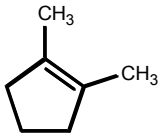
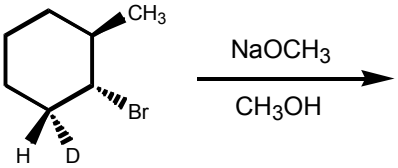
ORGANIC CHEMISTRY I – PRACTICE EXERCISE

Elimination Reactions and Alkene Synthesis

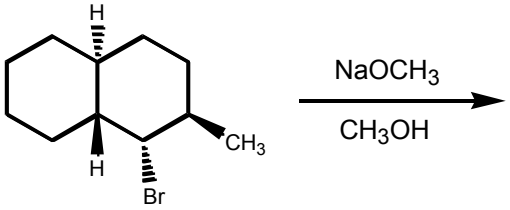
1) One of the products that results when 1-bromo-2,2-dimethylcyclopentane is heated in ethanol is shown below. Give a mechanism by which it is formed and give the name of this mechanism.



2) Provide the structure of the major organic product in the following reaction.

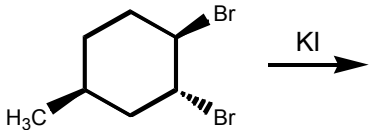


3) Provide the structure of the major organic product from following reaction.



4) Which diastereomer of 1-bromo-4-*t*-butylcyclohexane, the *cis* or the *trans*, undergoes elimination more rapidly when treated with sodium ethoxide? Explain your answer.

5) Provide the structure of the major organic product from the following reaction.



6) When 1-iodo-1-methylcyclohexane is treated with $NaOCH_2CH_3$ as the base, the more highly substituted alkene product predominates. When $KOC(CH_3)_3$ is used as the base, the less highly substituted alkene predominates. Give the structures of the two products and offer an explanation.

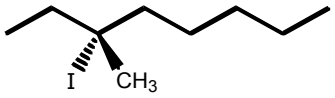
7) Which of the following statements apply to E1 reactions of alkyl halides? Choose as many as necessary.

I. Rate = k[base]
II. Rate = k[base][RX]
III. Rate = k[RX]
IV. The reactions occur in two or more distinct steps.
V. Rearrangements are sometimes seen.

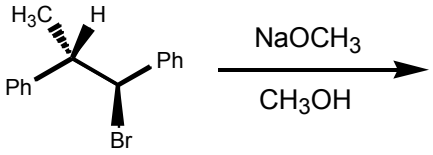
8) What is Saytzeff's rule?

9) What major product results when 2-bromo-2-methylbutane is treated with sodium ethoxide.

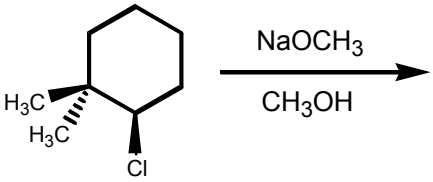
10) How many *distinct* alkenes can result from E2 elimination of the compound below? Give their structures and IUPAC names.



11) Give the major product and the mechanism of the following reaction.



12) Predict the most likely mechanism and the product for the reaction below.



13) Predict the most likely mechanism and the product from the reaction between 2-chloro-2-methylpentane and sodium ethoxide in ethanol.

14) The major product which results when 2-chloro-2-methylpentane is heated in ethanol is an ether. Show and name the mechanism by which this ether forms.

15) Which of the following mechanisms feature carbocation intermediates?

A) S_N1 only
B) S_N2 only
C) E1 only
D) E2 only
E) both S_N1 and E1

16) Which mechanism(s) give(s) alkenes as the major products, Sn1, Sn2, E1, or E2?

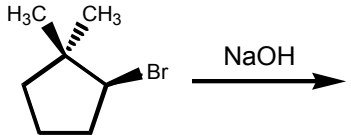
17) Which compound produces only one alkene when treated with sodium methoxide?

A) 2-chloro-2-methylpentane
B) 3-chloro-3-ethylpentane
C) 3-chloro-2-methylpentane
D) 2-chloro-4-methylpentane
E) 2-chloro-3-ethylpentane

18) When 3-iodo-3-ethylpentane is treated with sodium methoxide in methanol, the major organic product is an _____ that is generated through an _____ mechanism.

A) ether, S_N1 B) ether, S_N2 C) ether, E1 D) alkene, E2 E) alkene, E1

19) Provide the structure of the major alkene product of the reaction below.



20) Based on Saytzeff's rule, select the most stable alkene.

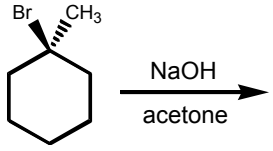
A) 1-methylcyclohexene
B) 3-methylcyclohexene
C) 4-methylcyclohexene
D) They are all of equal stability

21) Based on Saytzeff's rule, select the most stable alkene.

A) 1,2-dimethylcyclohexene
B) 1,6-dimethylcyclohexene
C) *cis*-3,4-dimethylcyclohexene
D) They are all of equal stability

FOR QS. 22-24, DRAW ALL ALKENE PRODUCTS AND CIRCLE THE PREDOMINANT ONE.

22)



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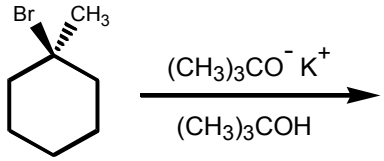
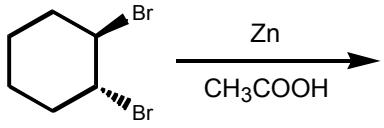
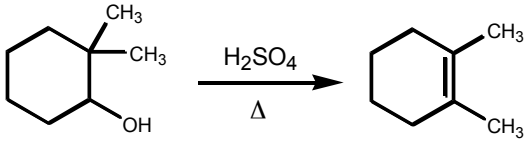


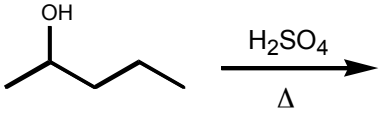
24)



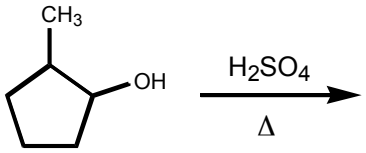
25) Propose a detailed, step-by-step mechanism for the reaction shown below.



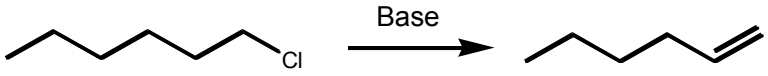
26) Draw all likely products of the following reaction and circle the product you expect to predominate.



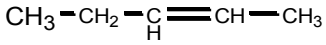
27) Draw all likely products of the following reaction and circle the product you expect to predominate.



28) Which base, ammonia (NH_3) or triethylamine [$(CH_3CH_2)_3N$], would be more effective to use for the following conversion?



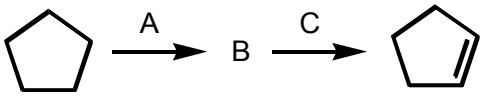
29) Which compound would undergoe dehydrohalogenation with strong base to give the alkene shown below as the only alkene product?



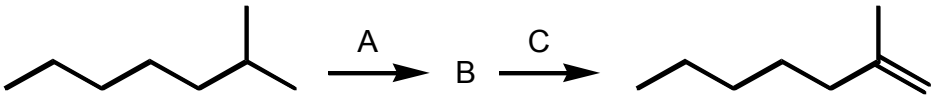
A) 1-chloropentane
B) 2-chloropentane
C) 3-chloropentane
D) 1-chloro-2-methylbutane
E) 1-chloro-3-methylbutane

FOR SYNTHESES # 30-32 GIVE THE MISSING REAGENTS AND STRUCTURES.

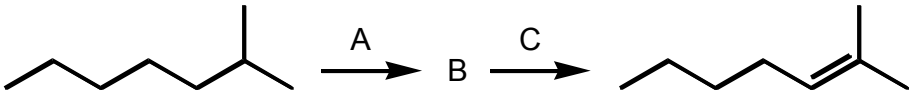
30)



31)



32)



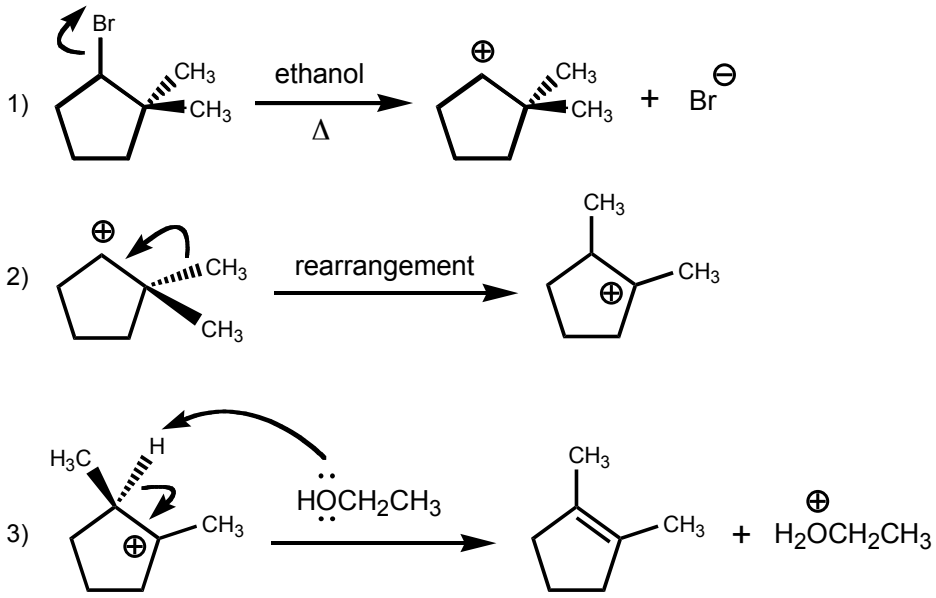
33) Which of the following statements applies to the E2 mechanism?

A) It occurs with inversion of stereochemistry.
B) It occurs with racemization of stereochemistry.
C) It proceeds through the more stable carbocation intermediate.
D) The C-H and C-X bonds that break must be anti.
E) Use of a bulky base gives the more highly substituted alkene product.

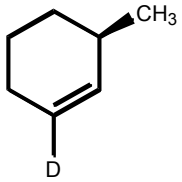
ANSWERS

1)

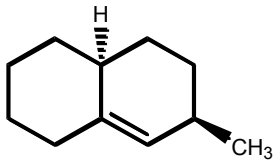
E1 mechanism with carbocation rearrangement



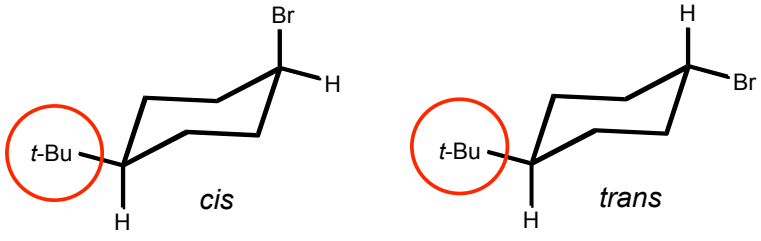
2) In questions 2 and 3, only the proton trans to the leaving group can eliminate.



3)

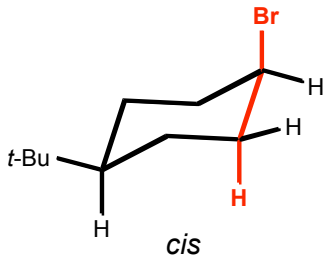


4) Due to the presence of the **bulky *t*-butyl group**, the ring is practically locked up in the most stable conformation with the bulky group being equatorial.



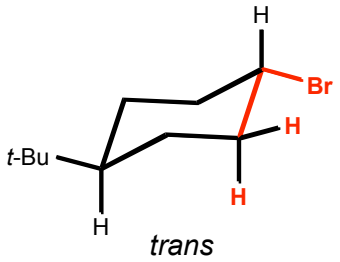
t-Bu = *t*-Butyl group

Of the two isomers, the *cis* is the only one that fulfills the anticoplanar arrangement for E2, where the leaving group and adjacent proton must be anti to each other and in the same plane.



cis

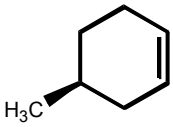
The atoms shown in red fulfill the *anticoplanar* requirement for E2. Elimination is possible and fast.



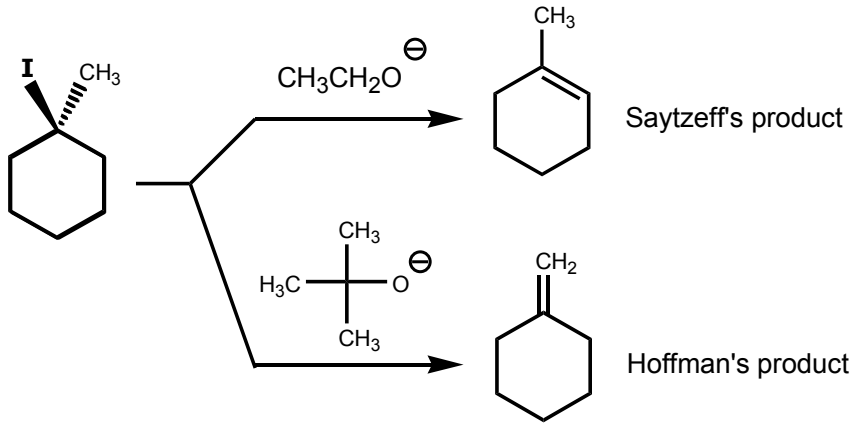
trans

The atoms shown in red **cannot** fulfill the *anticoplanar* requirement. Elimination is slower or not possible

5)



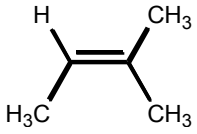
6) The small, unhindered base ethoxide yields the more stable alkene (Saytzeff's product, i.e. the more highly substituted alkene). When the bulky *t*-butoxide base is used, the most accessible hydrogen is removed. This results in the least highly substituted alkene (Hoffman's product).



7) III, IV, and V.

8) In elimination reactions, the most highly substituted alkene predominates.

9)



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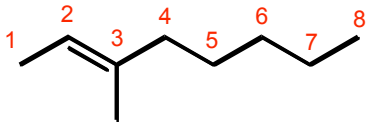
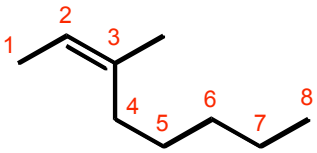
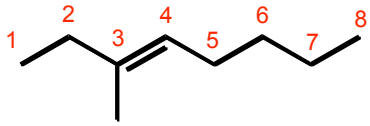


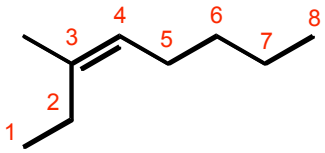
(*E*)-3-methyloct-2-ene



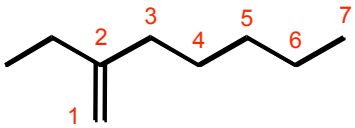
(*Z*)-3-methyloct-2-ene



(*E*)-3-methyloct-3-ene

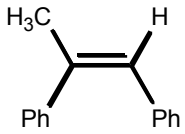


(*Z*)-3-methyloct-3-ene

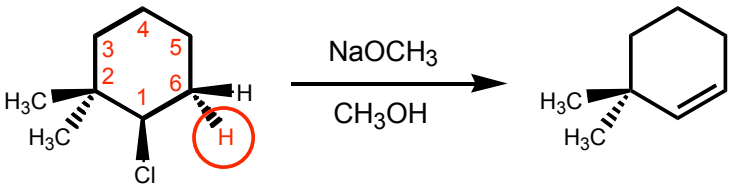


2-Ethylheptene

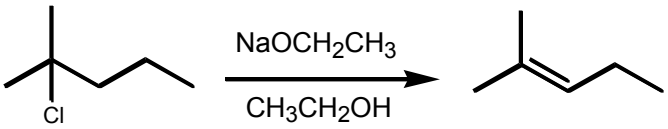
11) E2. The molecule must rotate around the central cabon-carbon bond to aquire the anticoplanar arrangement required for E2. This is a stereospecific reaction that results in formation of the product where the phenyl groups are *cis* to each other.



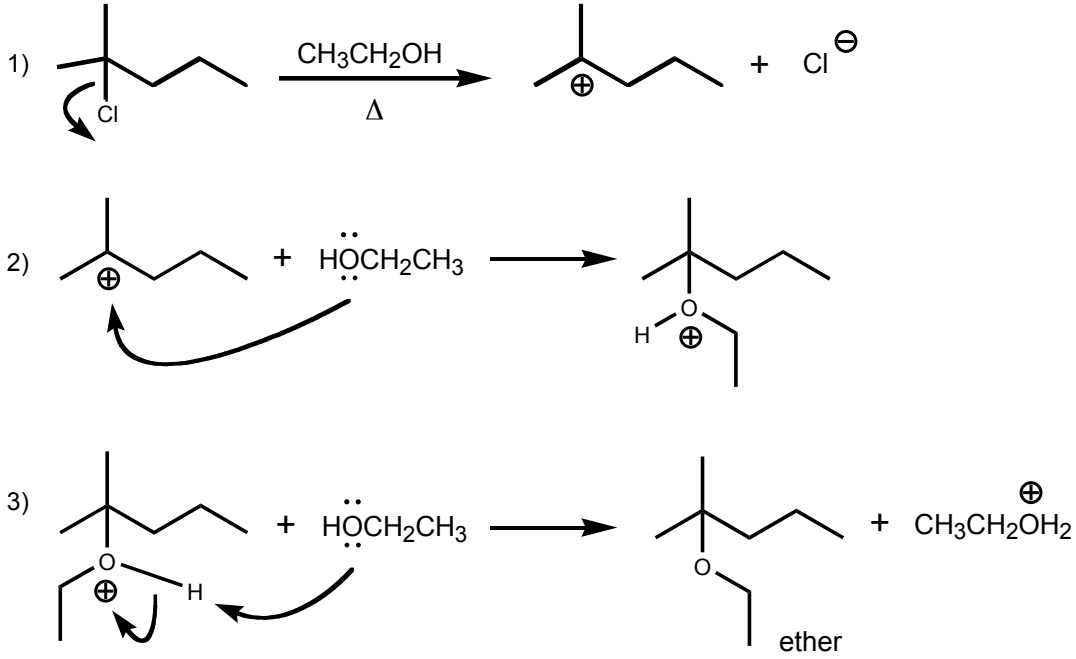
12) Strong base and bulky substrate favor E2. Only carbon 6 has protons *trans* to the leaving group. The pi bond can only form between carbons 1 and 6. Can you name the product by IUPAC rules?



13) Strong base and bulky substrate favor E2 with preferential formation of Saytzeff's product.

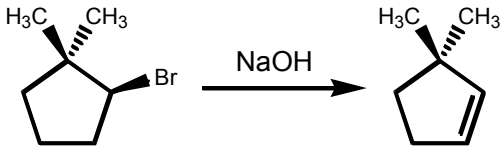


14) Weak nucleophile (ethanol, the solvent) and bulky substrate favor Sn1 as shown below. Can you tell which is the rate-determining step? Can you tell what type of reaction is involved in the last step?



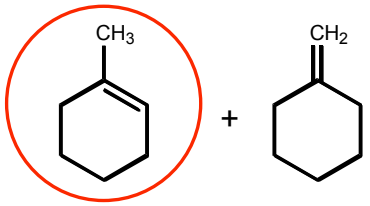
15) E 16) E1 and E2 17) B 18) D

19) The reacton is E2. See question 12 for a similar case.



20) A 21) A

22)



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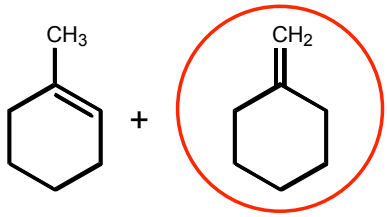
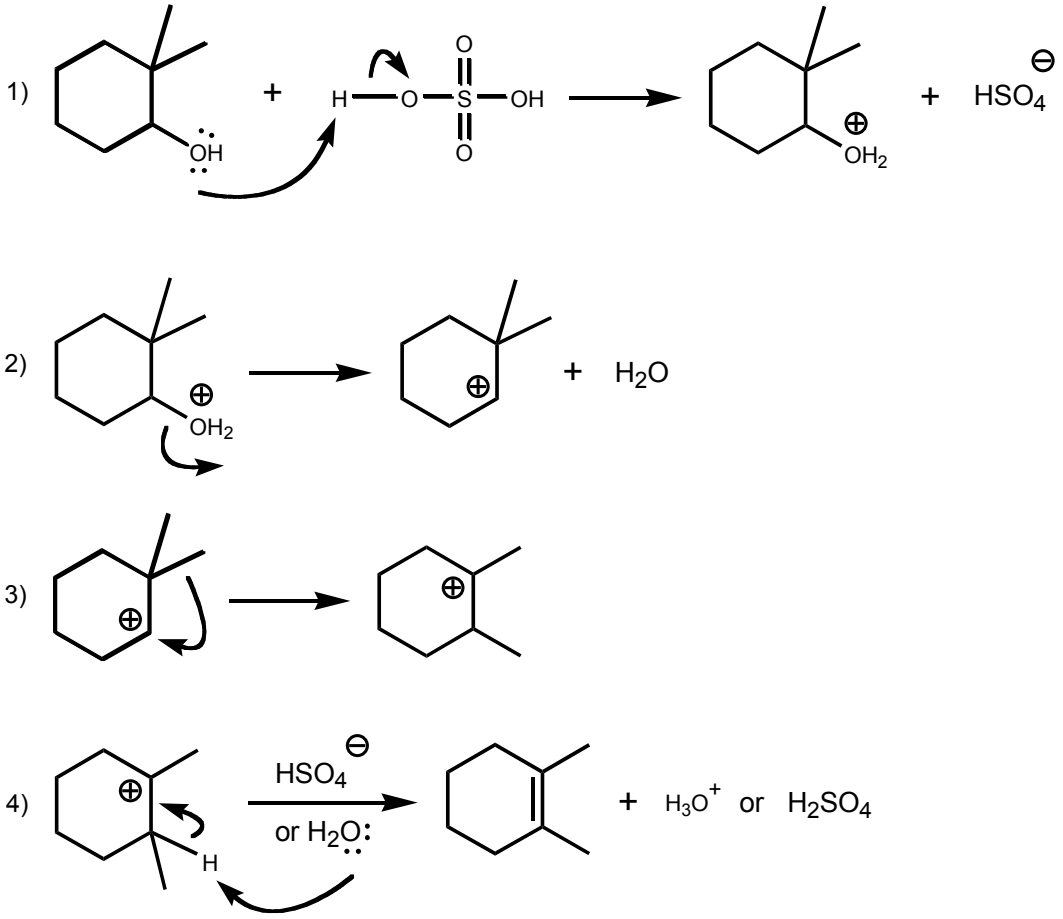


24)

25) First step is protonation of the alcohol by the strong acid to form a potential water molecule as a leaving group. Next is departure of the leaving group with formation of a carbocation. Next is a carbocation rearrangement from secondary to tertiary. The last step is an elimination step where the water abstracts the acidic proton next to the positive charge to form the alkene.



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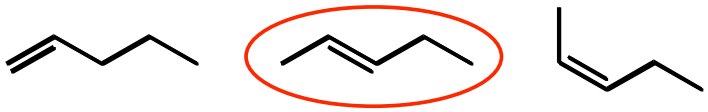

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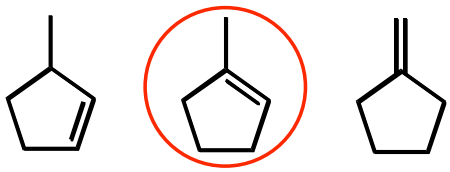
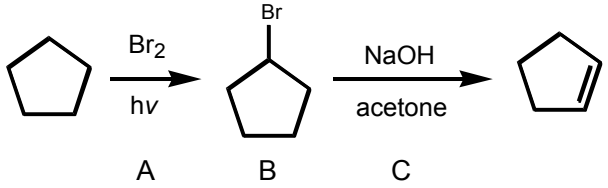


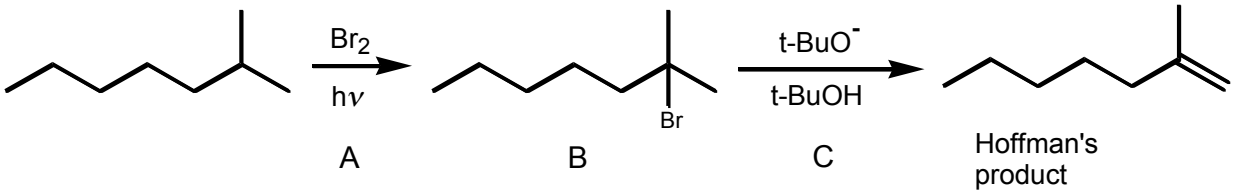
28) Triethylamine. Amines can be nucleophiles or bases. Increasing their steric bulk near the nitrogen atom diminishes their nucleophilicity while retaining the basicity. Since the substrate is sterically accessible to nucleophilic attack, a bulky base is needed to promote elimination.

29) C

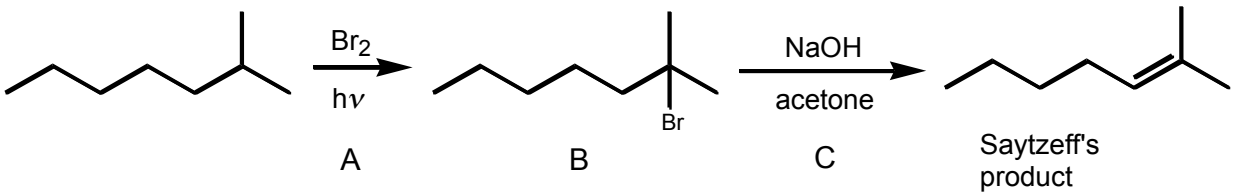
30) This is a typical example of a simple, multistep synthesis (in this case only two steps). This tests your ability to use previously learned reactions (e.g. from ch. 4) to design a synthesis towards a particular product, in this case cyclopentene. The last step is an elimination reaction. Any strong base combination will serve the same purpose as NaOH and acetone.



31) Similar to the previous problem, but this time Hoffman's product is desired. A bulky base must be used in the last step, such as *t*-butoxide ion.



32) Same as above, but this time Sayteff's product is desired. A small base must be used in the last step.



33) D