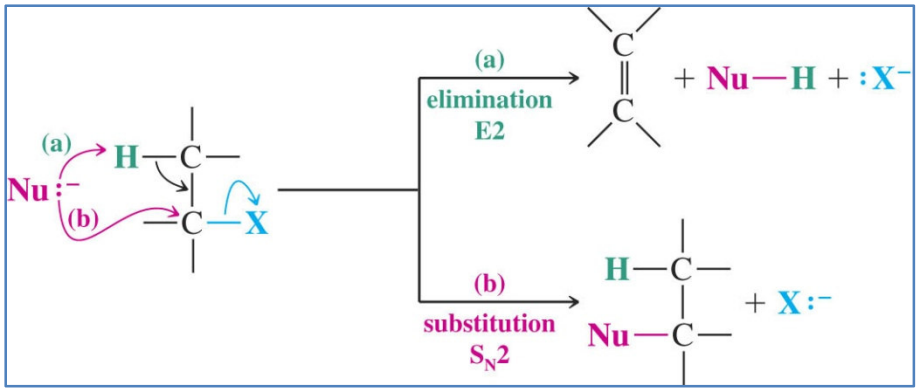
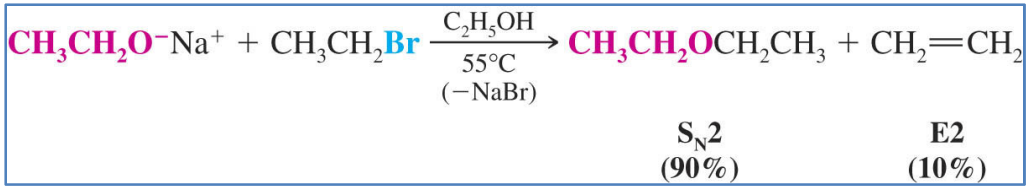
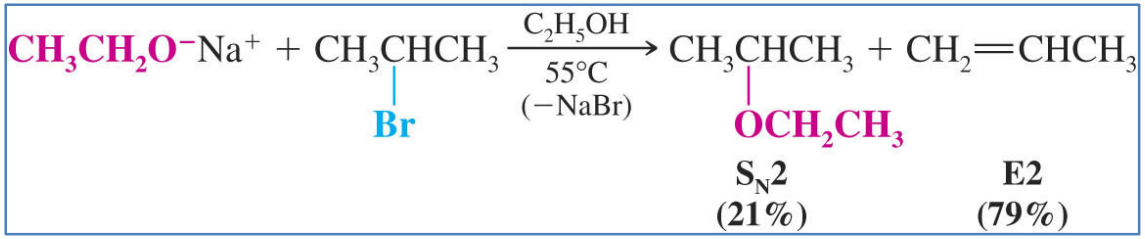
- Substitution versus Elimination
  - S_N2 versus E2



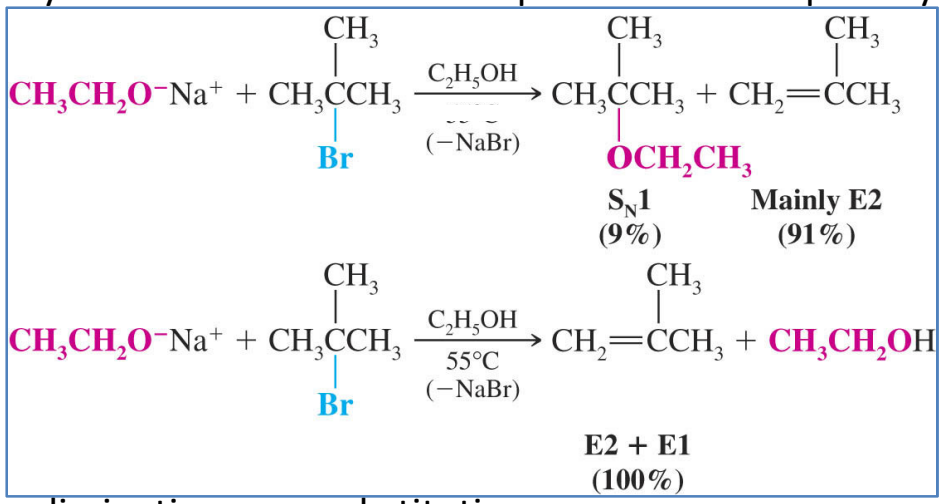
- Primary substrate
  - If the base is small, S_N2 competes strongly because approach at carbon is unhindered



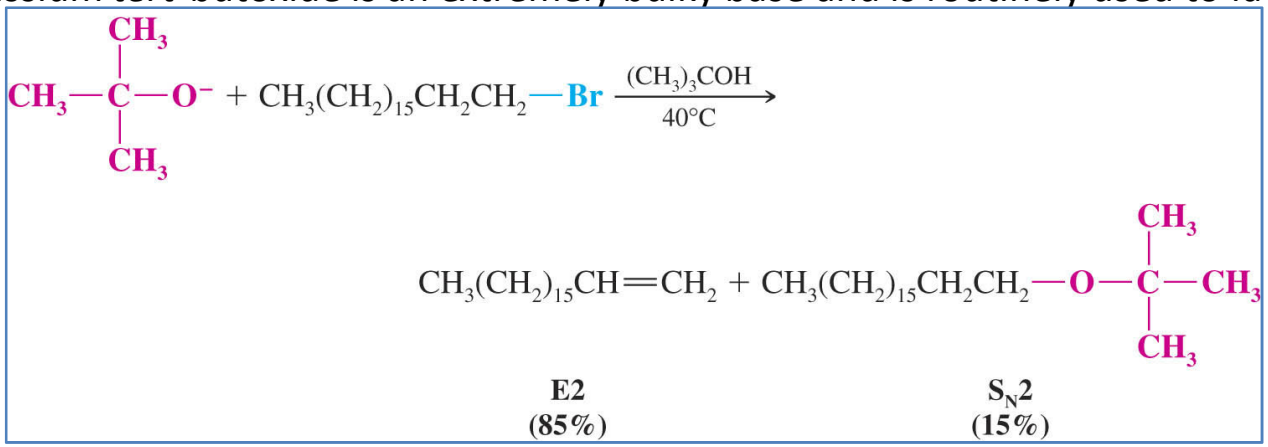
- Secondary substrate
  - Approach to carbon is sterically hindered and E2 elimination is favored



- Tertiary substrate
  - Approach to carbon is extremely hindered and elimination predominates especially at high temperatures

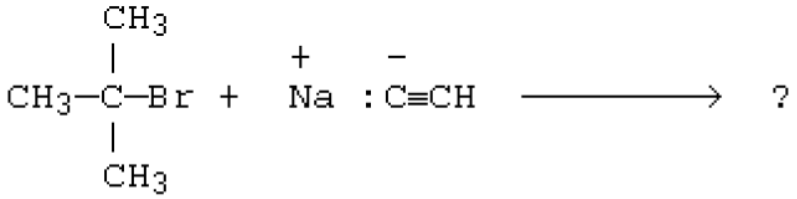


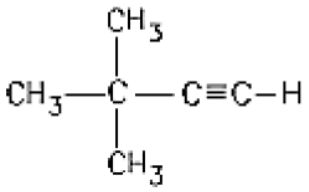
- Temperature
  - Increasing temperature favors elimination over substitution
- Size of the Base/Nucleophile
  - Large sterically hindered bases favor elimination because they cannot directly approach the carbon closely enough to react in a substitution
  - Potassium *tert*-butoxide is an extremely bulky base and is routinely used to favor E2 reaction



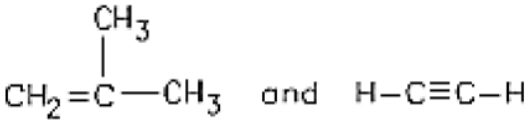
Selected Problems

6. What would you expect to be the chief organic product(s) when tert-butyl bromide reacts with sodium acetylide, i.e.,

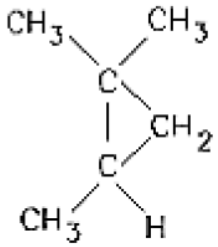




I



II



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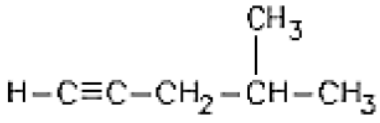
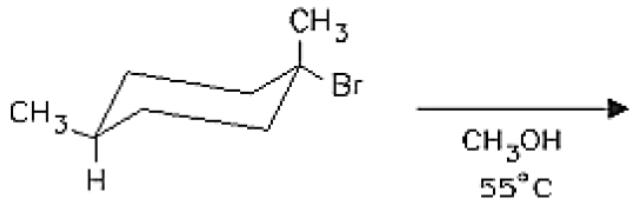
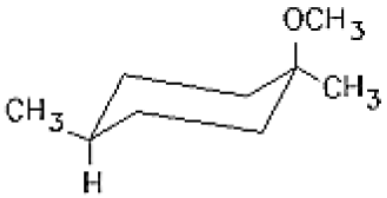


IV

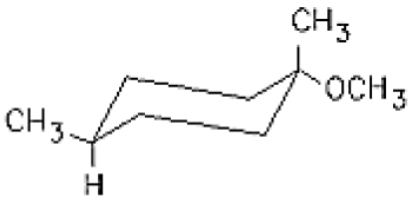
A) I
B) II
C) III
D) IV
E) None of these

10. Which would be formed in the following reaction?





I



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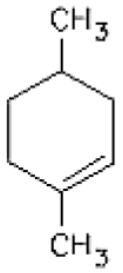

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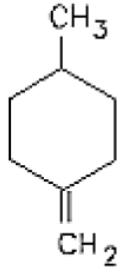
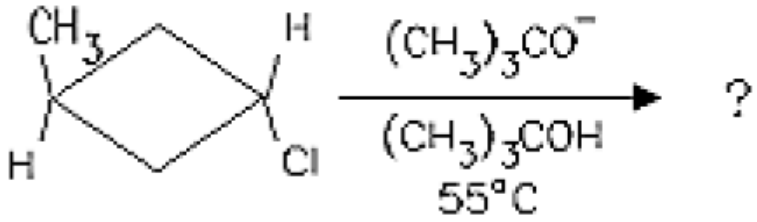
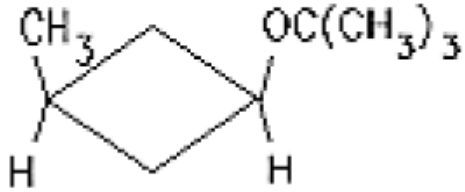


IV

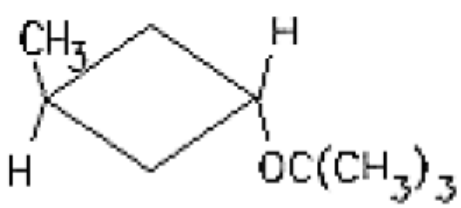
A) I
B) II
C) III
D) IV
E) All of the above

11. Which would be the major product of the following reaction?





I



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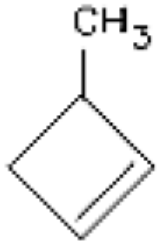
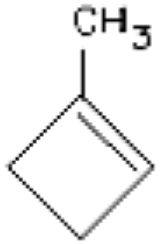


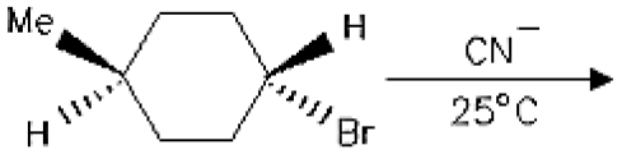
III

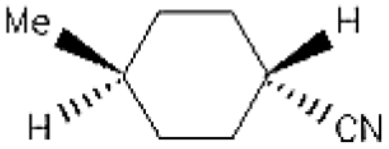


IV

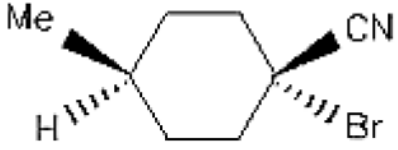
A) I
B) II
C) III
D) IV
E) None of the above

16. What would be the major product of the following reaction?

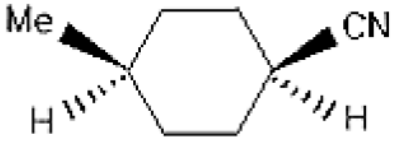




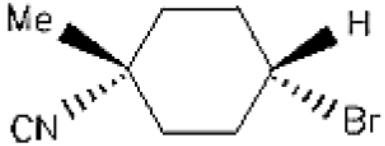
I



II



III



IV

A) I
B) II
C) III
D) IV
E) Equal amounts of I and III

17. You want to synthesize 2-methyl-1-butene from 2-chloro-2-methylbutane. Which reagent would you use?

A) $NaOH/H_2O$
B) KOH/H_2O
C) CH_3ONa/CH_3OH
D) CH_3CH_2ONa/CH_3CH_2OH
E) $(CH_3)_3COK/(CH_3)_3COH$

20. Reaction of sodium ethoxide with 1-bromopentane at 50°C yields primarily:

A) $CH_3CH_2CH_2CH{=}CH_2$

B) $CH_3CH_2CH{=}CHCH_3$

C) $CH_3CH_2CH_2CH_2CH_3$

D) $CH_3CH_2CH_2CH_2CH_2OH$

E) $CH_3CH_2CH_2CH_2CH_2OCH_2CH_3$

67. Consider the substitution reaction that takes place when (R)-3-bromo-3-methylhexane is treated with methanol. Which of the following would be true?

A) The reaction would take place only with inversion of configuration at the stereogenic center.

B) The reaction would take place only with retention of configuration at the stereogenic center.

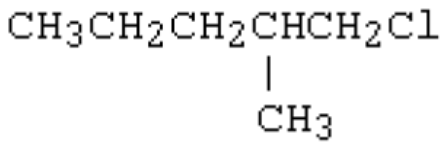
C) The reaction would take place with racemization.

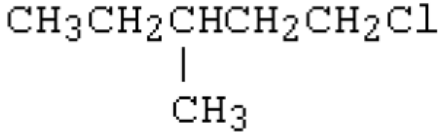
D) No reaction would take place.

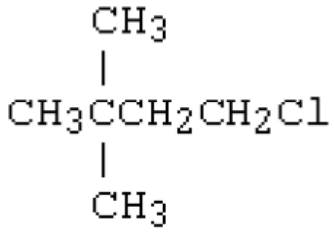
E) The alkyl halide does not possess a stereogenic center.

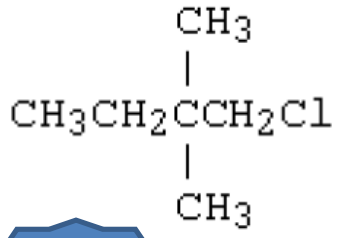
88. Which alkyl chloride, though primary, is essentially unreactive in S_N2 reactions?

A) $CH_3CH_2CH_2CH_2CH_2CH_2Cl$

B) 

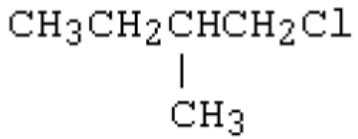
C) 

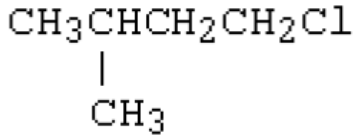
D) 

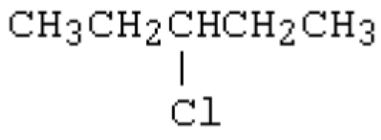
E) 

92. Which of these compounds would give the largest E2/S_N2 product ratio on reaction with sodium ethoxide in ethanol at 55°C?

A) $CH_3CH_2CH_2CH_2CH_2Cl$

B) 

C) 

D) 

E) $(CH_3)_3CCH_2Cl$