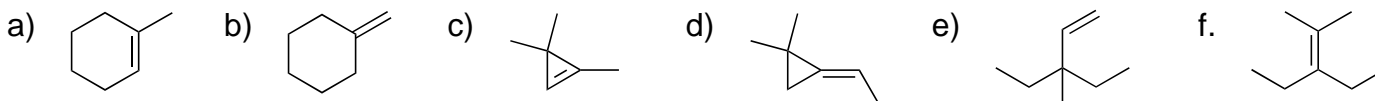
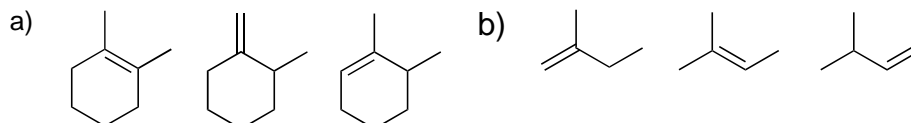


1. Classify each of the following alkenes as mono-substituted, di-substituted, tri-substituted, or tetra-substituted:

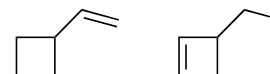


2. Arrange each set of isomeric alkenes in order of increasing stability

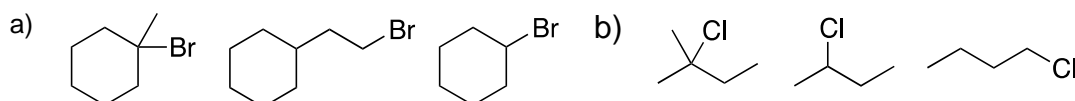


3. Consider the following two isomeric alkenes.

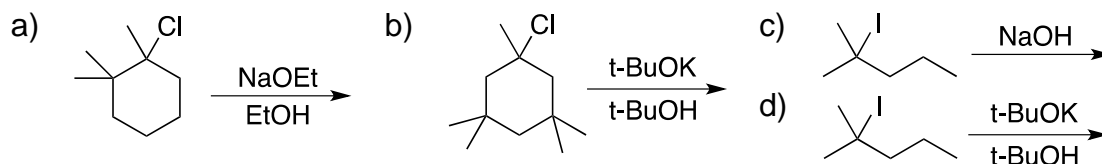
The first isomer is a mono-substituted alkene, while the second isomer is a di-substituted alkene. We might expect the second isomer to be more stable, but heats of combustion for these two compounds indicate that the first isomer is more stable. Offer an explanation. (hint: angle strain of the cyclic compound)



4. Arrange each set of compounds in order of increasing reactivity toward an E2 process.



5. Identify the major and minor products for each of the following E2 reactions



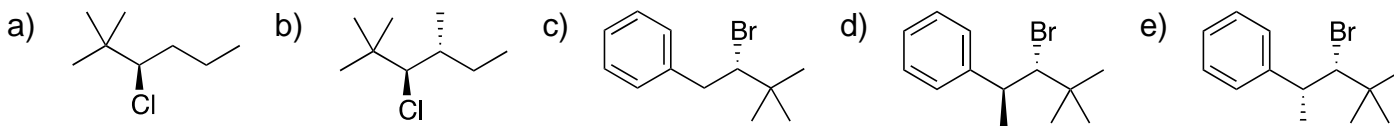
t-BuOK = potassium tert-butoxide (conjugate base of tert-butanol)

NaOEt = Sodium ethoxide (conjugate base of ethanol)

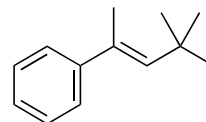
6. Show two different methods for preparing each of the following alkenes (one method using a sterically hindered base and the other method using an unhindered base):



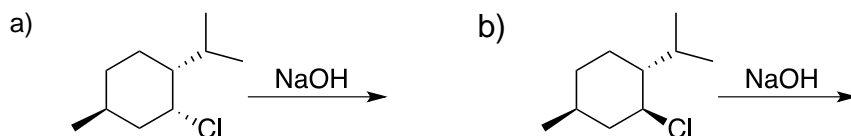
7. Identify the major and minor products for the E2 reaction that occurs when each of the following substrates is treated with a strong base



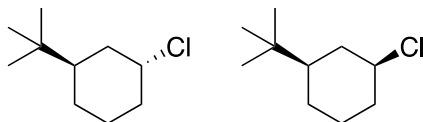
8. Identify an alkyl halide that could be used to make the following alkene via an E2 reaction:



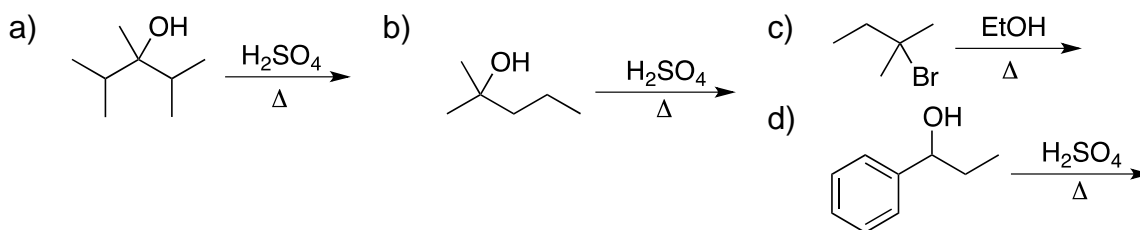
9. Draw the major E2 products from each of the following alkyl halides.



10. Predict which of the following two compounds will undergo an E2 reaction more rapidly:

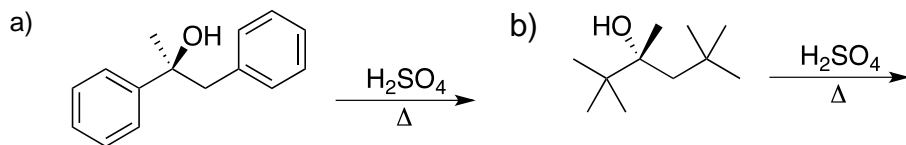


11. Identify the major and minor products for each of the following E1 reactions

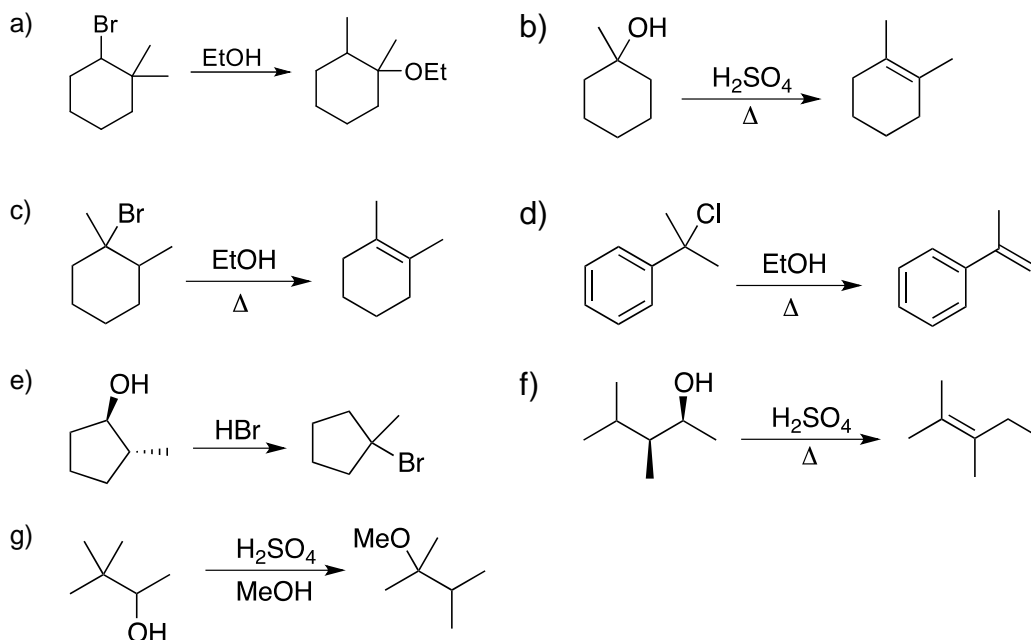


12. Identify two different starting alcohols that could be used to make 1-methylcyclohexene. Then determine which alcohol would be expected to react more rapidly under acidic conditions. Explain your choice.

13. Draw only the major product for each of the following E1 reactions:



14. Draw the mechanism for each of the following S_N1 or E1 processes (Hint: Look at the product drawn to decide whether the process is S_N1 or E1)



15. Identify the mechanism(s) expected to operate when 1-bromobutane is treated with each of the following reagents:

- a) NaOH b) NaSH c) t-BuOK d) NaOMe

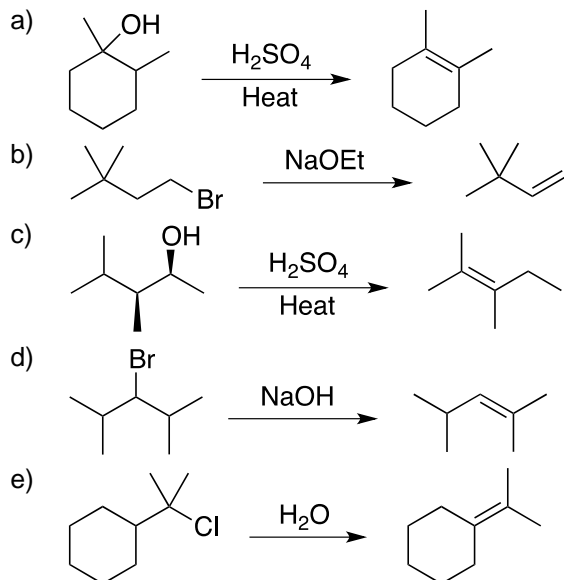
16. Identify the mechanism(s) expected to operate when 2-bromobutane is treated with each of the following reagents:

- a) NaOEt b) NaI in DMSO c) NaOH d) t-BuOK

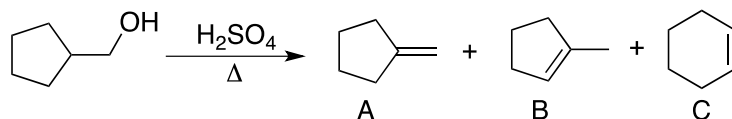
17. Identify the mechanism(s) expected to operate when 2-bromo-2-methylpentane is treated with each of the following reagents:

- a) EtOH b) t-BuOK c) NaI d) NaOEt

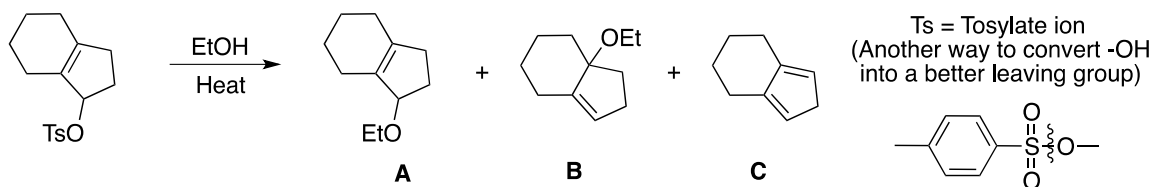
18. Propose a mechanism for each of the following transformations: (N.B. Decide first whether the reaction is E1, E2, S_N1 or S_N2)



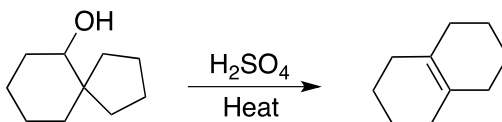
19. Propose a mechanism of formation for each of product A, B and C. Additional products may be formed, but your mechanism only needs to explain the products shown.



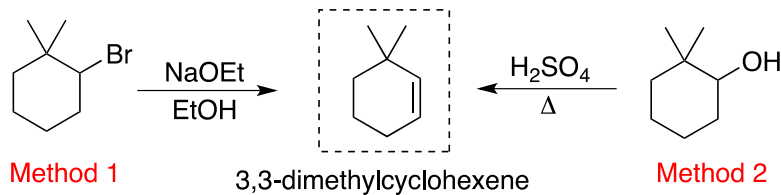
20. Propose a mechanism of formation for each of product A, B and C. . Additional products may be formed, but your mechanism only needs to explain the products shown.



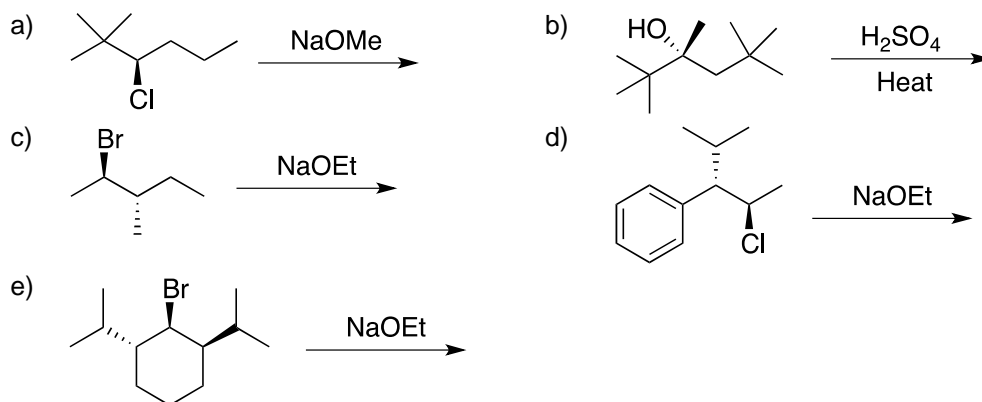
21. Propose a mechanism for the following transformation.



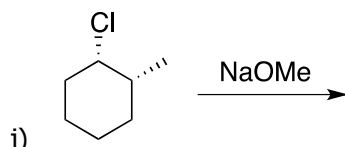
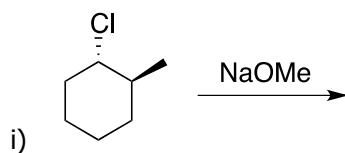
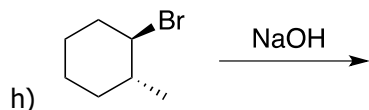
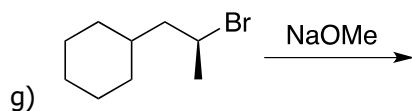
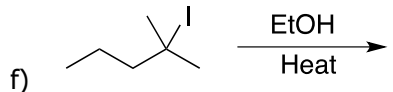
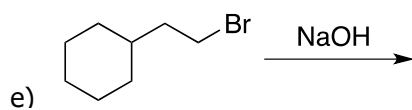
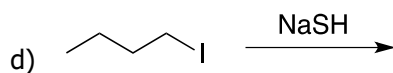
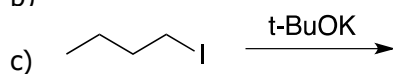
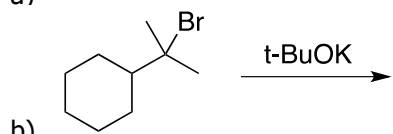
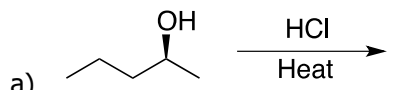
22. Identify which of the following methods is more efficient for producing 3,3-dimethylcyclohexene. Explain your choice.

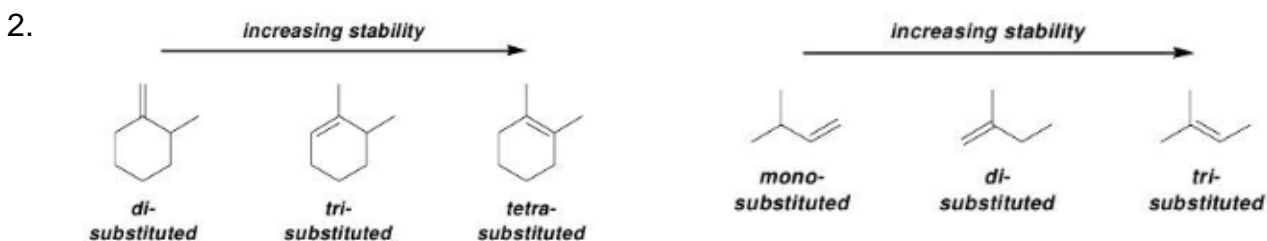
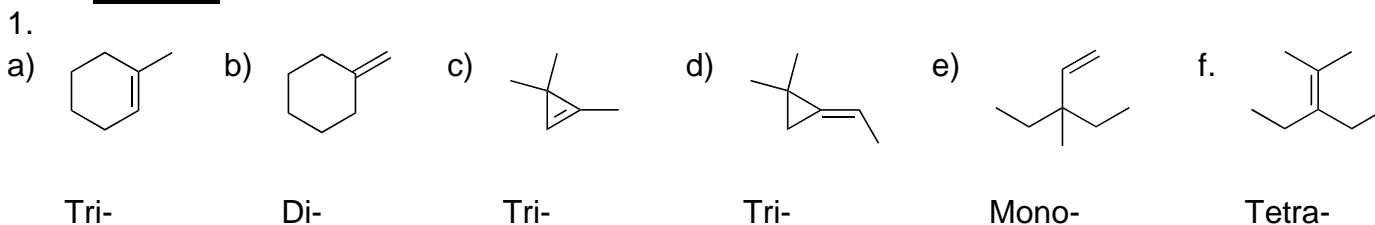


23. Compound A and compound B are constitutional isomers with molecular formula C_3H_7Cl . When compound A is treated with sodium methoxide, a substitution reaction predominates. When compound B is treated with sodium methoxide, an elimination reaction predominates. Propose structures for compounds A and B.
24. Predict the major product(s) with the correct stereochemistry for each of the following reaction: (N.B. for some molecules, drawing the Newman projection of the starting material can be very helpful, again decide first whether the reaction is $E1$, $E2$, S_N1 or S_N2)

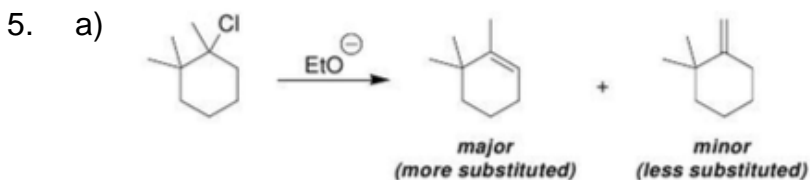
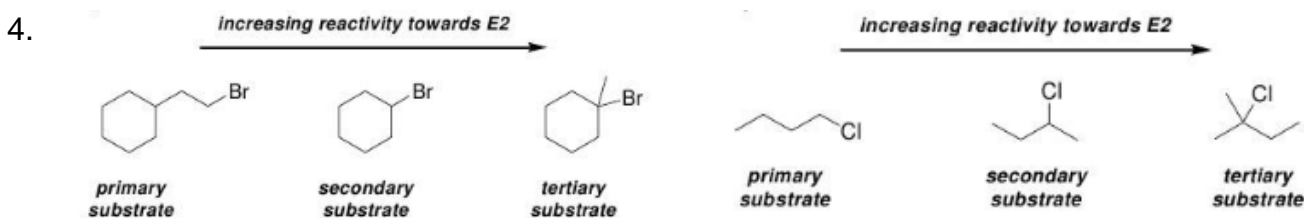
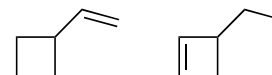


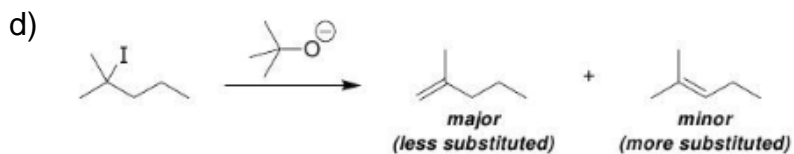
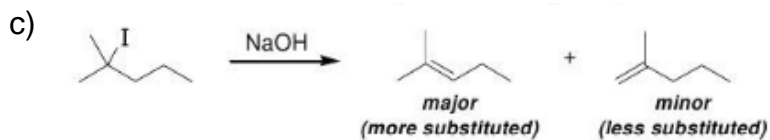
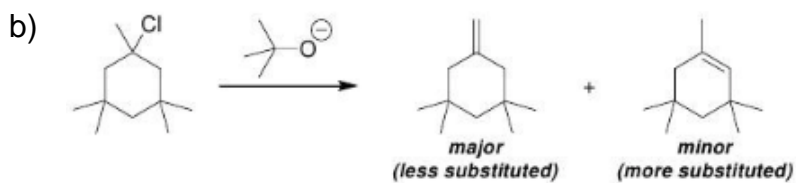
25. Identify the major and minor product(s) that are expected for each of the following reactions. (N.B. Decide first whether the reaction is E1, E2, S_N1 or S_N2)



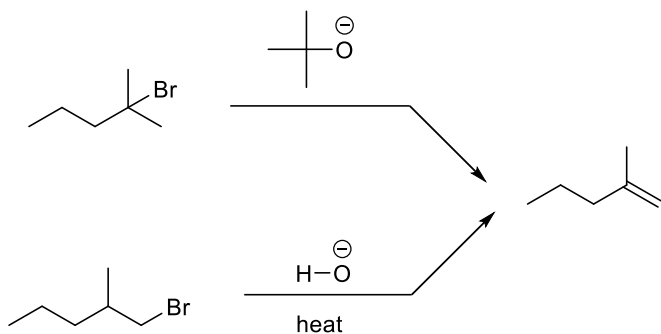
Solutions

3. In the first compound (left), all of C atoms of the ring are sp^3 -hybridized and tetrahedral. As a result, they are supposed to have bond angles of around 109.5° , but their actual bond angles are compressed due to the ring (and are almost 90°). In other words, the compound exhibits angle strain characteristic of small rings. In the second compound, two of C atoms are sp^2 -hybridized and trigonal planar. As a result, they have bond angles of approximately 120° , but their bond angles are compressed due to the ring (also $\sim 90^\circ$). The resulting angle strain ($120^\circ \rightarrow 90^\circ$) is greater than the angle strain in the first compound ($109.5^\circ \rightarrow 90^\circ$). Therefore, the second compound is higher in energy despite the fact that it has a more highly substituted double bond.

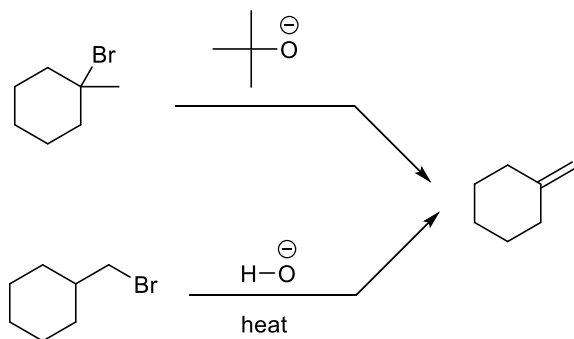




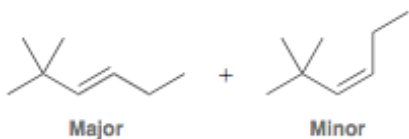
6. a)



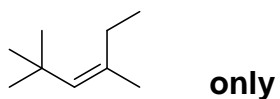
b)

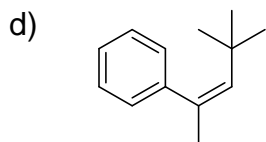
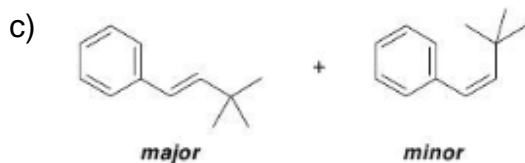


7. a)

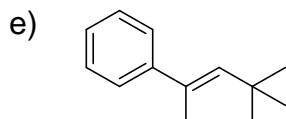


b)



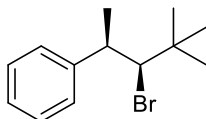


The only E2 product



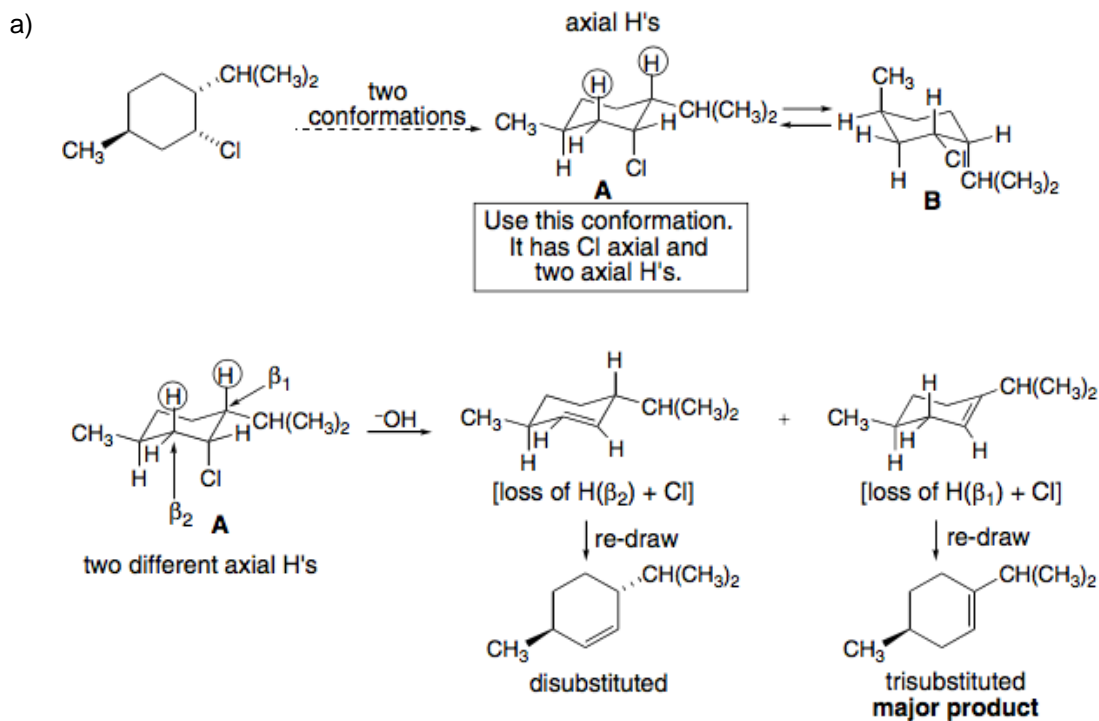
The only E2 product

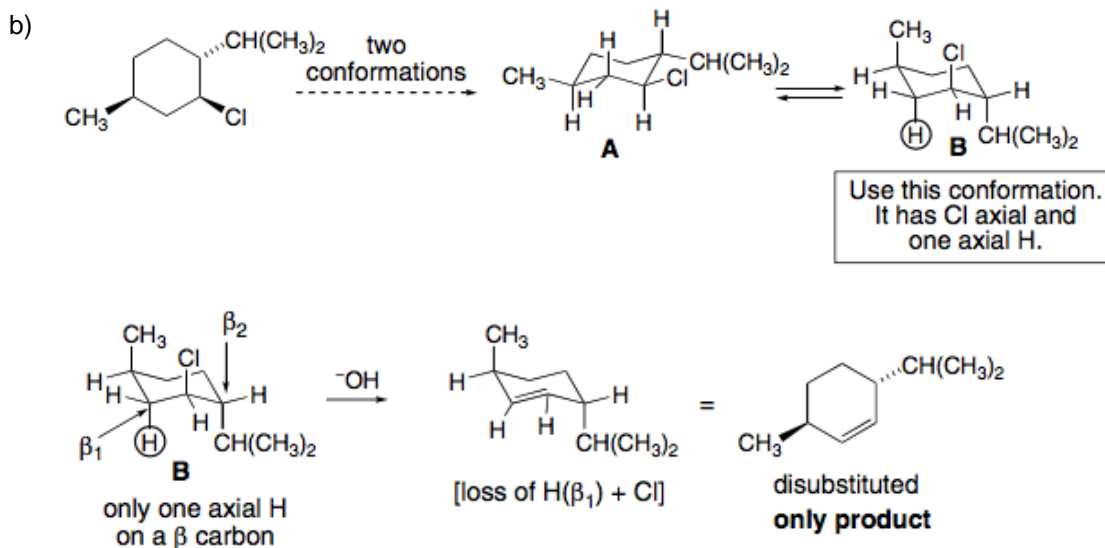
8. Multiple structures are possible



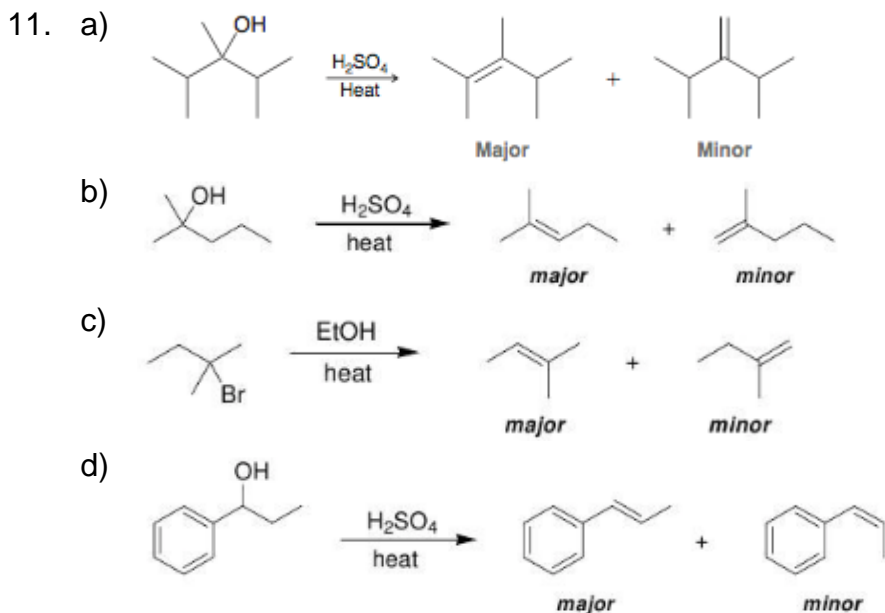
Remember to be careful of both regio- and stereochemistry

9. Draw the major E2 products from each of the following alkyl halides.

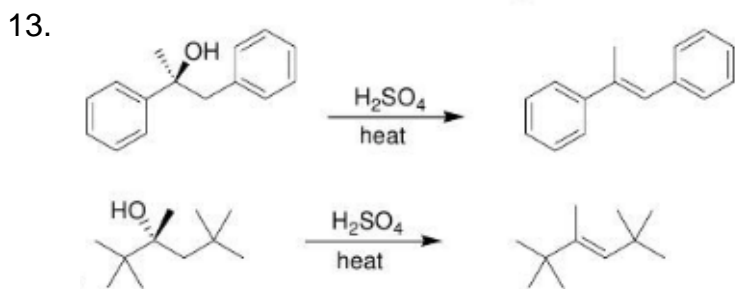
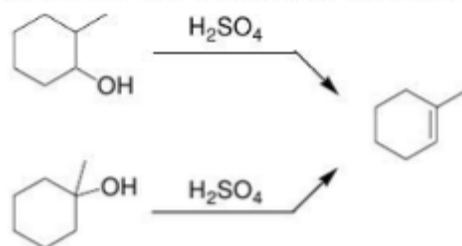




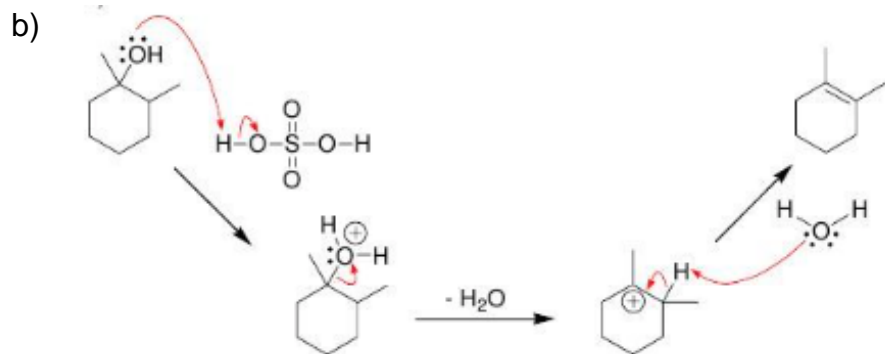
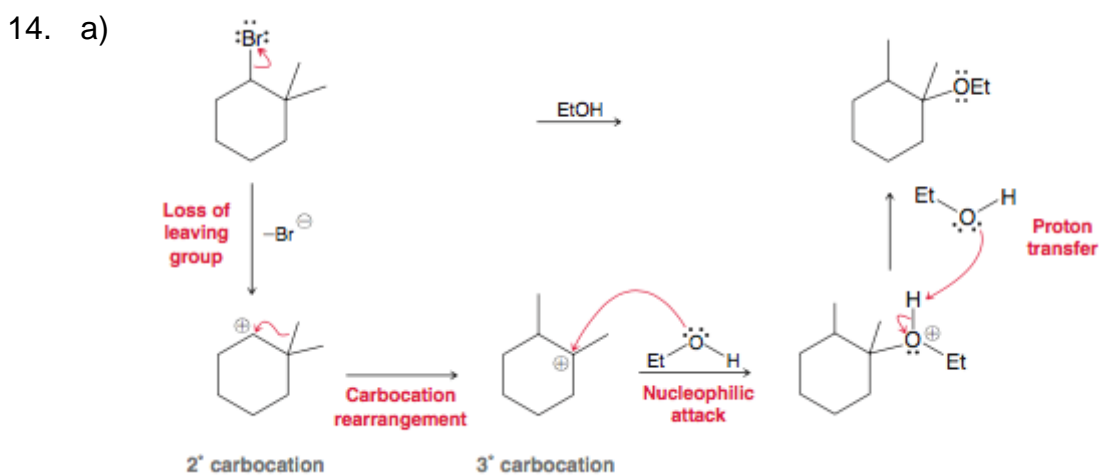
10. Because of the bulky tert-butyl group, the second compound (right) is essentially locked in a chair conformation in which the chlorine is placed equatorially. This conformation is unlikely to undergo E2 reactions because the leaving group is not anti-periplanar to a beta-proton. However, the first compound is locked in a chair conformation in which chlorine atom is placed axially. This conformation rapidly undergoes an E2 reaction. Therefore, the first compound is expected to be more reactive towards an E2 than the second compound.

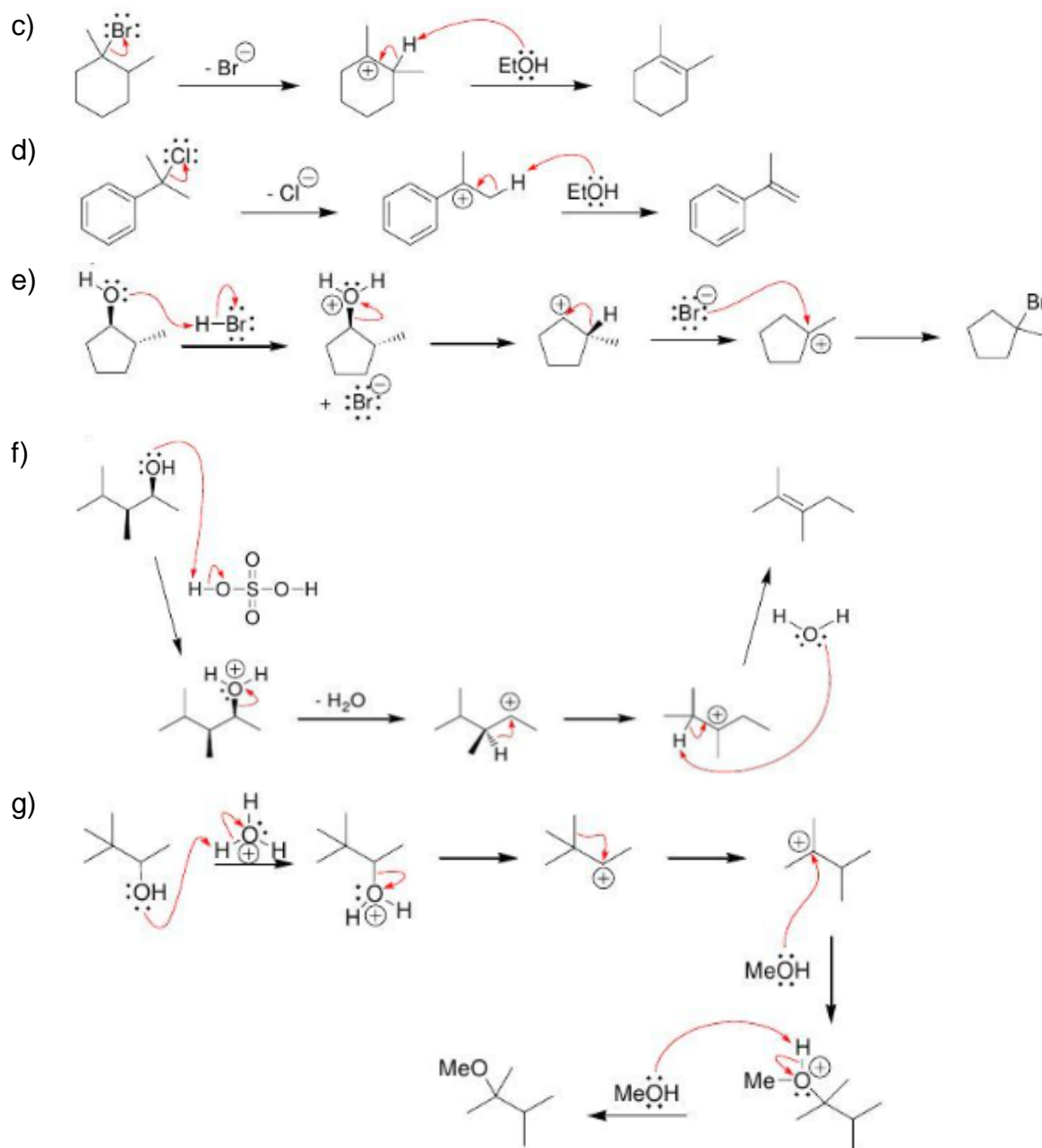


12. Both alcohols below can be used to form the product. The tertiary alcohol below will react more rapidly because the rate determining step involves the formation of a tertiary carbocation rather than a secondary carbocation.



E1 reactions are not stereospecific – that is, they do not require anti-periplanarity in order for the reaction to occur. When cis and trans products are possible, we generally observe a preference for formation of the **trans** stereoisomer.





15. Identify the mechanism(s) expected to operate when 1-bromobutane is treated with each of the following reagents:

- | | | | |
|--------------------------------------|-----------------------|-----------|--------------------------------------|
| a) NaOH | b) NaSH | c) t-BuOK | d) NaOMe |
| S _N 2 (Major), E2 (minor) | Only S _N 2 | Only E2 | S _N 2 (Major), E2 (minor) |

16. Identify the mechanism(s) expected to operate when 2-bromobutane is treated with each of the following reagents:

- | | | | |
|--------------------------------------|-----------------------|--------------------------------------|-----------|
| a) NaOEt | b) NaI in DMSO | c) NaOH | d) t-BuOK |
| E2 (Major), S _N 2 (Minor) | Only S _N 2 | E2 (Major), S _N 2 (Minor) | Only E2 |

17. Identify the mechanism(s) expected to operate when 2-bromo-2-methylpentane is treated with each of the following reagents:

a) EtOH

Both S_N1 and E1

b) t-BuOK

Only E2

c) NaI

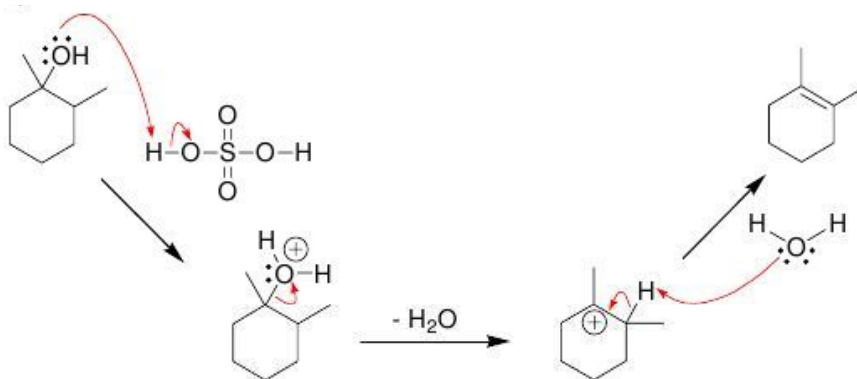
Only S_N1

d) NaOEt

Only E2

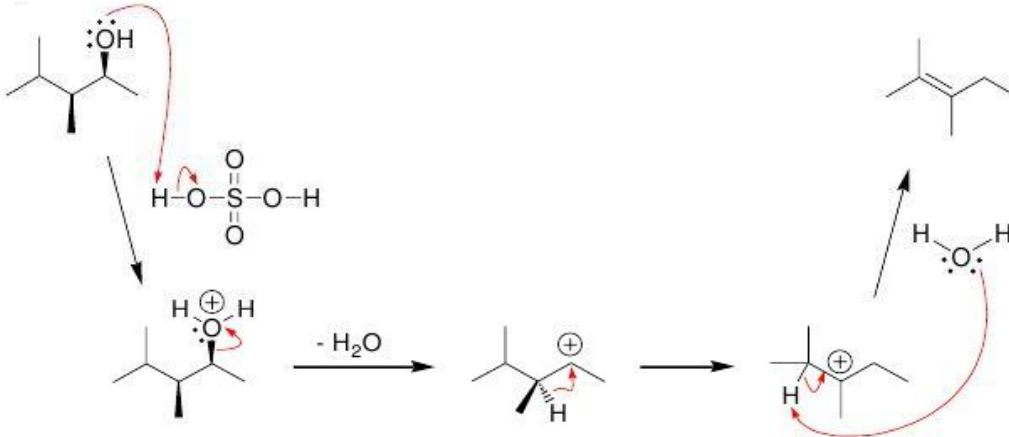
18.

a) E1



b) E2

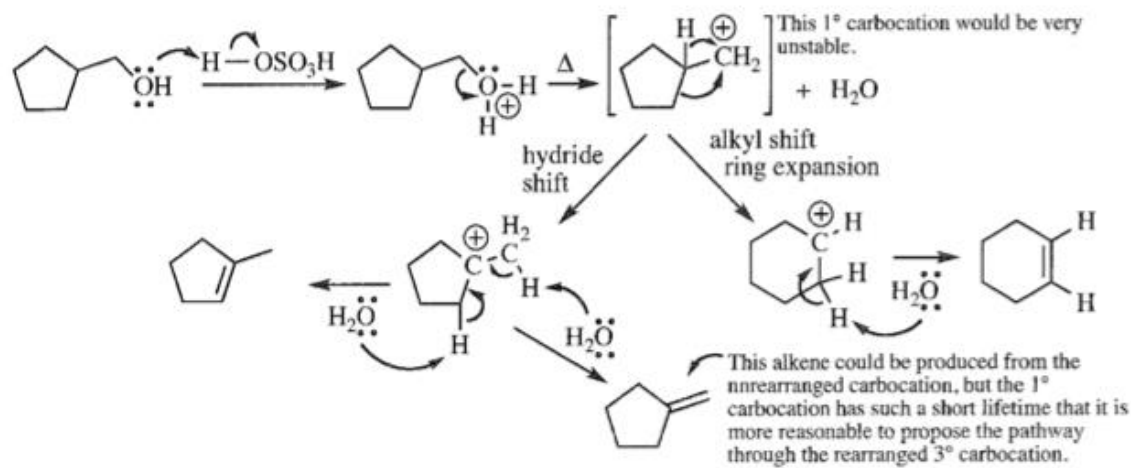
c) E1



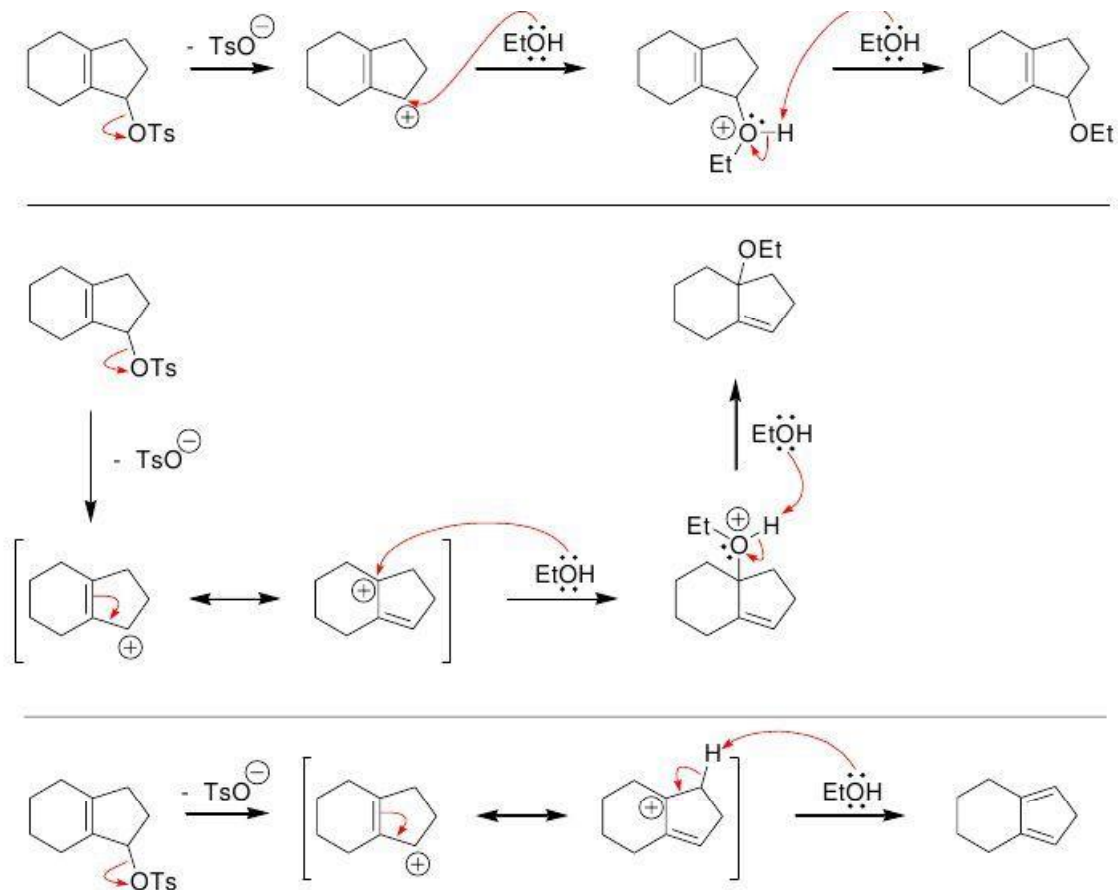
d) E2

e) E1

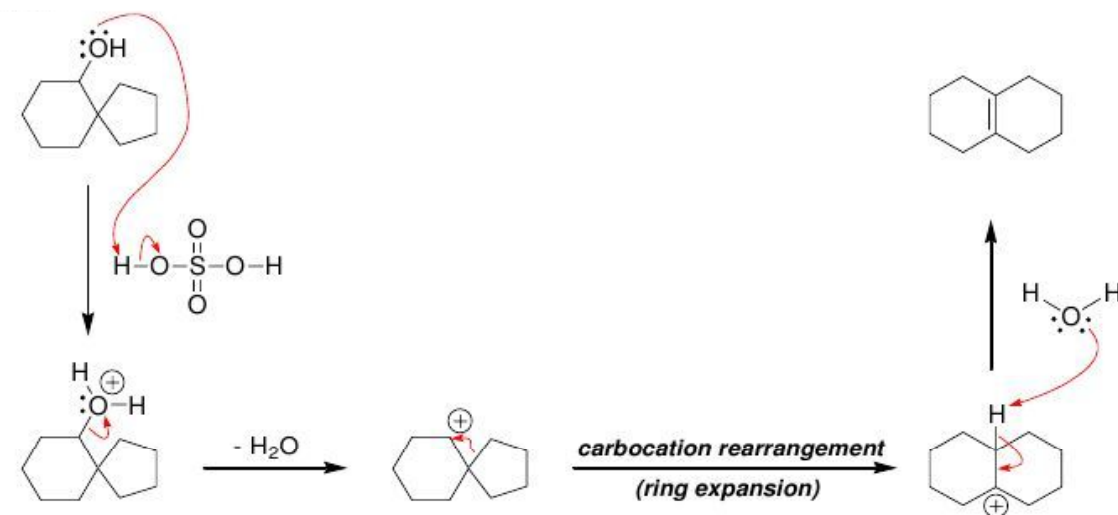
19.



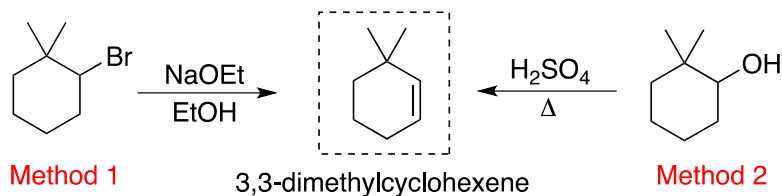
20.



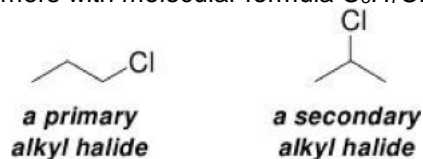
21.



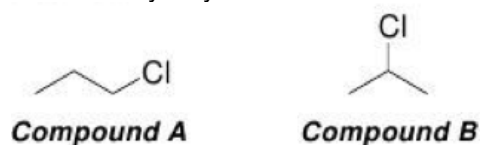
22. The first method is more efficient because it employs a strong base to promote an E2 process for a secondary alkyl halide bearing a good leaving group. The second method relies on an E1 process occurring at a secondary alcohol, which will be slow and will involve a carbocation rearrangement to produce a different product.



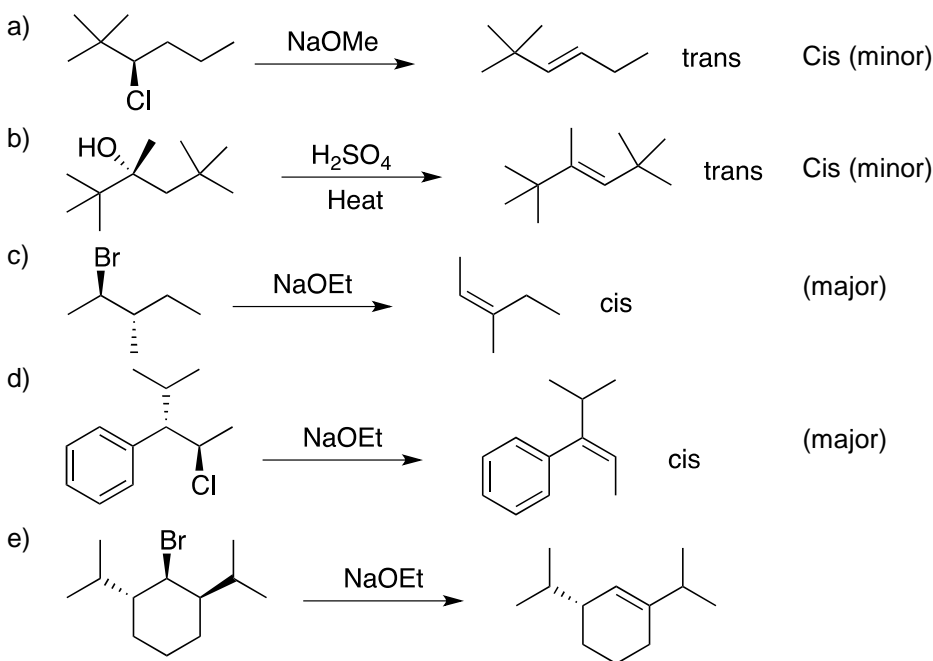
23. There are only two constitutional isomers with molecular formula C_3H_7Cl :



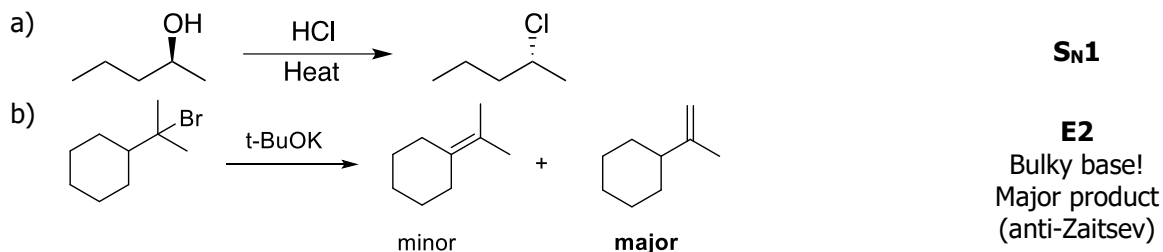
Sodium methoxide is both a strong nucleophile and a strong base. When compound A is treated with sodium methoxide, a substitution reaction predominates. Therefore, compound A must be the primary alkyl chloride above. When compound B is treated with sodium methoxide, an elimination reaction predominates. Therefore, compound B must be the secondary alkyl chloride:

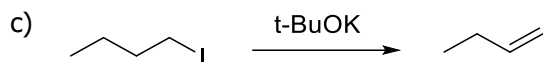
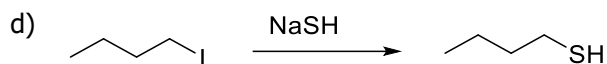


24.

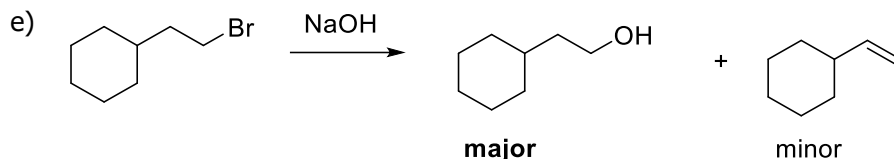


25.

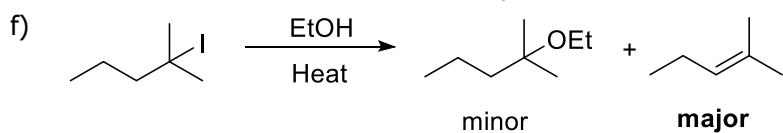


**E2****S_N2**

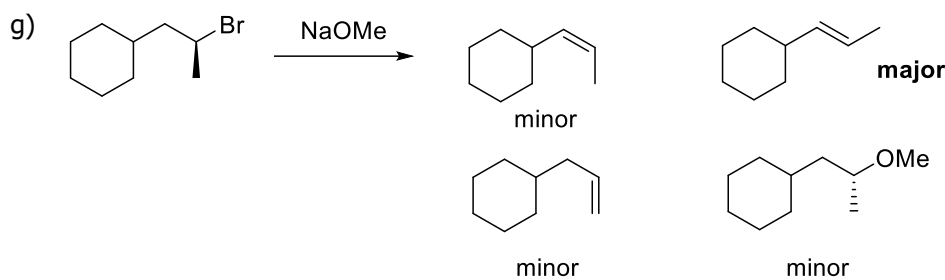
SH is a good nucleophile, but a poor base!



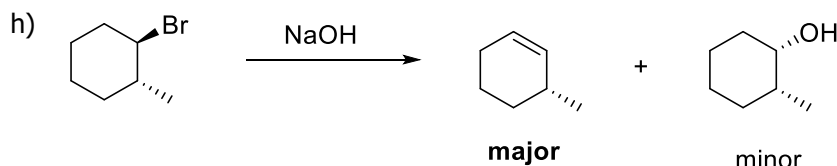
S_N2 (major)
1° AH + small strong Nu



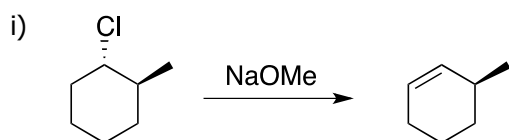
E1 and S_N1
Heat favours elimination over substitution



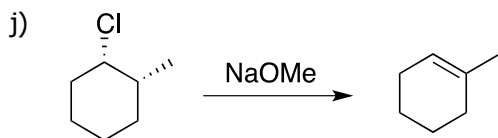
E2 (major)
Watch for Stereochemistry of the reactant and regioselectivity



E2 (major)
2° AH + small strong base



E2 major
Draw the chair conformation and look for a beta hydrogen anti-periplanar to Cl



E2 major
Draw the chair conformation and look for a beta hydrogen anti-periplanar to Cl