

ELIMINATION REACTIONS

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Building Upon:

- S_N1 and S_N2
- Newman projections
- Chair conformations
- Alkynes as bases

Learning Objectives:

- Draw mechanisms for $E1$, $E2$ and $E1cB$ reactions
- Describe the factors that affect which mechanism operates
- Predict the stereochemistry and regiochemistry of the products
- Understand why $E1$ and S_N1 can compete.

Alkyl Halides

From last time:



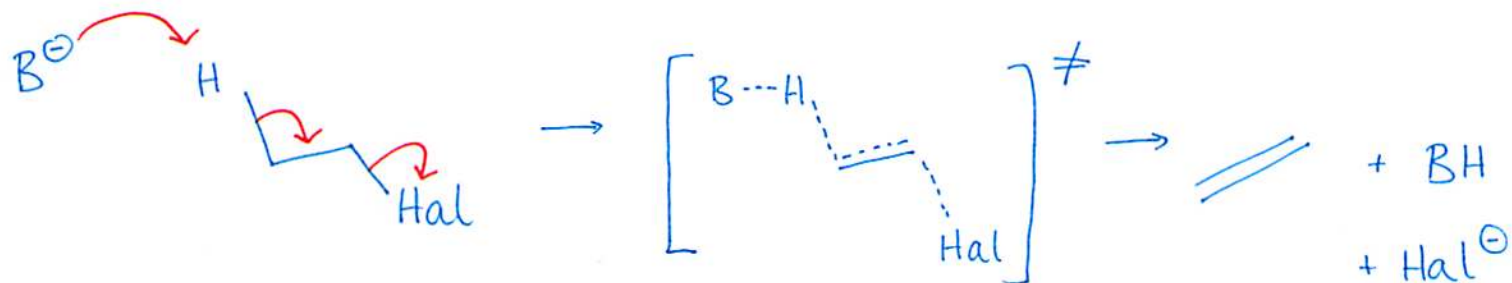
But what if the "nucleophile" attacks hydrogen instead of carbon? (i.e. it acts as a base)



Again, there are two possible mechanisms

The E2 Mechanism

elimination bimolecular



- Single step

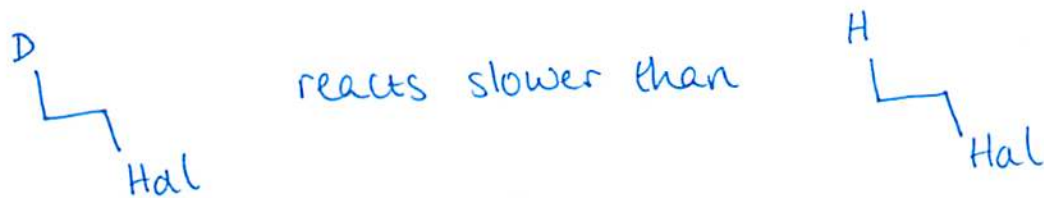
What is the evidence for this reaction?

- Second order kinetics $rate = k[B^-][alkyl\ halide]$

Kinetic Isotope Effect

$C-D \leftarrow$ stronger bond

$C-H$



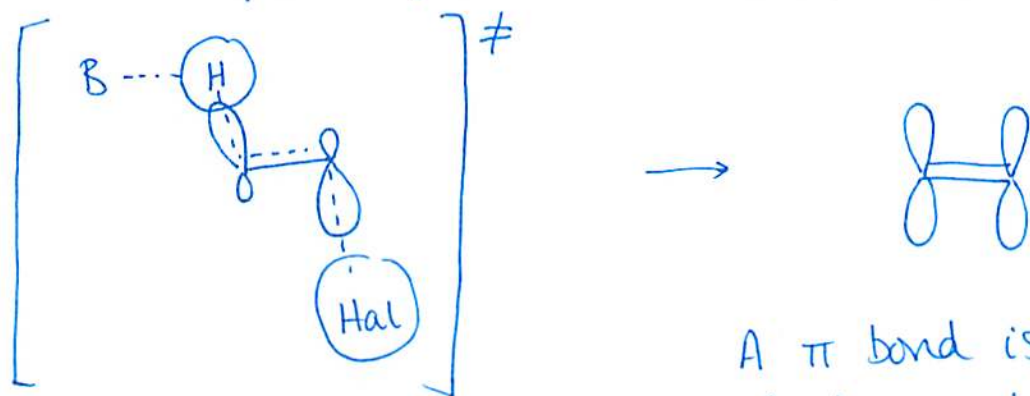
This implies that the $C-D/H$ bond must be broken in the rate determining step.

Stereochemistry of Product

3

E2 reactions occur with periplanar geometry.

This is because the H, 2 carbons, and Hal must all be in the same plane for correct orbital overlap.



A π bond is being formed which requires the orbitals to be parallel.

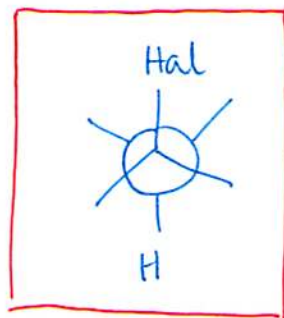
This requires all the orbitals to be in the same plane in the transition state.

There are two periplanar options:



syn

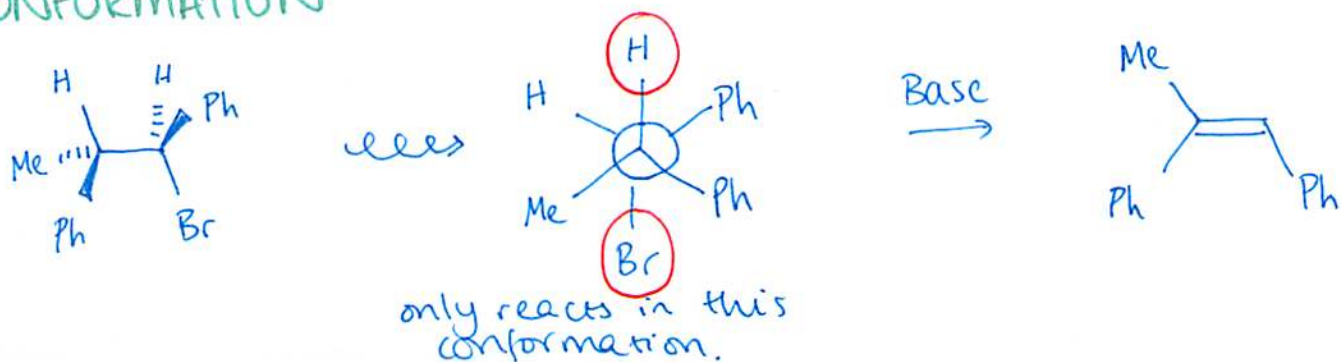
or



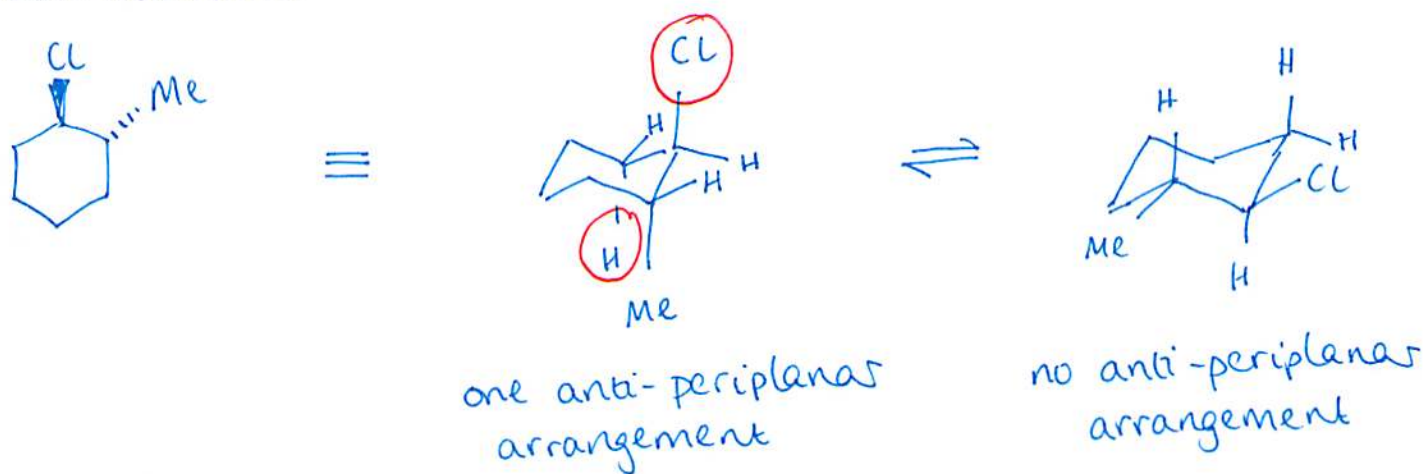
anti

← staggered is preferred.

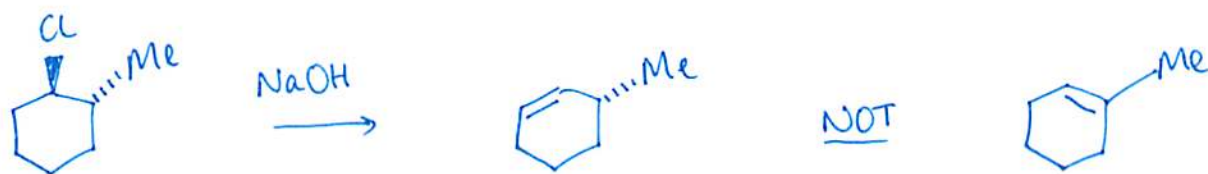
E2 ELIMINATIONS TAKE PLACE FROM THE ANTIPERIPLANAR CONFORMATION



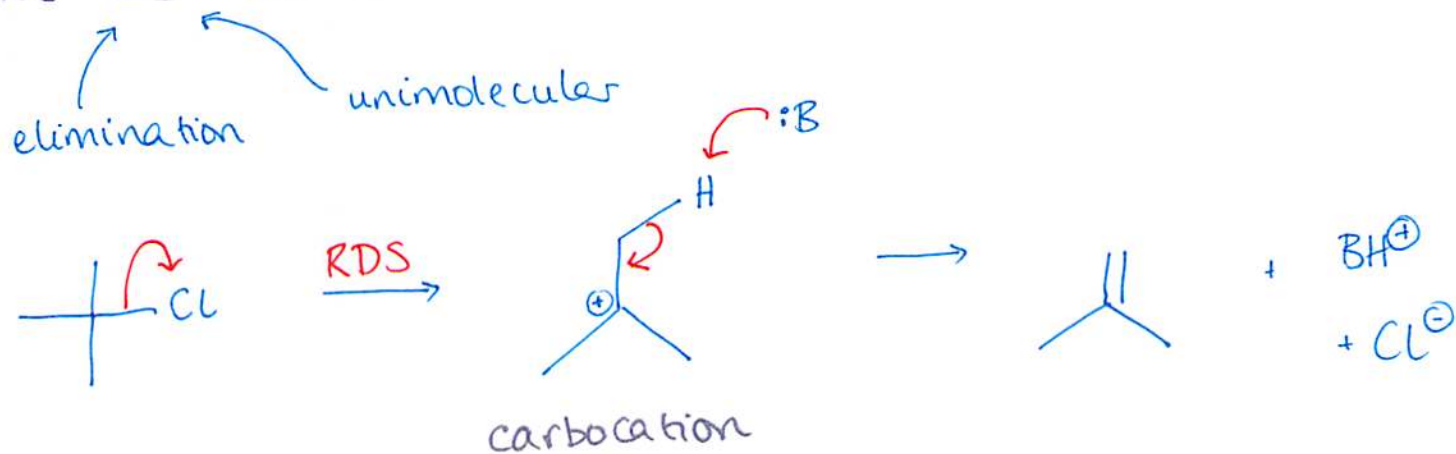
In a chair, the proton and leaving group have to be trans diaxial



Thus:



The E1 Mechanism

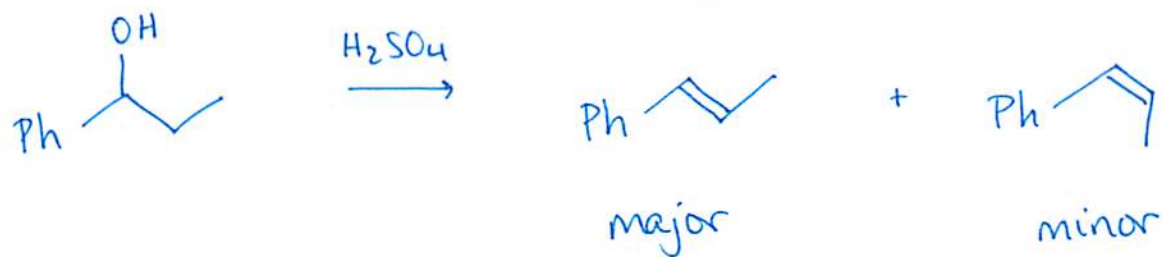


• First order kinetics $\text{rate} = k [\text{alkyl halide}]$

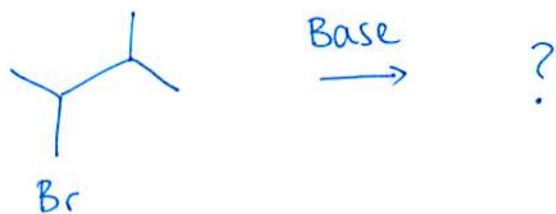
• No deuterium isotope effect

• No requirement for antiperiplanar geometry

The E alkene is generally preferred over the Z alkene (sterics in the transition state)



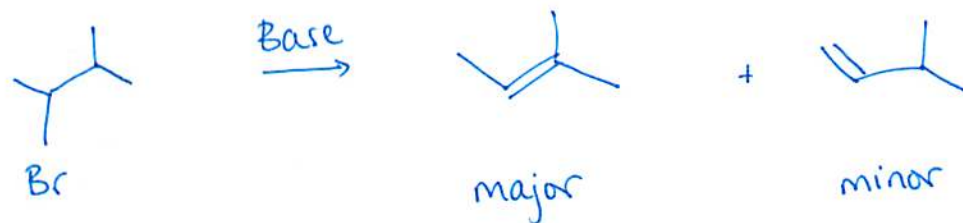
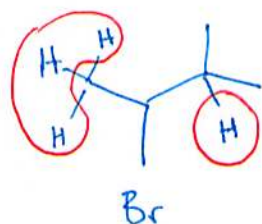
Regiochemistry of Product



There are two different hydrogen sites:

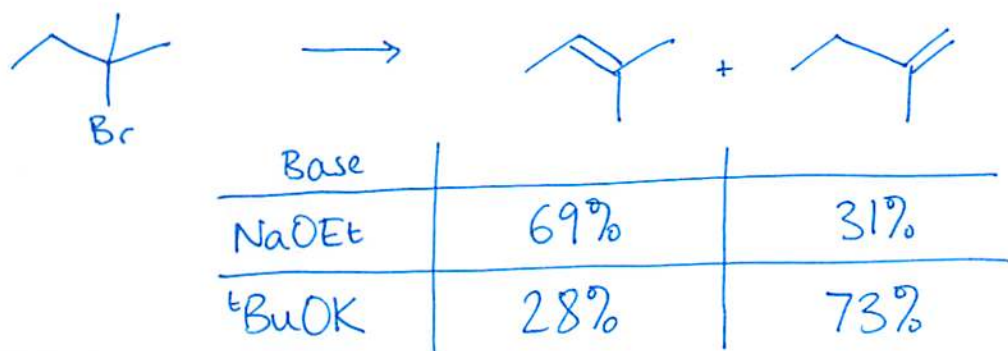
Zaitsev's Rule:

You get the more stable alkene product i.e. the more substituted product



This applies to both E1 and E2

However: you must also ~~consider~~ consider the size of the base:



E1 or E2?

(6)

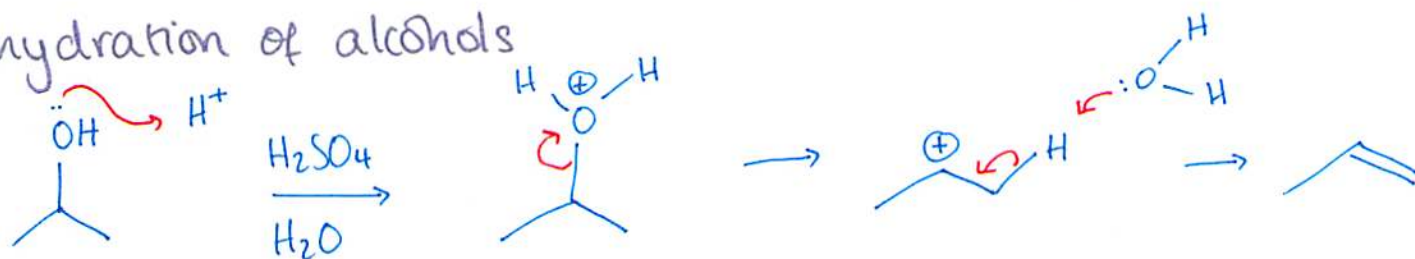
Nucleophilic substitutions are very sensitive to sterics, so 3° substrates do not react via S_N2 .

However, eliminations are a lot less sensitive to sterics (think about the mechanism), so generally with a good base E2 will take place.

Increasing the concentration of base favours E2.

E1 will only occur if a stable carbocation can be formed.

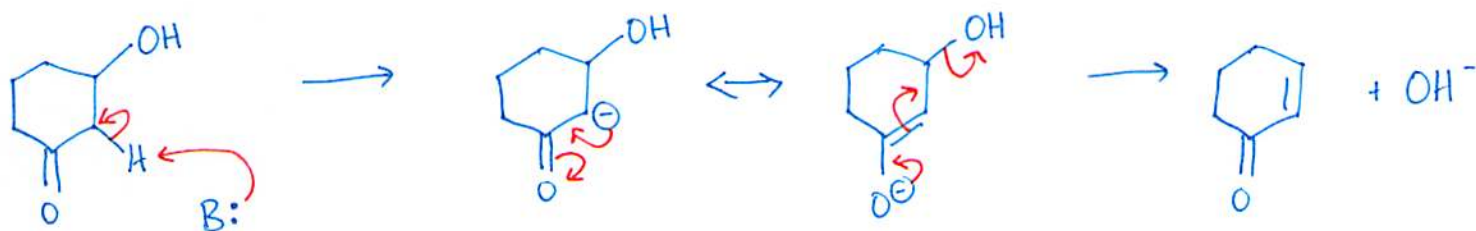
A common example of E1 is the acid-catalysed dehydration of alcohols



A third (quite rare!) mechanism:

The E1CB mechanism

↑ conjugate base

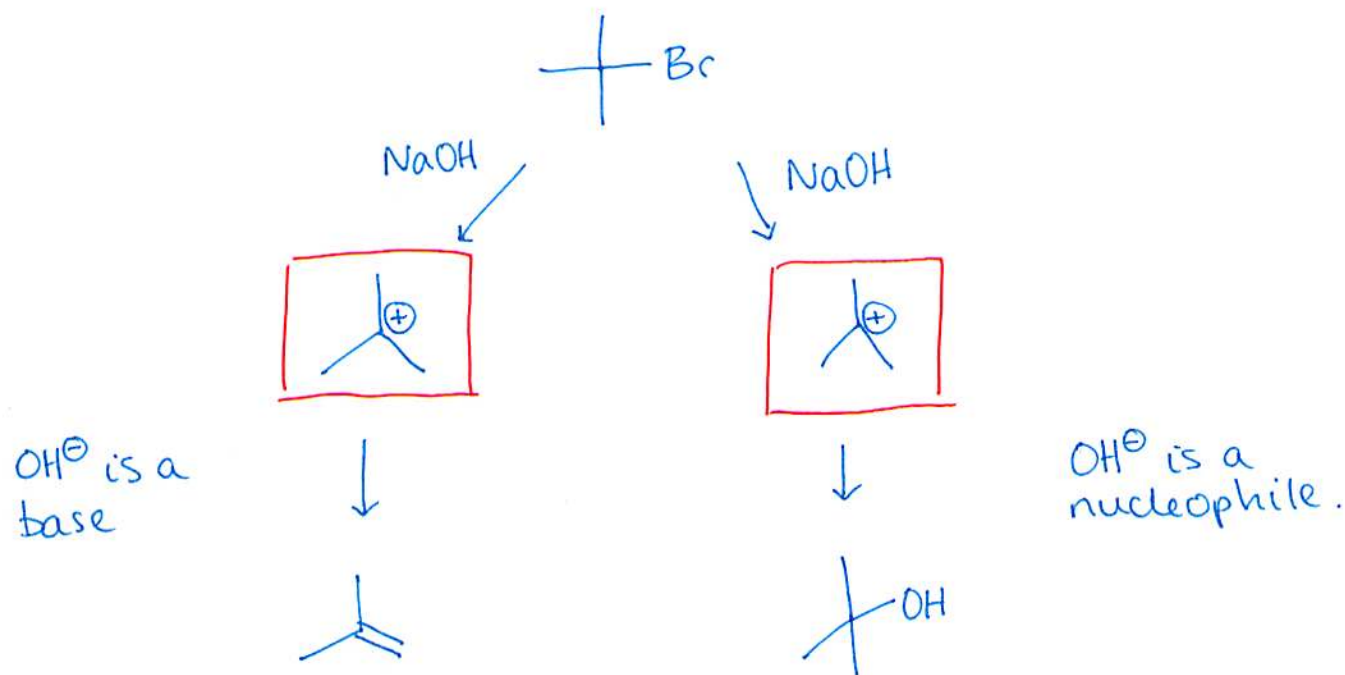


carbanion intermediate

- Common for reactions where you have a poor leaving group and something in the molecule that will stabilise the carbanion (e.g. a carbonyl group)
- Kinetically the same as E2

Competition between elimination and substitution

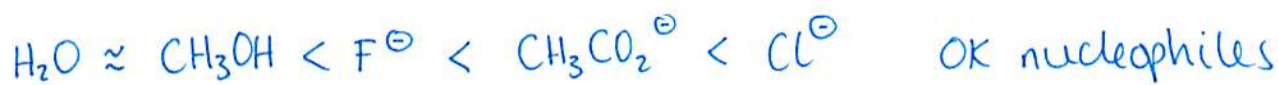
For $E1$ and S_N1 , both reactions have identical RDS and identical intermediates:



So which reaction takes place?

Unfortunately you often get a mixture of products.

Is the attacking species a better base or a better nucleophile?



It is often difficult to predict whether $\ddot{\text{O}}\text{H}^\ominus$ and $\ddot{\text{O}}\text{R}^\ominus$ will act as nucleophiles or bases 😞

Generally small species with high charge density are good bases e.g. OH^-

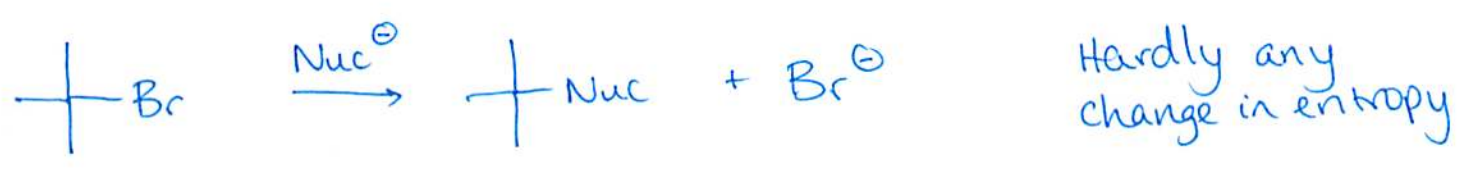
Larger species that are less charge dense are good nucleophiles e.g. I^-



Always acts as a base.
Too sterically hindered to be a nucleophile.
Also written as tBuO^-

Temperature

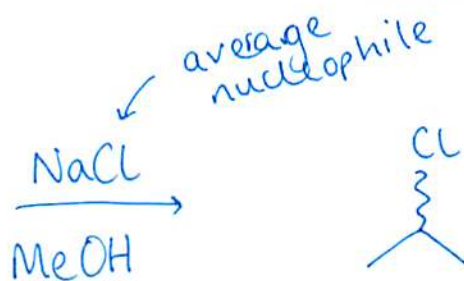
You can favour E1 over $\text{S}_{\text{N}}1$ by raising the temperature
(Gen Chem 2)



$$\Delta G = \Delta H - T\Delta S$$

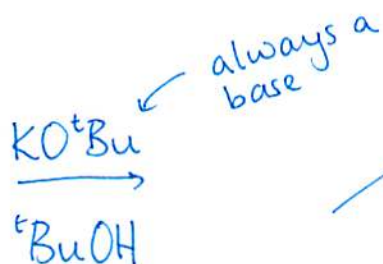
If you increase the temperature, $T\Delta S$ increases a lot for an E1 reaction, making ΔG more favourable.

Summary

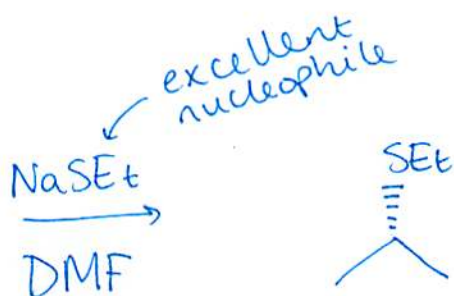


S_N1

polar protic solvent



E2



S_N2

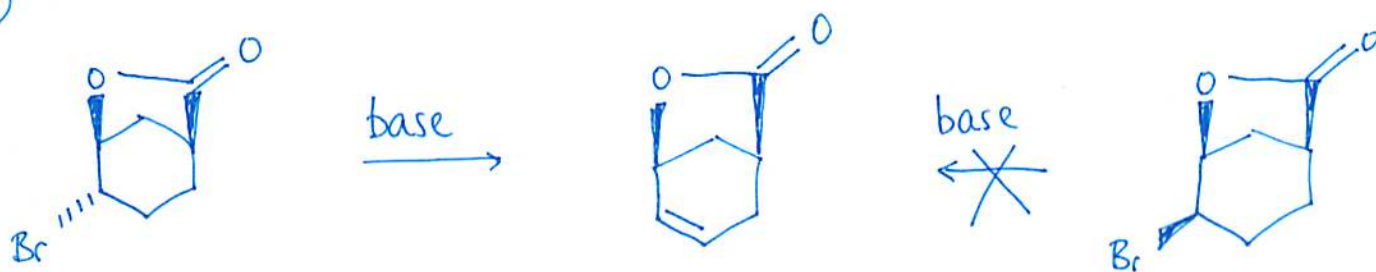
polar aprotic solvent

Questions:

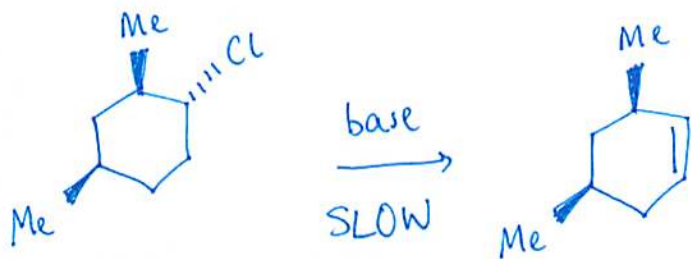
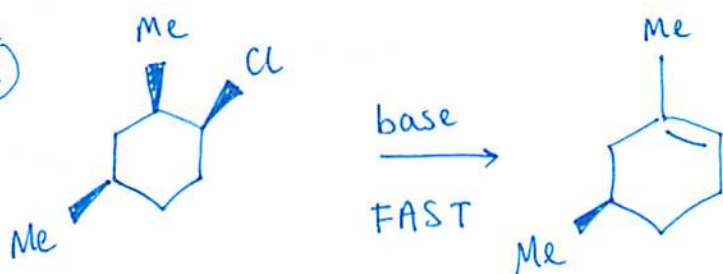
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Explain the following results:

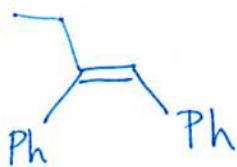
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③ Draw an alkyl halide that could be used to prepare:



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