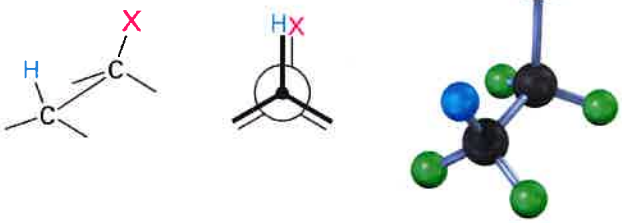
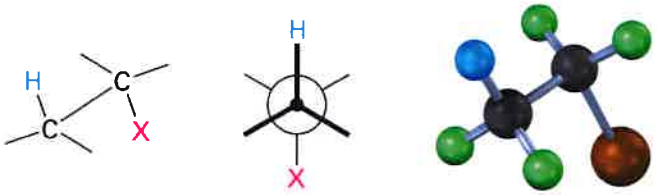
Geometry of Elimination - E_2

E2 reactions have **periplanar** geometry, meaning that all four reacting atoms (hydrogen, the two carbons and the leaving group all lie in the same plane) there are 2 possibilities…

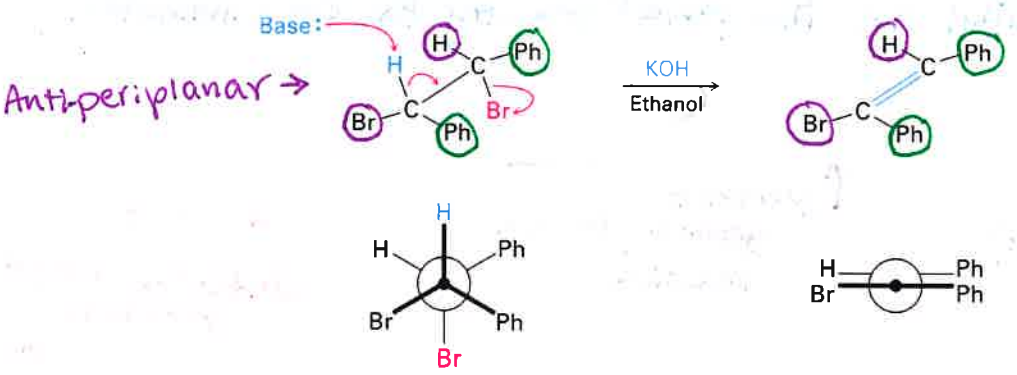
Syn-periplanar - the H and the halide (X) are on the same side of the molecule



Anti-periplanar - the H and the halide (X) are on opposite sides of the molecule, this allows orbital overlap and minimizes steric interactions



Anti periplanar is energetically preferred because it allows the substituents on the two carbons to adopt a staggered relationship where as syn periplanar requires the substituents to be eclipsed.



***meso*-1,2-Dibromo-1,2-diphenylethane (anti periplanar geometry)**

(*E*)-1-Bromo-1,2-diphenylethylene

What stereochemistry do you expect for the alkene obtained by E2 elimination of **(1S,2S)-1,2-dibromo-1,2-diphenylethane?**

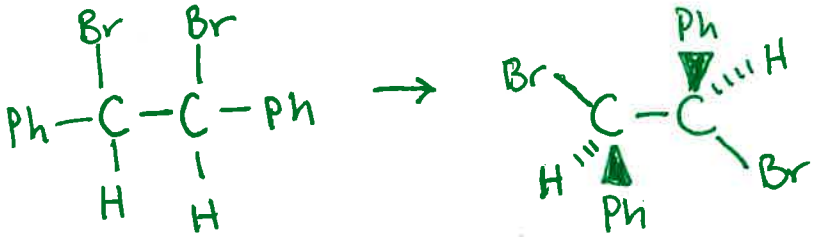
↳ see last 2 pages

anti periplanar eliminations have specific stereochemical consequences. They will result in 100% E or 100% Z (cis or trans)

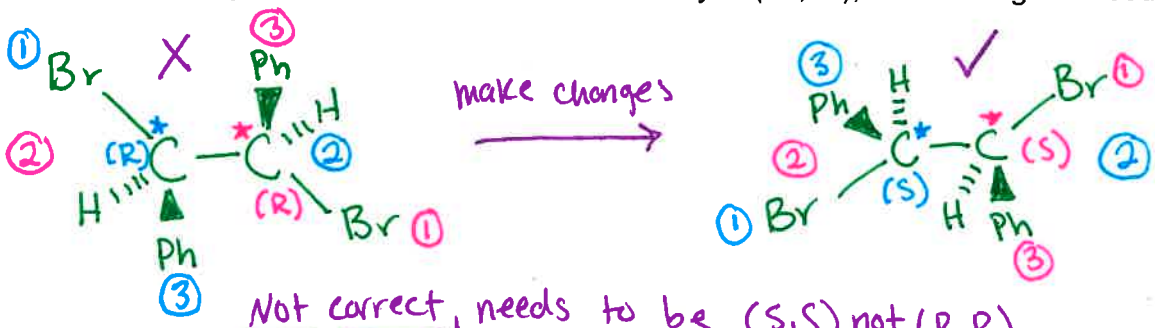
Z E

What stereochemistry do you expect for the alkene obtained by E2 elimination of **(1S,2S)-1,2-dibromo-1,2-diphenylethane?**

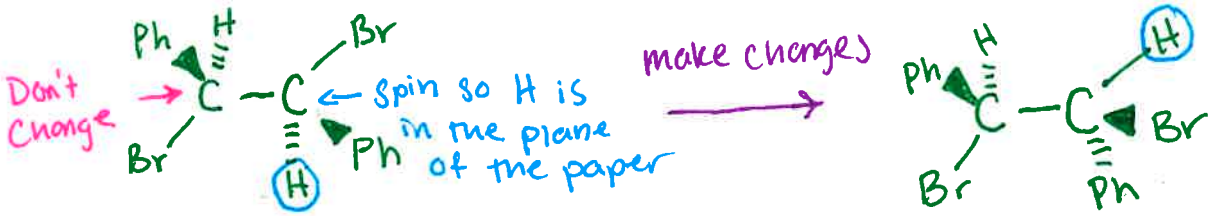
1. Draw the correct structure for 1,2-dibromo-1,2-diphenylethane. Note: it might be easier to draw it without stereochemistry at first but then you should convert it to a three dimensional drawing by using wedges and dashes to indicate stereochemistry



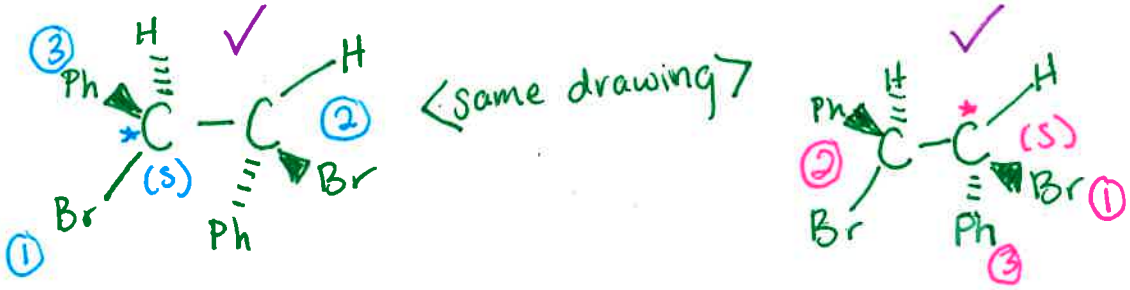
2. Confirm you have the correct stereochemistry of (1S,2S), make changes if needed.



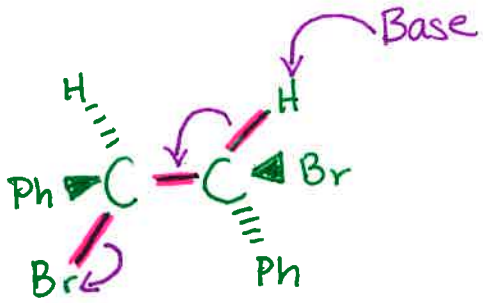
3. Draw the structure again but spin one of the carbons in the drawing so you have the abstracted proton and the leaving group in the plane of the paper.



4. It doesn't hurt to confirm your stereochemistry again at this point. You just changed your drawing so make sure you changed it correctly and retained the proper stereochemistry.

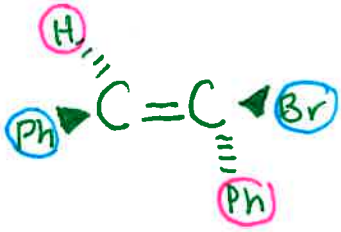


5. Draw the mechanism for the E2 elimination reaction.

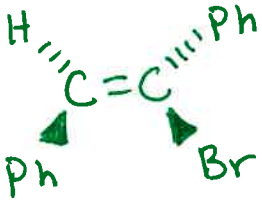


Pink = in the plane of the paper & takes part in the E2 elimination

6. Draw the product for the E2 elimination reaction and remember if the atom is sticking back into the paper, keep it there. Or if it is sticking out of the paper, keep it there.



OR



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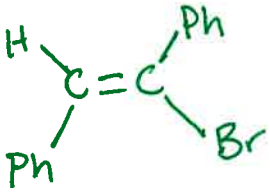
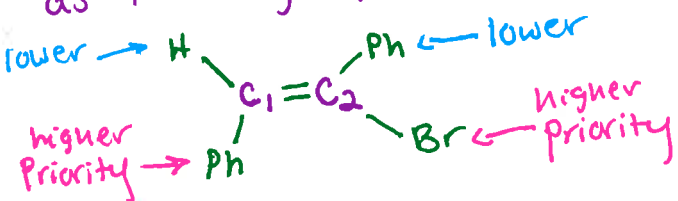


Pink = sticking back into the paper

Blue = sticking out towards you

Note: the product is cis because the large group on C_1 is on the same side as the large group on C_2.



- Chair geometry is ridgid and forces the substituents into particular arrangements

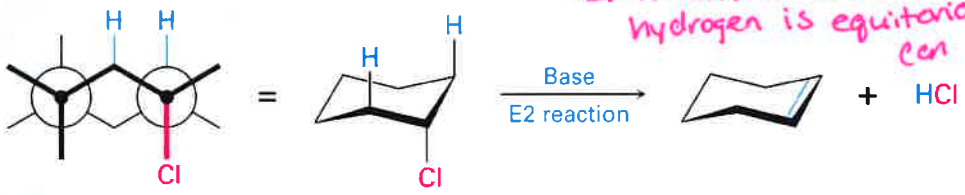
Elimination from Cyclohexanes

The abstracted proton and leaving group should align **trans-diaxial** to be anti periplanar in approaching transition state

Equatorial groups are not in proper alignment

- Anti-periplanar requirement for E2 reactions overrides Zaitzev's rule
  - ↳ hydrogen and leaving group must be trans-diaxial
  - ↳ If either the leaving group or the hydrogen is equitorial, E2 elimination can not occur.

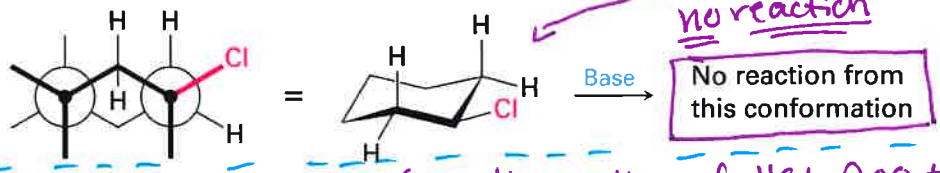
Axial chlorine: H and Cl are anti periplanar



Equatorial chlorine: H and Cl are not anti periplanar

Example of transdiaxial requirement:

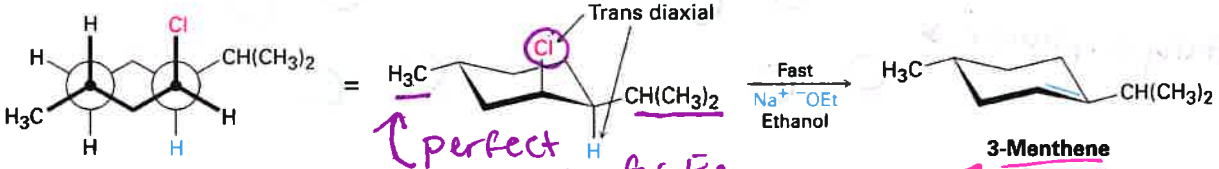
chlorine is equitorial so no reaction



(A) neomenthyl chloride undergoes E2 elimination of HCl 200 times faster than (B)

* neomenthyl has the perfect geometry for E2 elimination

(A)(a)



(A) Neomenthyl chloride

↑ perfect geometry for E2 reactions

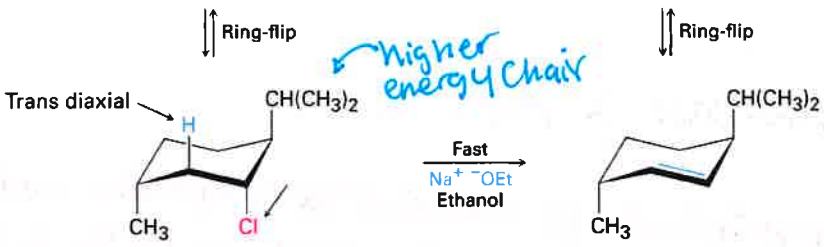
↑ different major products

(B) (b)

lower energy chair

(B) Menthyl chloride

(B) menthyl chloride must undergo a ring flip to a higher energy chair conformation to make all substituents axial ... it then results in the non-Zatizev product

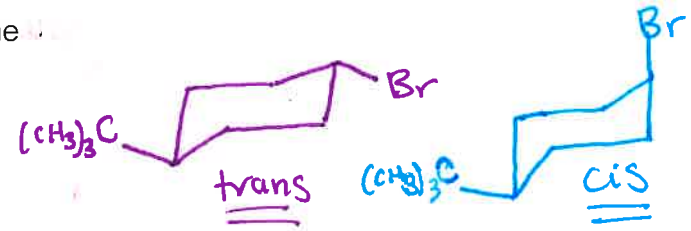


E2 = Leaving group and the hydrogen must both be axial for anti periplanar elimination to occur

What isomer would you expect to undergo E2 elimination faster?

trans-1-bromo-4-tert-butylcyclohexane

★ cis-1-bromo-4-tert-butylcyclohexane



The more stable conformations of each of the two isomers are pictured above; the larger tert-butyl group is always equitorial in the more stable conformation. The cis isomer reacts faster under E2 conditions because Br and H are in the anti periplanar arrangement that favors E2 elimination

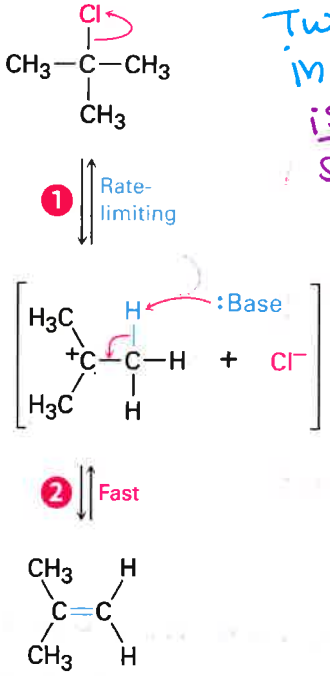
The E1 Reaction

E2 similer to SN2
E1 similar to SN1

1 Spontaneous dissociation of the tertiary alkyl chloride yields an intermediate carbocation in a slow, rate-limiting step.

Carbocation

2 Loss of a neighboring H^+ in a fast step yields the neutral alkene product. The electron pair from the C–H bond goes to form the alkene π bond.

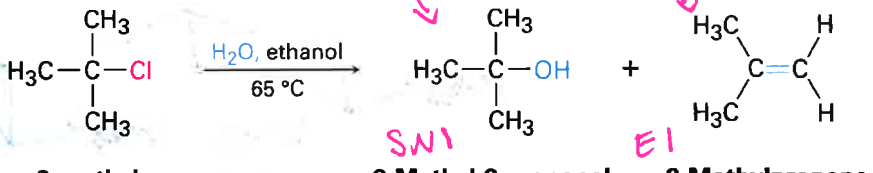


Two separate steps are involved. The 1st step is the rate limiting step. Also like SN1, a carbocation intermediate is formed.

Begins with the same unimolecular dissociation to give a carbocation that we saw in the SN1 reaction, but the dissociation is followed by loss of a H^+ from the adjacent carbon rather than by substitution.

Stereochemistry of E1 Reactions

competes w/ S_N1 and E_2 at 3° centers



substitution ↓ elimination ↓

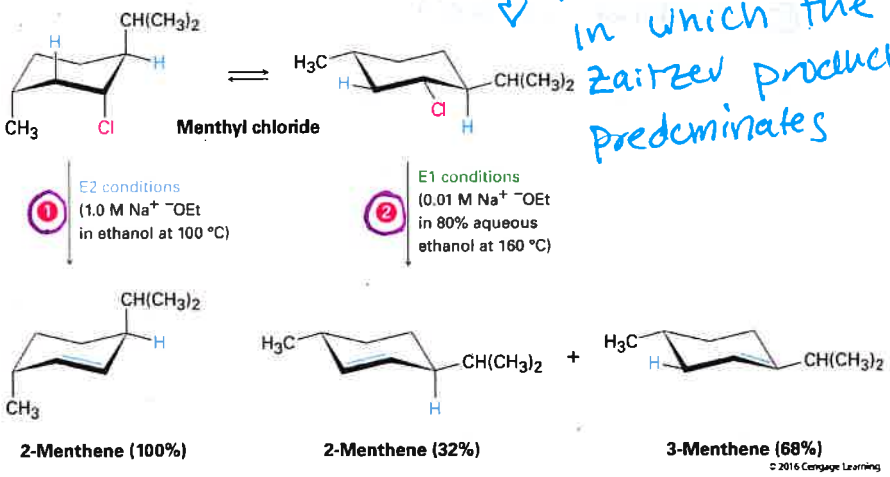
SN1 E1

2-Chloro-2-methylpropane → **2-Methyl-2-propanol (64%)** + **2-Methylpropene (36%)**

E_1 and S_N1 normally occur together whenever the alkyl halide is treated in a protic solvent with a non-basic nucleophile. The best E_1 substrates are also the best S_N1 substrates and mixtures of the E_1 and S_N1 reaction products are often obtained.

Comparing E1 and E2

- Strong base is needed for E_2 but not for E_1
- E_2 is stereospecific, E_1 is not
- E_1 gives Zaitzev product



↓ mixture of alkenes in which the Zaitzev product predominates

① E_2 conditions (strong base in 100% ethanol) led to 2-menthene through anti periplanar elimination of E_2

② Dilute base in 80% ethanol lead to a mixture of 2-menthene and 3-menthene

No geometric requirement on the E_1 Reaction because the halide and the hydrogen are lost in separate steps.