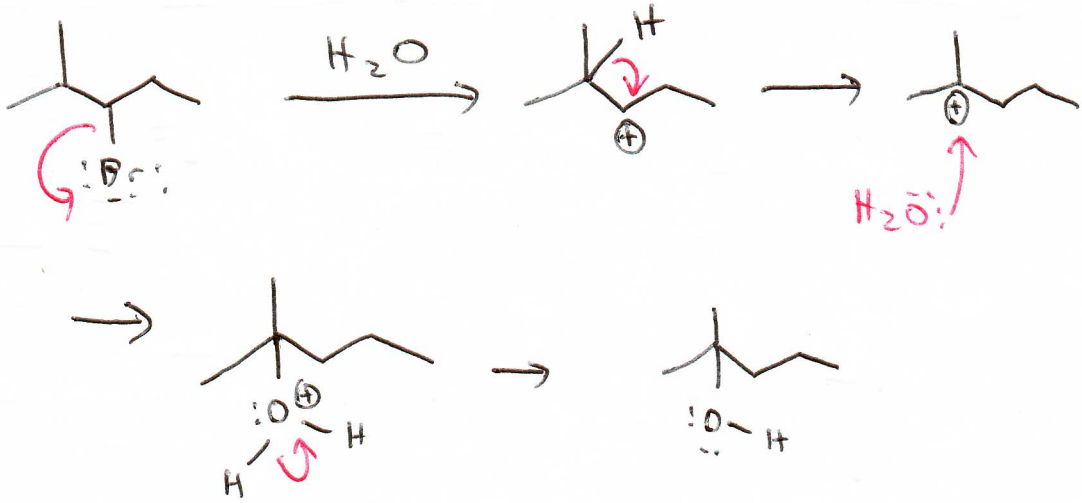
6) Regiochemistry

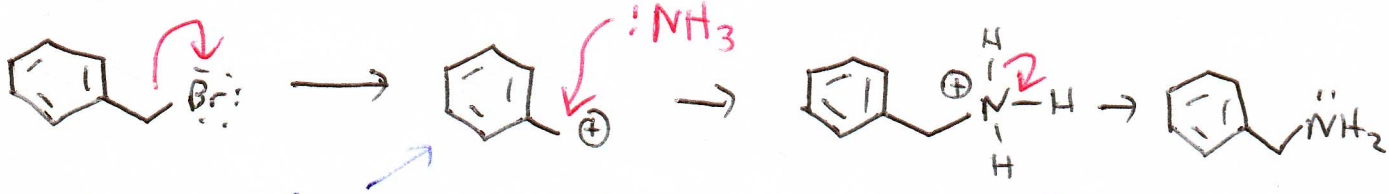


1) substrate

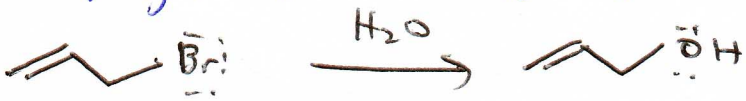
$3^\circ \gg\gg 2^\circ > 1^\circ \sim$ methyl

reactivity in S_N1 rxns

3° substrates are far more reactive in S_N1 rxns since 3° carbocations are far more stabilized by hyperconjugation.



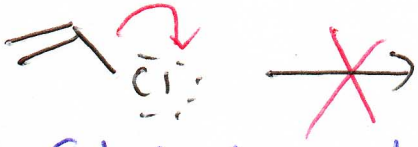
Even though it's primary, this carbocation forms due to conjugation of the ⊕ with benzene.



1° allyl substrates are also reactive.

vinyl 

vinyl → attached to the double bond.



$= \oplus + Cl^-$

Vinyl substrates do not undergo S_N1 rxns because vinyl carbocations are not stable (orbitals with more s-character better tolerate negative charges, but are worse at tolerating ⊕ charges).

In SN2 rxns, vinyl substrates do not react because the π electrons in the C=C bond repel the approaching nucleophile.

2) nucleophiles

For SN1 rxns, poor nucleophiles → particularly, non-basic nucleophiles → must be used, since the rxn will only occur if the carbocation has time to form.

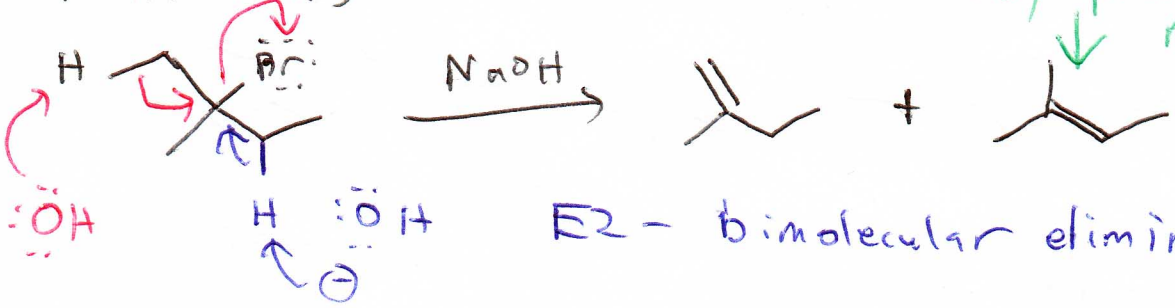
3) leaving groups

Good leaving groups are conjugate bases of strong acids.

4) solvent

In SN1 rxns, polar protic solvents are normally used, and the solvent itself is often also the nucleophile.

Eliminations

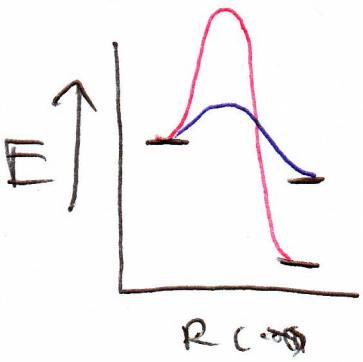


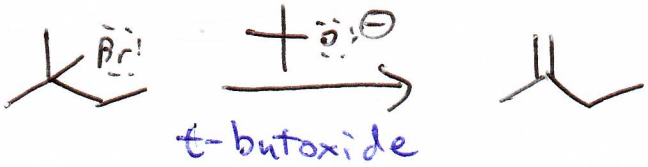
More likely product since it is more thermodynamically stable.

E2 - bimolecular elimination

More substituted alkenes are more thermodynamically stable.

Zaitsev's rule - In eliminations, the more heavily substituted alkene will be the most one to form.*



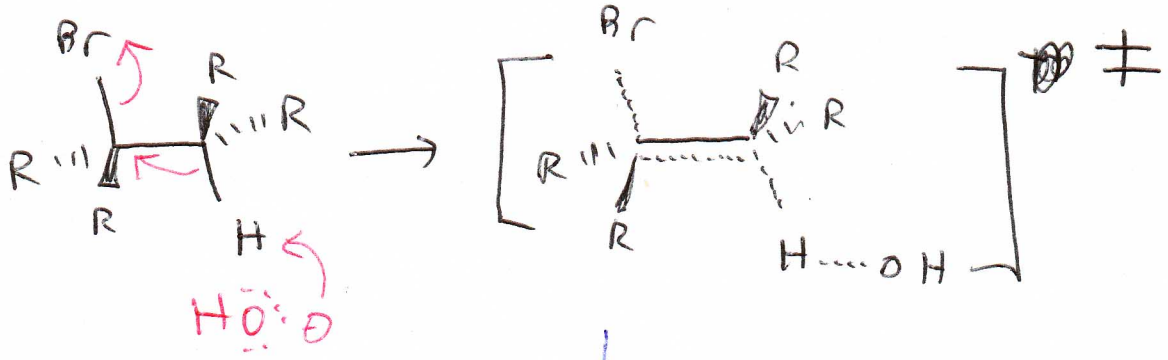


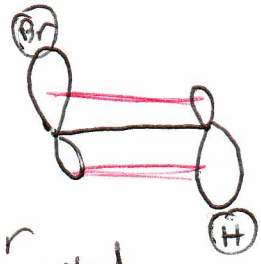
major product

If a nucleophile is very sterically hindered, it can cause the formation of a <u>less</u> stable alkene due to kinetic effects (more hindered nucleophiles make it more difficult to remove more hindered hydrogens).

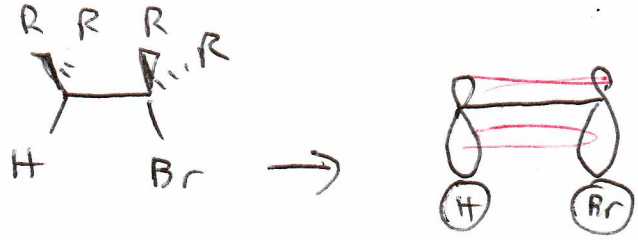
E2

1) utility → alkyl halide → alkenes
2) reagents → basic strong nucleophiles
3) conditions → polar aprotic solvents
5) stereochemistry



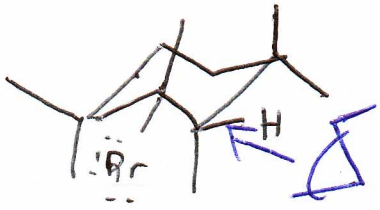


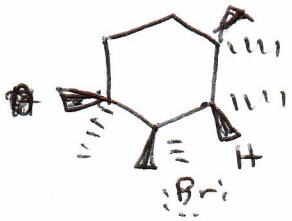
antiperiplanar (parallel but pointed 180° opposite).



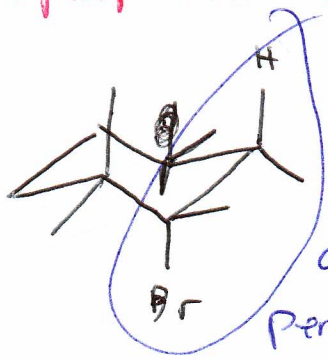
synperiplanar (like parallel)

Eliminations can only occur if the hydrogen removed is synperiplanar or antiperiplanar to the leaving group.





ring flip



anti-periplanar