

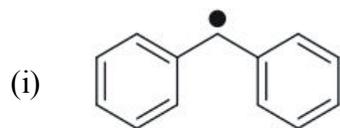
### Unit III

5. (a) A careful study of the photo initiated addition of HBr to 1-hexene established the following facts : 4

(i) The products are 1-bromohexane, 2-bromohexane, and 3-bromohexane. The amounts of 2- and 3-bromohexane formed are always nearly identical and increase from about 8% at 4°C to about 22% at 63°C.

(ii) During the reaction, a small amount of 2-hexene can be detected. Write a suitable mechanism that is consistent with these results.

(b) Rank the following free radicals in order of decreasing stability and provide a suitable justification : 4



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Total Pages : 07

LMDE/M-24

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ORGANIC CHEMISTRY-II

CHEM-203

Time : Three Hours]

[Maximum Marks : 60

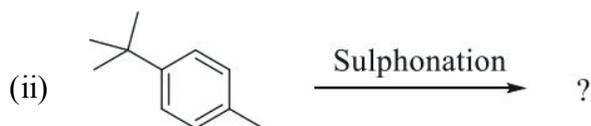
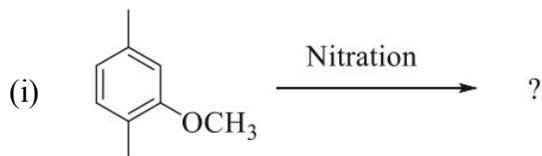
**Note :** Attempt *Five* questions in all, selecting at least *one* question from each Unit. All questions carry equal marks.

### Unit I

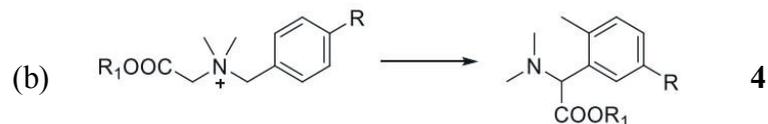
1. (a) Although N, N-dimethylaniline is extremely reactive toward electrophilic aromatic substitution and is readily substituted by weak electrophiles, such as diazonium and nitrosonium ions, this reactivity is greatly diminished by the introduction of an alkyl substituent in an *ortho* position. Explain with a mechanism. 4

(b) Rearrangement of phenolic esters in the presence of aluminium chloride yields ortho- or para-hydroxy ketones. What is the mechanism of this reaction? Is it a one-step or two-step process? 4

- (c) Predict the product(s) for each of the following reactions with proper justification : 4



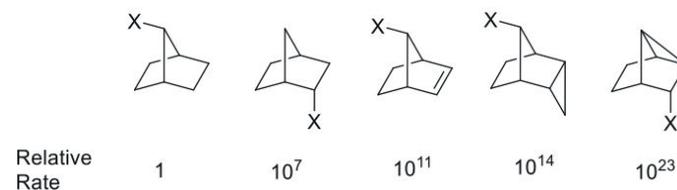
2. Solve the following organic transformation and provide a suitable mechanism :



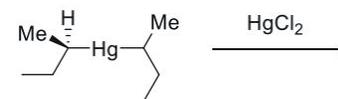
### Unit II

3. (a) Relative rate data are given below for a wide range of reactivities for rings related to the bicyclo[2.2.1]heptyl (norbornyl) system. Offer a

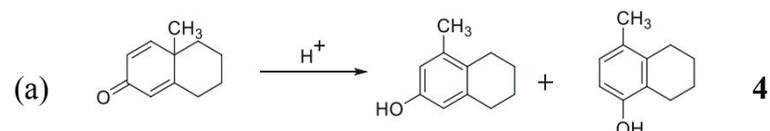
discussion with suitable mechanisms of the structural effects that are responsible for the observed relative rates. 4

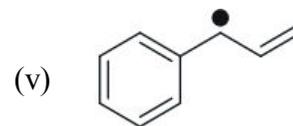
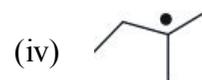
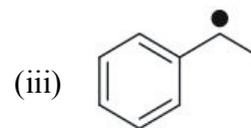
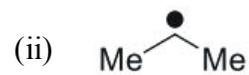


- (b) Discuss the solvolysis of erythro and threo isomer of 3-phenyl-2-butyl tosylates in acetic acid and provide a suitable mechanism for each reaction. 4
- (c) Considering the following reaction proves that under different sets of conditions, the product has one-half of the original activity. What conclusion have you made from this observation? Explain with a mechanism. 4



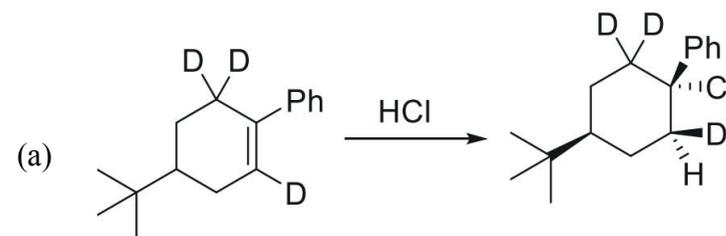
4. Rationalize the following organic transformation and suggest a suitable mechanism :

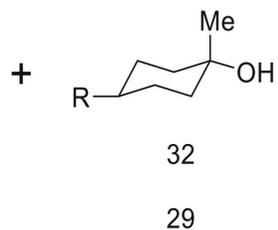
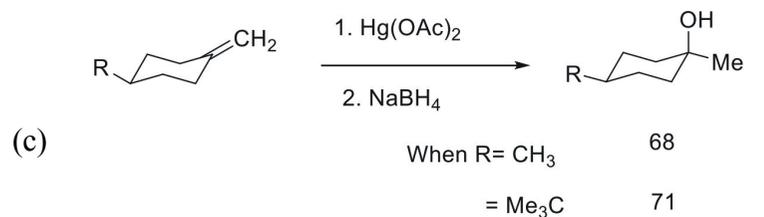
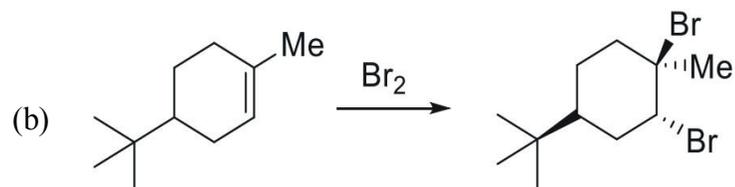




(c) Briefly explain the homolytic aromatic substitution with suitable examples. 4

6. Discuss the factors and mechanisms that are responsible for the regiochemistry and stereochemistry observed for the following reactions. 4+4+4





#### Unit IV

7. (a) An aromatic aldehyde A [Mol formula : C<sub>7</sub>H<sub>6</sub>O] on reaction with diethyl malonate in the presence of pyridine (base) gives product B and compound B on hydrolysis with aq KOH and further acidification give product C, which on heating give compound D. Explain each reaction and provide the suitable mechanism for each step. Also, provide the synthesis of compound D using the Perkin reaction.      4

- (b) Briefly discuss the following with a suitable mechanism :      4+4

- (i) Reformatsky reaction  
 (ii) Wittig Reaction.

8. (a) By taking a proper example discuss the significance of pH control during the addition-elimination reactions of ketones with phenylhydrazine.      4
- (b) In benzoin condensation “p-dimethylaminobenzaldehyde is not an acceptor but only a donor”. How will you prove this statement? Solve with a mechanistic approach.      4
- (c) Define the term transesterification. What are the suitable conditions required to carry out the desired transesterification reaction? Explain with a suitable mechanism.      4