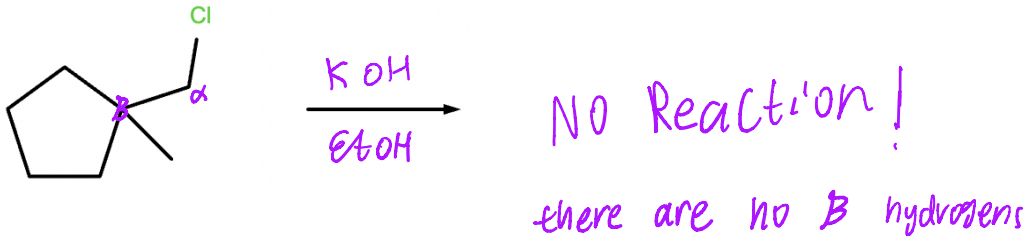
minor

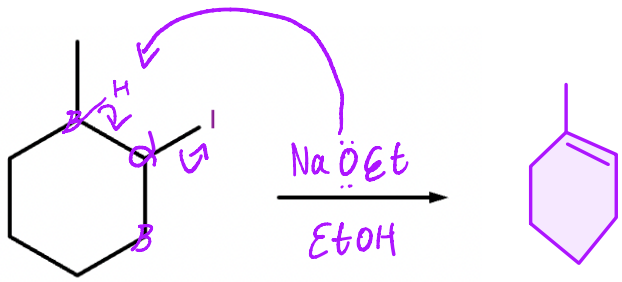
zaitzev

Practice: E2 ~~mechanism~~ with major products in mind







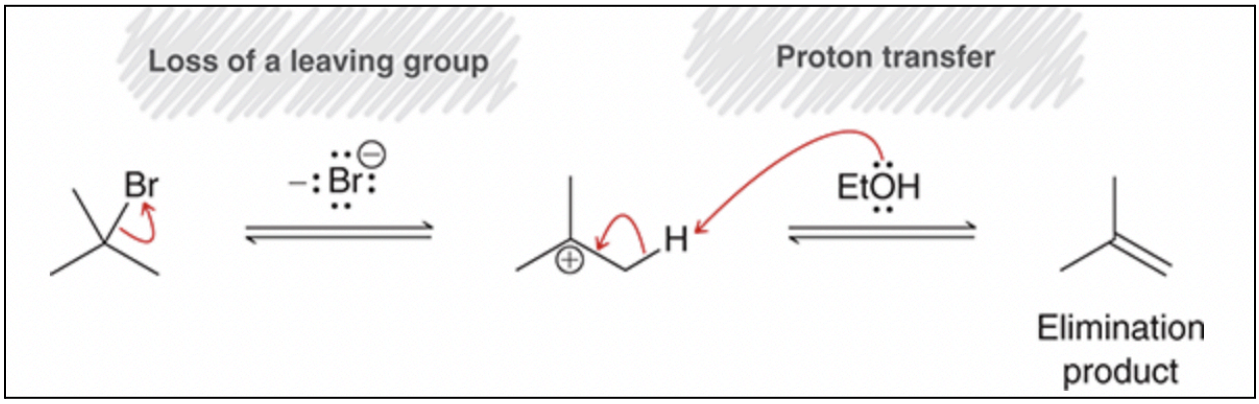


E1 Reactions

E1

E1 uses a Step-wise mechanism

Requires a weak base



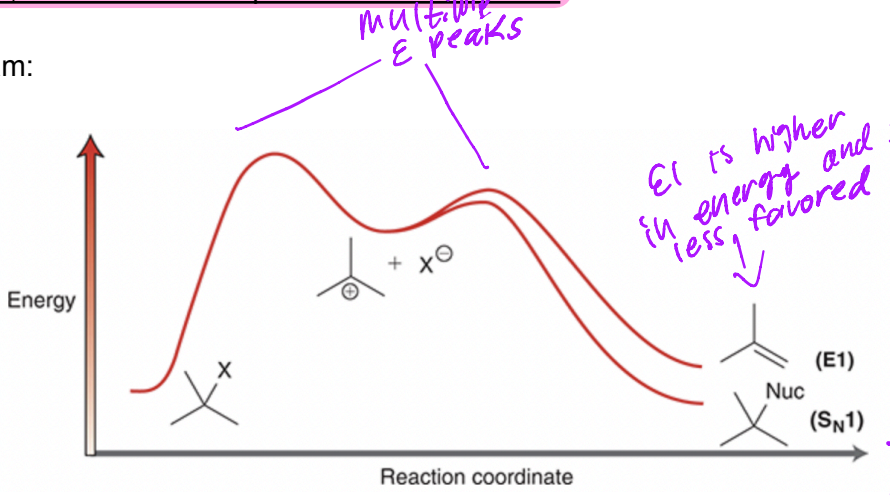
Kinetics: 1st order

Rate = K [sub]

E1 can only react with a 3° alkyl halide

In this reaction, both E1 and Sn1 products can be formed

Energy diagram:



Stepwise

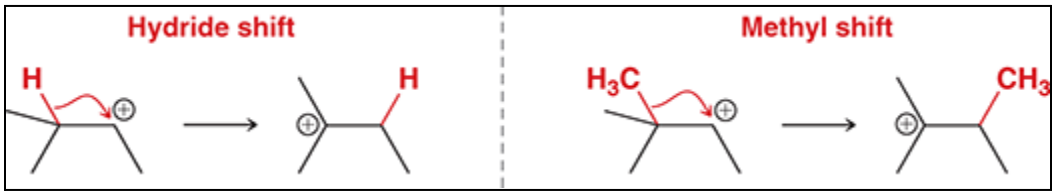
E1 is higher in energy and is less favored

typically major prod.

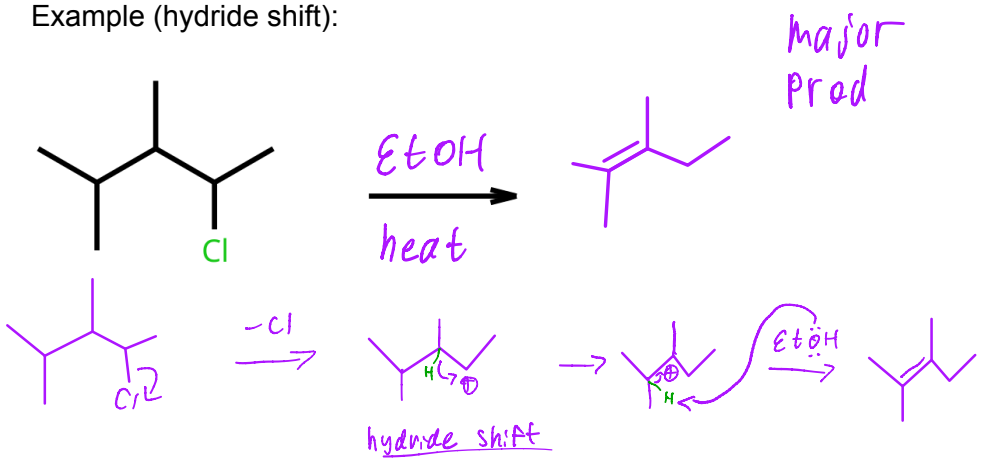
Types of weak bases

H_2O	ROH (MeOH) (EtOH)	COOH

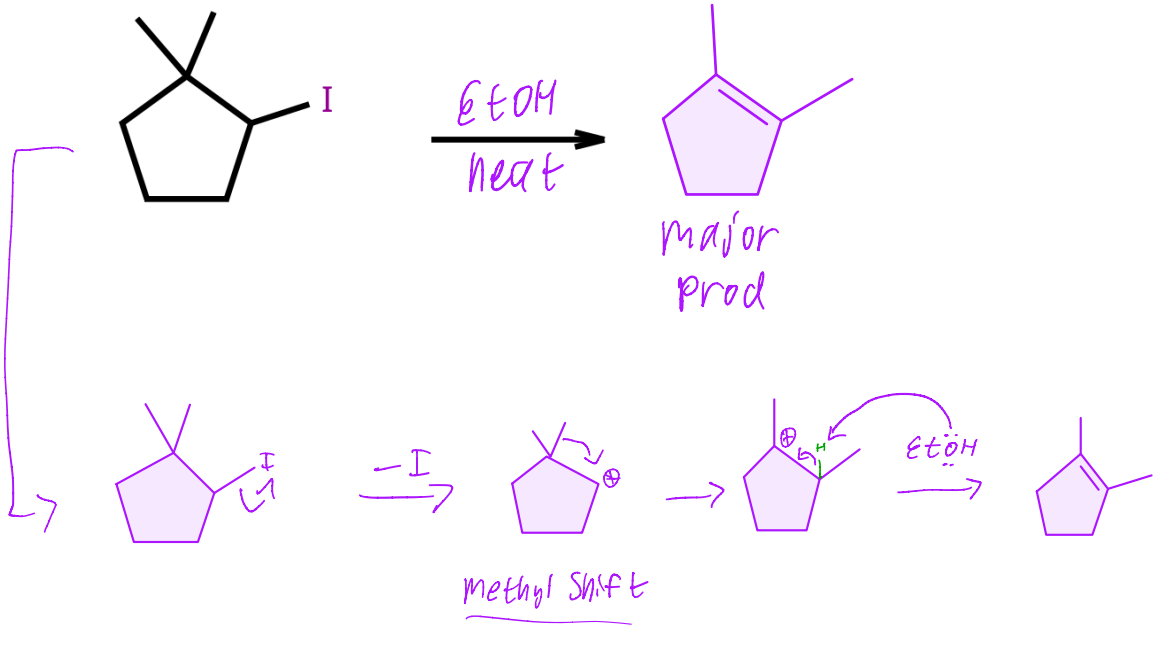
Just like with Sn1, our carbocation can undergo rearrangement to form the most stable product



Example (hydride shift):



Example (methyl shift):



Substitution/Elimination Reactions 101: How to determine when you're using Sn1/E1/Sn2/E2

1. **Determine the function of the reagent:**

Elimination: uses bases

Substitution: uses nucleophiles

Strong base Weak nucleophile	Strong base Strong nucleophile	Weak base Strong nucleophile	Weak base Weak nucleophile
DBN DBU	$HO^{\ominus}$ $MeO^{\ominus}$ $EtO^{\ominus}$	$I^{\ominus}$ $Br^{\ominus}$ $Cl^{\ominus}$ $RS^{\ominus}$ $HS^{\ominus}$ RSH H_2S	H_2O MeOH EtOH

2. **Look at your substrate to determine the mechanism**

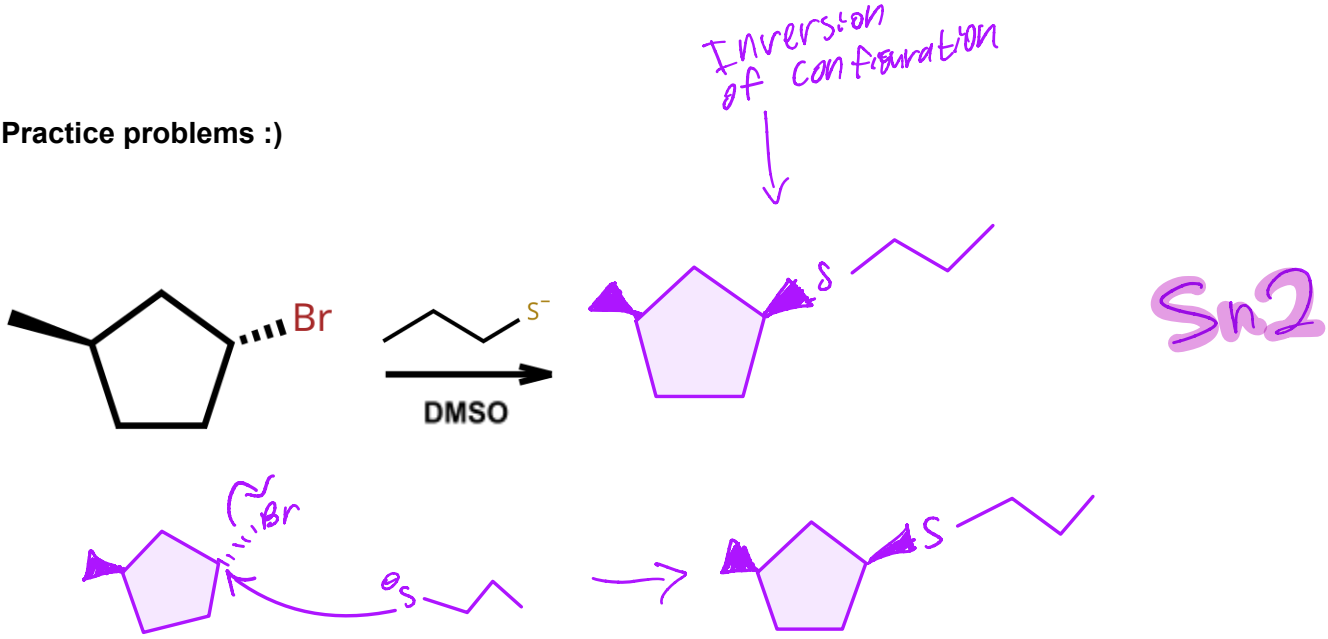
Memorize this diagram!!

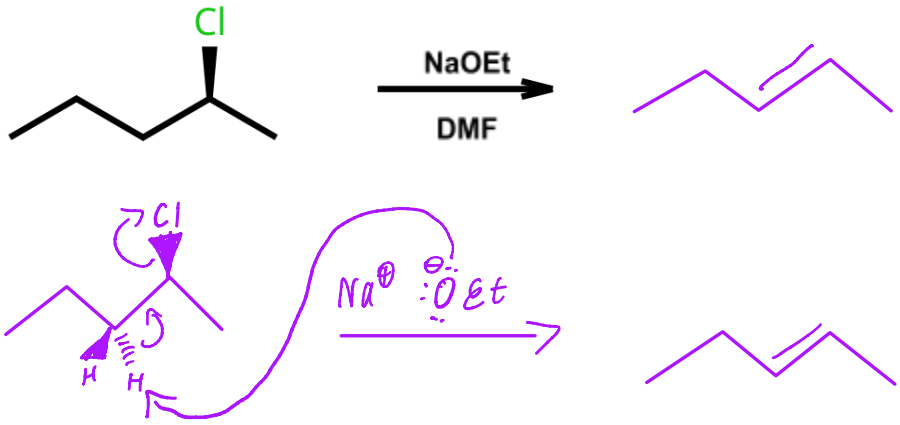
	Strong base Weak nucleophile	Strong base Strong nucleophile	Weak base Strong nucleophile	Weak base Weak nucleophile
1°	E2	E2 S_N2	S_N2	✗
2°	E2	E2 S_N2	S_N2	✗
3°	E2	E2	S_N1	S_N1 E1

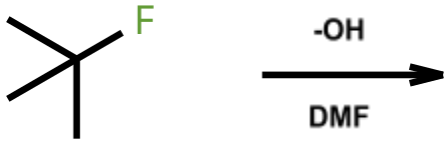
3. **Consider any regiochemistry or stereochemistry**

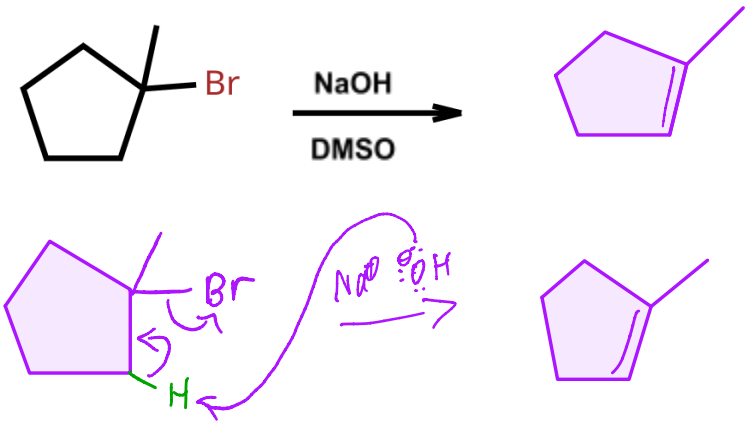
	Regiochemistry	Stereochemistry
Sn2	nuc$^{\ominus}$ attacks α carbon	Inversion of configuration
E2	Zaitsev prod is major unless using a sterically hindered (bulky) base	-stereoselective: trans major prod. -stereospecific: only if there's 1 β hydrogen
Sn1	nuc$^{\ominus}$ attacks carbocation	Racemic mixture
E1	Zaitsev is always major product	-stereoselective: trans-favored prod.

Practice problems :)



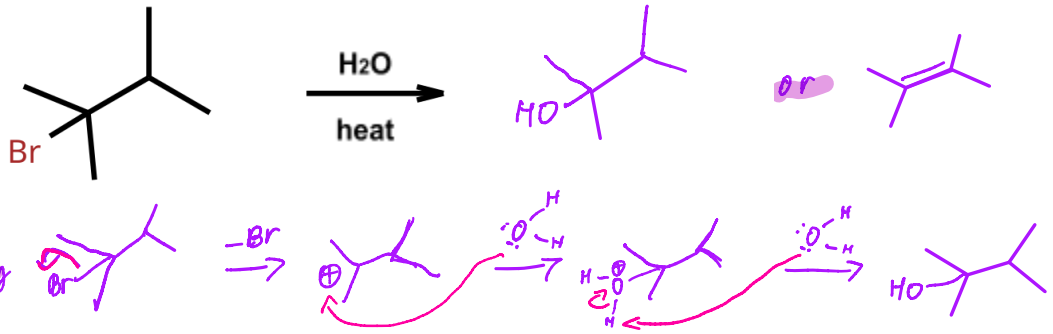




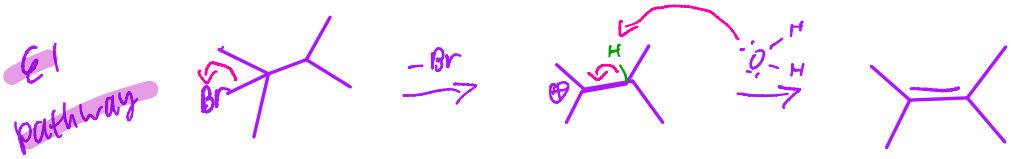


E2

Sn1 prod E1 prod



Sn1 / E1



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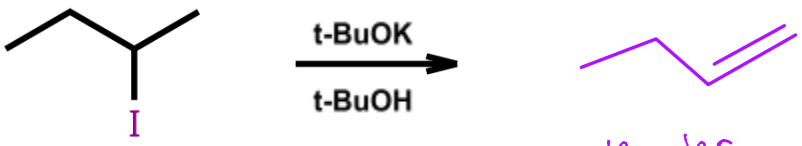
bulky base! —> Hofmann prod.



major prod.

E2