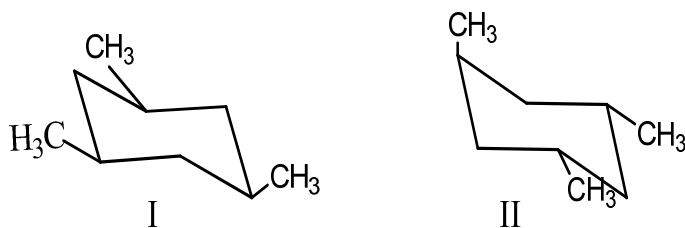
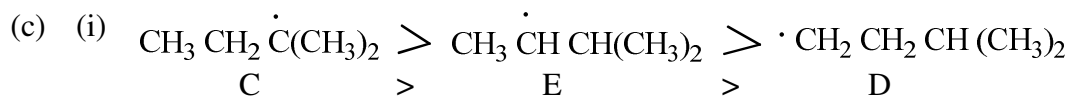
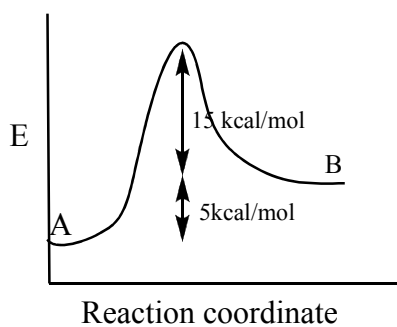


1. (a) (i)

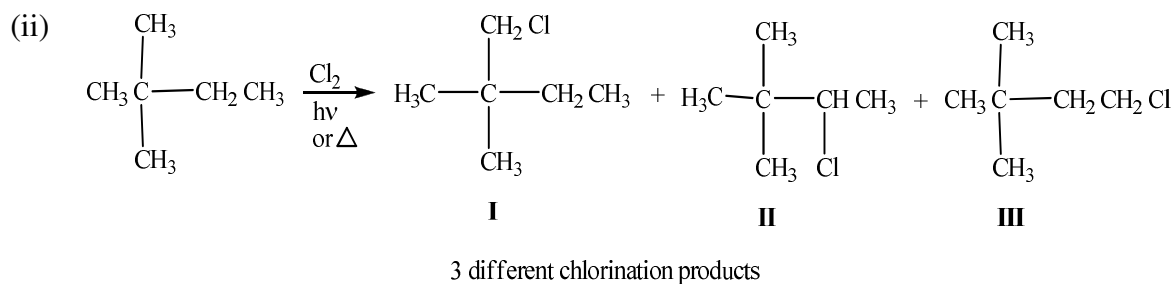


(ii) I has the most stable chair conformation because all the three methyl substituents are located at the equatorial positions in its more stable conformation. There is very minimum 1, 3 – diaxial interactions. The more stable chair conformation for II has only two methyl substituents in the equatorial positions.

(b)



Decreasing stabilization of radical by hyperconjugation in the order $3^\circ > 2^\circ > 1^\circ$



Relative amount of each product = no. of H x relative reactivity

$$\begin{array}{lclcl}
 \text{I} & : & 9 \times 1 & = & 9 \\
 \text{II} & : & 2 \times 3.8 & = & 7.6 \\
 \text{III} & : & 3 \times 1 & = & 3
 \end{array}$$

∴ % of each :

$$\text{I} : \frac{9}{9+7.6+3} \times 100\% = 45.9\%$$

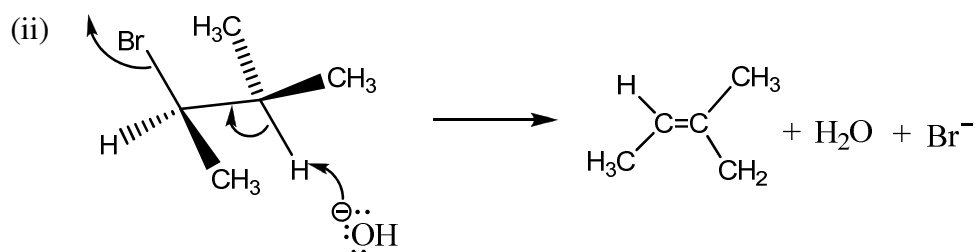
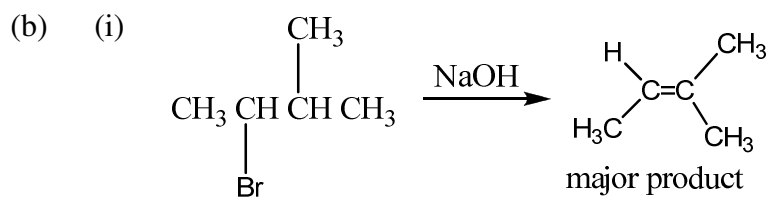
$$\text{II} : \frac{7.6}{19.6} \times 100\% = 38.8\%$$

$$\text{III} : \frac{3}{19.6} \times 100\% = 15.3\%$$

2 (a)



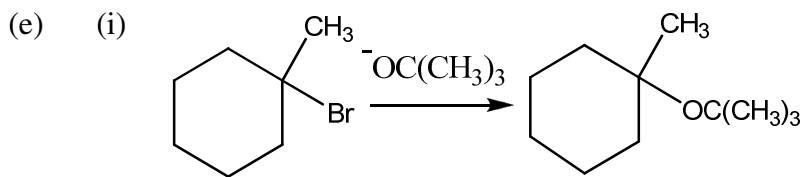
The rate of an $\text{S}_{\text{N}}1$ reaction is determined by the first step, i.e. the ionization of the substrate (R-X) to give the carbocation. The more stable the carbocation the faster it is formed because the transition state leading to it is more stable (c.f. Hammond's Postulate). On the basis that 3° carbocations are more stable than 2° carbocations and 2° is more stable than 1° , which more stable than CH_3^+ , and that I^- is a better leaving group than Br^- which is a better leaving group than Cl^- (basicity of halide ions decreases according to $\text{Cl}^- > \text{Br}^- > \text{I}^-$), the above order of reactivity is predicted.



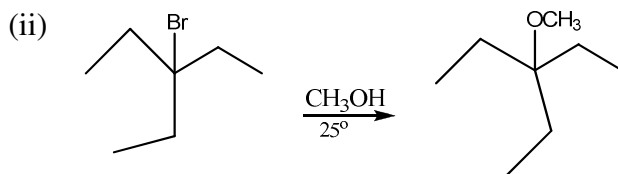
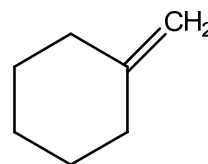
An E2 elimination is expected and this only occurs via a trans-periplanar conformation.

(c) $(\text{CH}_3\text{CH}_2)_2\text{N}$ is the better choice because it is a strong bulky base (i.e. a sterically hindered base and nucleophile) as compared to NH_3 . It would be easier for the triethylamine to abstract out the H to form the alkene than for it to undergo a substitution reaction as compared to NH_3 .

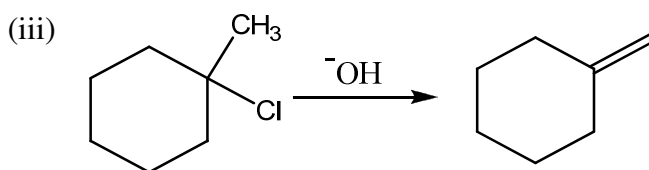
(d) The heat of hydrogenation of cyclobutene is exothermic . Being higher in value, than that of cyclopentene shows that the reaction occurs more readily. This is because a four-membered ring with a double bond has extra ring strain by virtue of the small ring and also the 90° bond angles compress the angles of the sp^2 -hybird carbons (normally 120°) more than they compress the sp^3 -hybird angles (normally 109.5°) in cyclobutane. The extra ring strain in cyclobutene makes its double bond more reactive than a typical double bond.



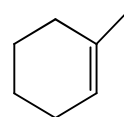
$\text{OC}(\text{CH}_3)_3^-$ is a strong bulky base/sterically hindered base that will direct the reaction mechanism to E2. $\text{OC}(\text{CH}_3)_3^-$ cannot function as a nucleophile in the $\text{S}_{\text{N}}2$ displacement of Br^- from the 1-bromo-1-methylcyclohexane, but will function as a base attracting a β -H, from the more accessible β -carbon. The actual product is

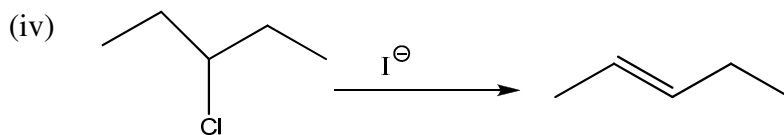


CH_3OH is a weak nucleophile (unlike CH_3O^-). If conversion of the bromide to an ether is to occur, the process will have to involve ionization of the bromide to a carbocation first. 25° is room temperature. Reaction would most likely not occur as the first step involves the formation of a carbocation which is a highly endothermic step. Since there is very little energy to break the C-Br bond, the process would be very, very slow or impossible to occur.

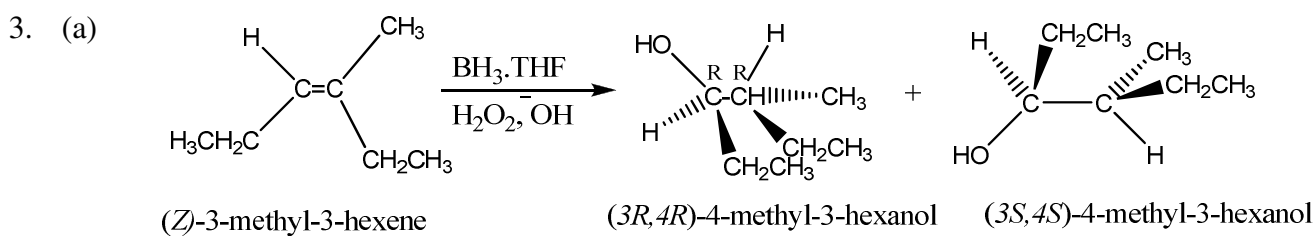


OH^- is a strong base but it is not bulky. It would therefore give the more highly substituted alkene as the major product i.e.



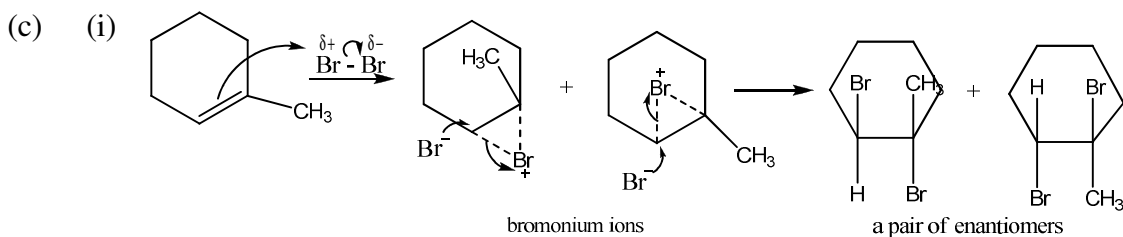
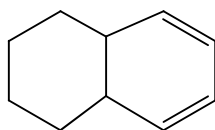


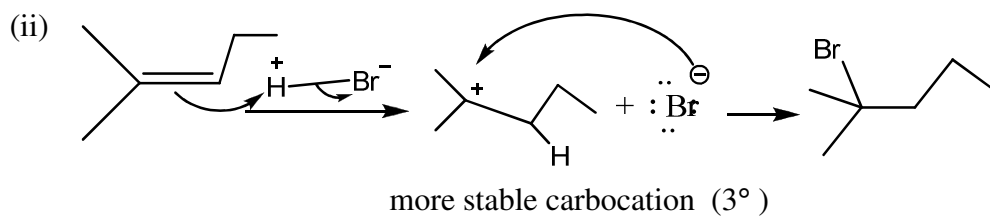
Actual product is as I^- can easily replace the Cl^- in an S_N2 reaction.



Hydroboration-oxidation is a anti Markovnikov addition of H_2O to an alkene. The stereochemistry of addition is syn. The two products are a pair of enantiomers,

- (b) Unknown F will have the carbon skeleton the same as G and with two double bonds conjugated to each other as seen by the oxidative cleavage. The structure of F is





4. (a) (i) A and B are constitutional isomers
 A and C are constitutional isomers
 B and C are diastereomers (cis and trans)
 C and D are enantiomers

- (ii) A is achiral
 B is achiral
 C is chiral
 D is chiral

(iii) C and D alone are optically active

(iv) A and B

(v) $B > A$
 $B > C$
 C and D are the same

(vi) B

(vii) No. It will be a racemic mixture.

(viii) Yes as only C is optically active.

(b) (i)
$$\text{e.e.} = \frac{10}{24} \times 100\% = 41.7\%$$

(ii) $[\alpha]$ = observed specific rotation

$$\frac{[\alpha]}{24^\circ} \times 100\% = 80\%$$

$$[\alpha] = \frac{80}{100} \times 24^\circ$$

$$= 19.2^\circ$$