

This question paper contains 16+4+2 printed pages]

H.P.A.S. (Main)—2013

CHEMISTRY

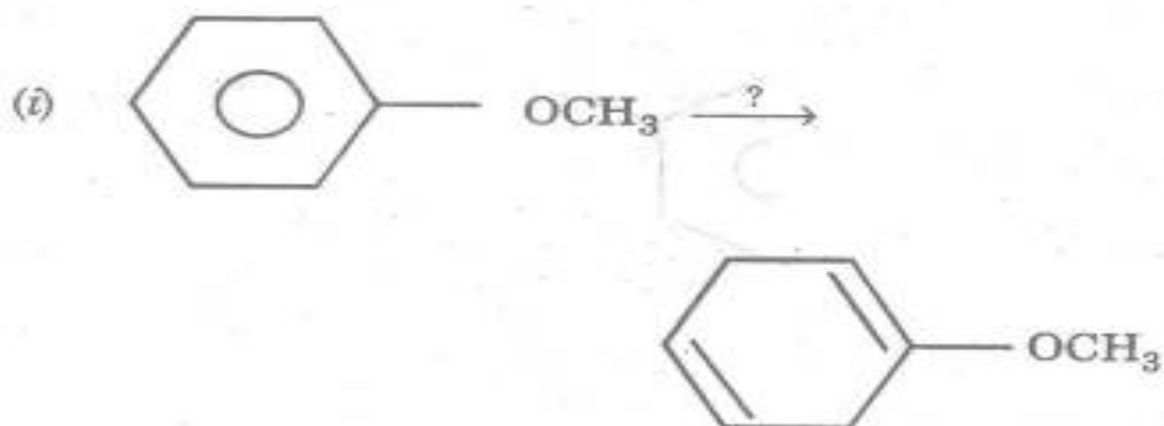
Paper II

Time : 3 Hours

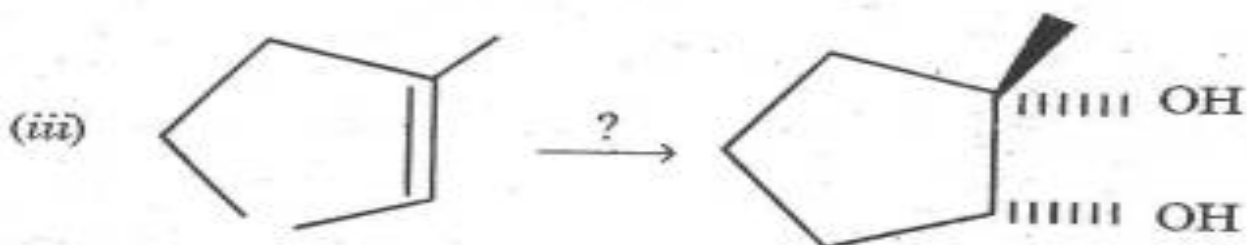
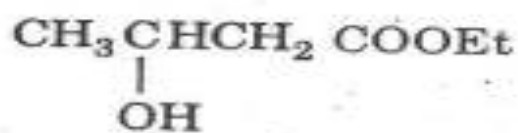
Maximum Marks : 150

Note :— Question No. 1 is compulsory and attempt any other *four* questions out of the remaining seven questions. Attempt *five* questions in all. All parts of a question must be attempted in continuation at one place.

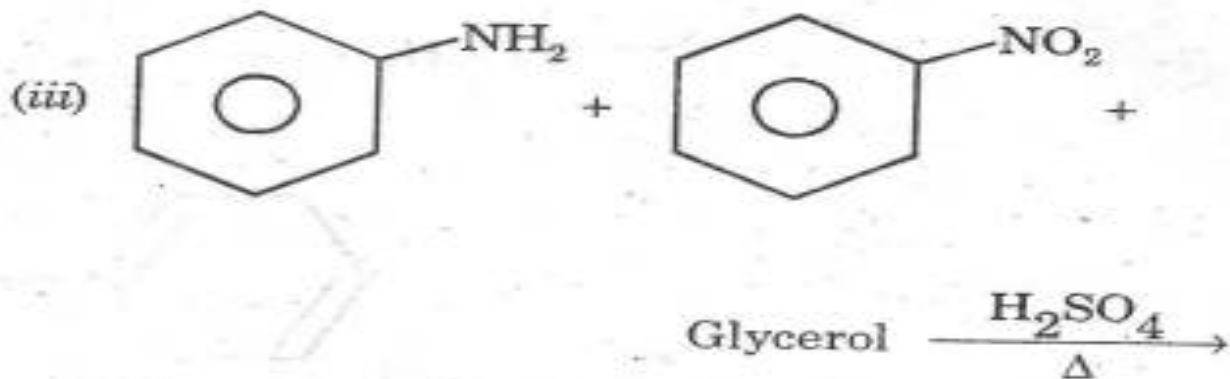
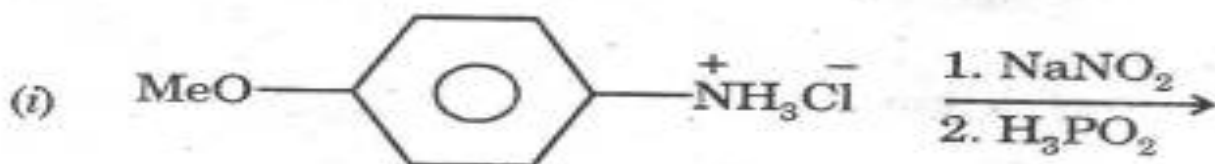
1. (a) Give reagents for the following reactions :



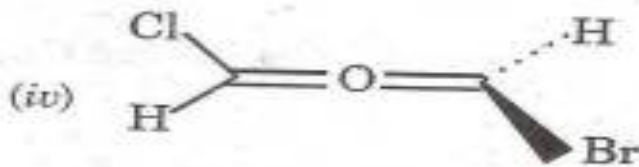
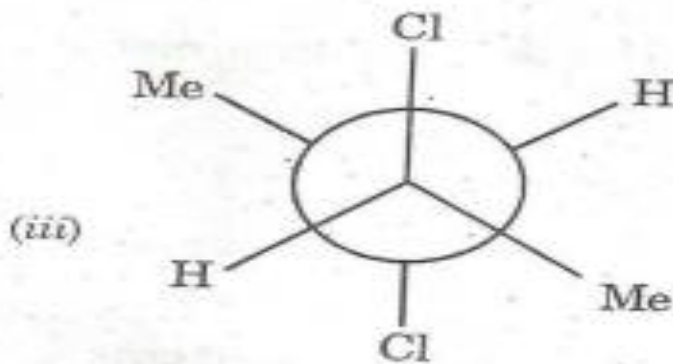
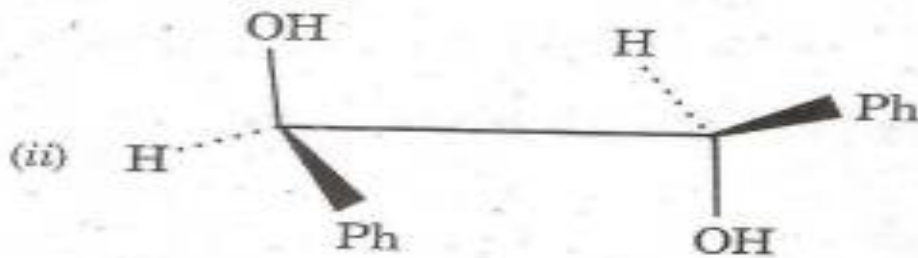
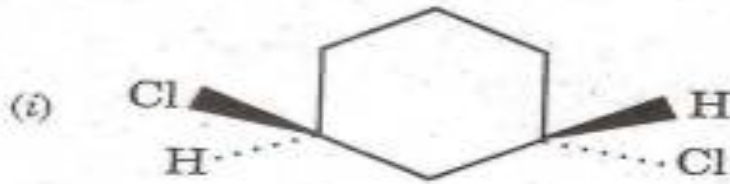
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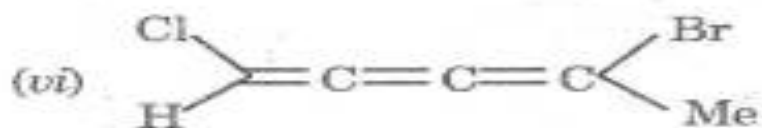
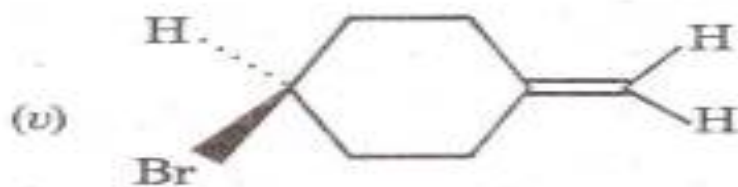


(b) Give reaction products in the following reactions :



- (c) Identify which of the following compounds are chiral ?



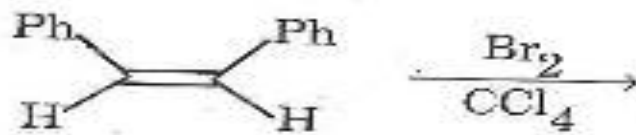


- (d) Explain the terms stereospecific, stereoselective and regioselective with examples.
- (e) Explain why 3-bromocyclopropene gives white precipitate with silver nitrate readily. Write the reaction and product.
- (f) Complete the following statements :
- (i) The reactive intermediate in Curtius and Lossen rearrangements is

- (ii) The carbonyl group of esters shows frequency in IR spectrum than carbonyl group of ketones.
- (iii) The reaction of benzaldehyde with acetic anhydride in presence of sodium acetate is known as
- (g) Give the structure of 18-crown-6. How does it enhance the oxidation of toluene with KMnO_4 ?
- (h) Attempt the following :
- (i) How can you distinguish between *o*-hydroxy benzaldehyde and *p*-hydroxy benzaldehyde by IR spectrum ?

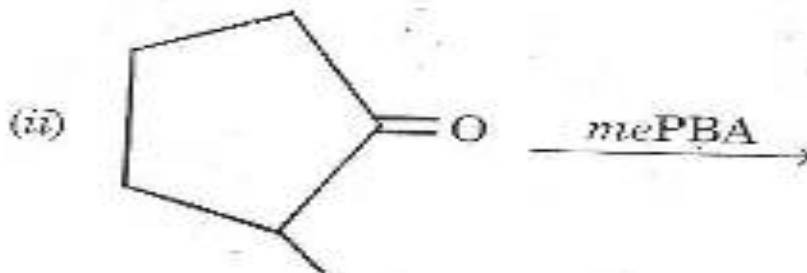
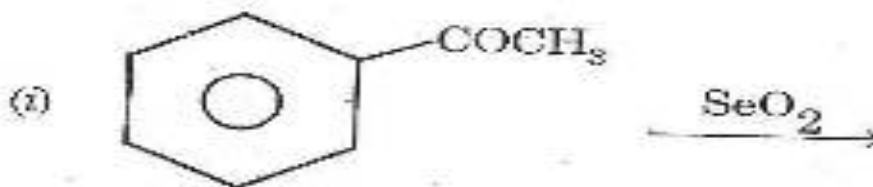
- (ii) How can you distinguish between methyl benzoate and phenylacetate by proton NMR ?
- (i) The reaction of *m*-bromoanisole with NaNH_2 in liquid ammonia leads to preferential formation of :
- (i) *o*-amino anisole
 - (ii) *m*-amino anisole
 - (iii) *p*-amino anisole
 - (iv) 1, 4-Diaminobenzene.
- (j) Explain the terms aromaticity, anti-aromaticity and homoaromaticity with suitable examples.

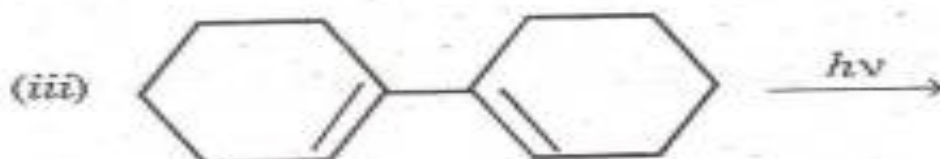
2. (a) Write the product(s), their ratios and relationship, if any, for the following reaction :



- (b) Draw Jablonski diagram. What is the difference between phosphorescence and delayed phosphorescence ?

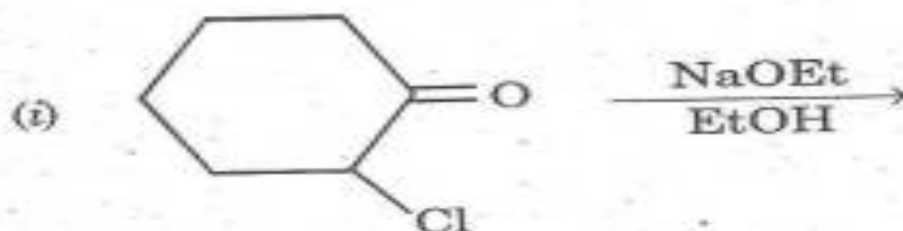
- (c) Complete the following reactions :

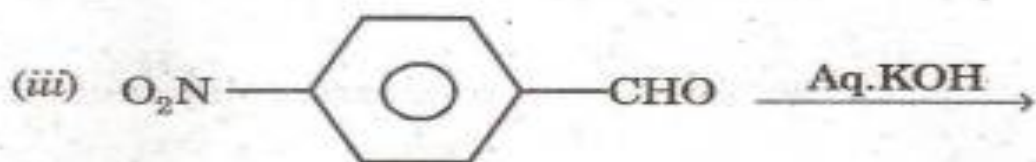
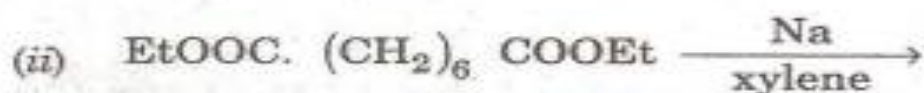




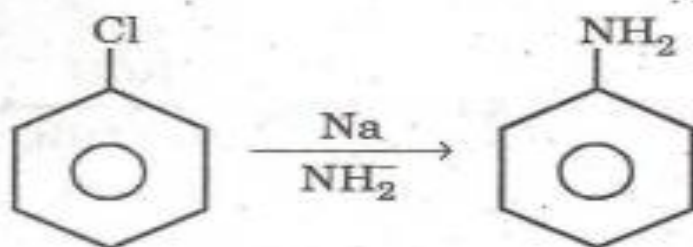
- (d) Intramolecular aldol condensation of 2, 5-heptanedione with dilute NaOH yields two enone products in the ratio of 9 : 1. The major product has two singlet absorptions in $^1\text{H NMR}$ at δ 1.65 and 1.90. There are no absorptions in the range δ 3–10. Identify the major product.

- (e) Complete the following reactions and name them :





3. (a) The following reaction proceeds by SET mechanism :



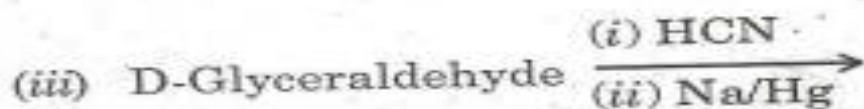
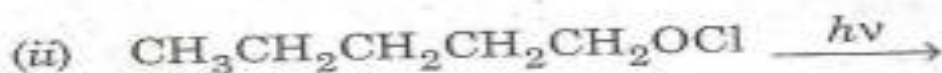
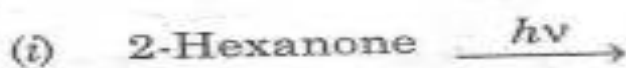
Write all the steps of the mechanism.

- (b) Justify disrotatory thermal ring closure of 1, 3, 5-hexatriene by FMO approach.
- (c) What is supramolecular chemistry ? Explain briefly with suitable examples.

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(d) Complete the following reactions and name them.

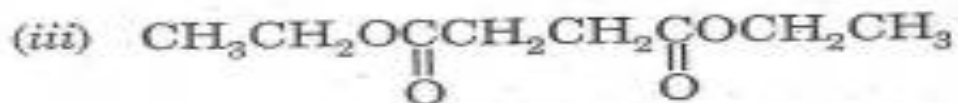
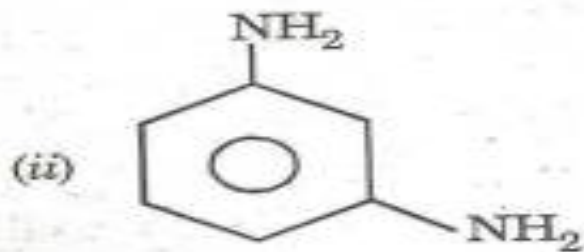
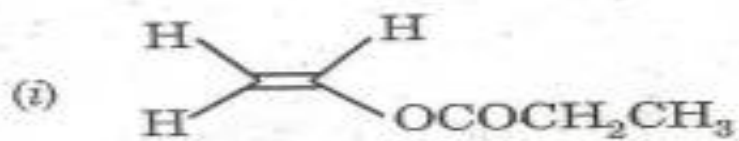
Write all the products, wherever possible :



(e) What is meant by number average and mass average molar mass in a polymer? Give monomers of poly (methyl methacrylate), polycarbonate and teflon.

(a) Comment on the number of signals and their multiplicity in PMR of the following

compounds :



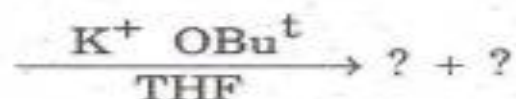
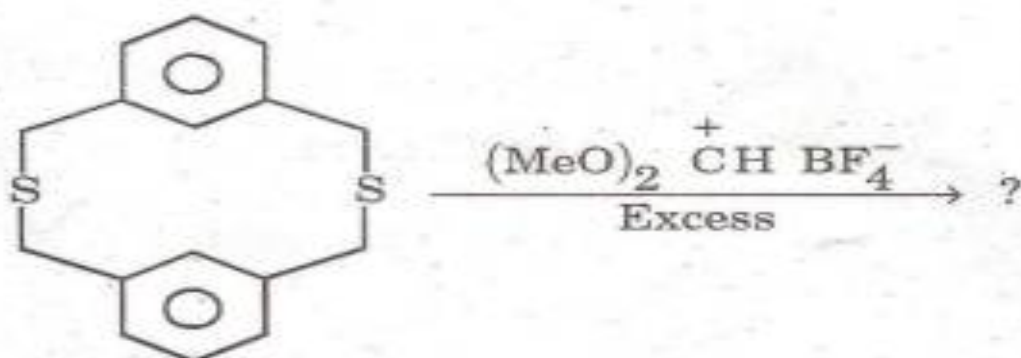
(b) Complete the following reactions with examples :

(i) Fischer-Indole

(ii) Von Richter

(iii) Bischler-Napieralski.

(c) Write the product(s) and name the reaction :



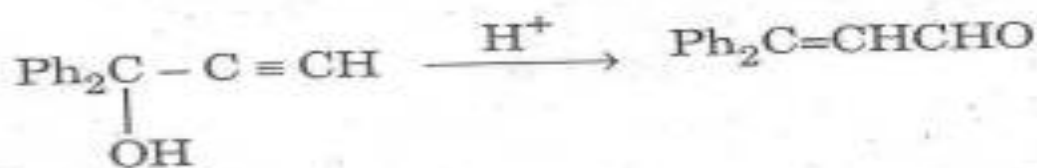
- (d) Explain the significance of σ (sigma) and ρ (rho) (both sign and magnitude) in Hammett equation. What is the importance of Hammett equation ?
- (e) The rates of ethanolysis of $\text{PhCH}_2\text{CH}_2\text{Br}$, $p\text{-(OMe)C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br}$ and $p\text{-(OH)C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{Br}$ are in the order $\ll 1, 1$ and 10^6 . Explain the order of ethanolysis.

5. (a) Complete the following statements :

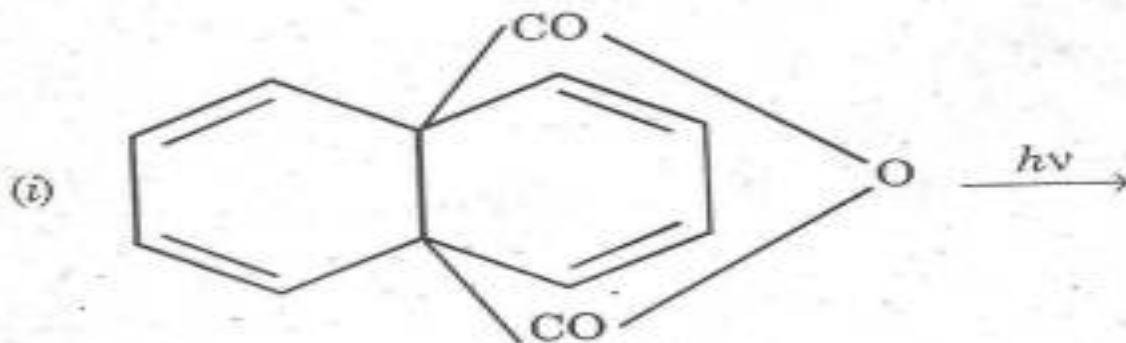
- (i) The boiling point of enol form of ethyl acetoacetate is than keto form of ethyl acetoacetate.
- (ii) The least aromatic compound amongst pyrrole, furan and thiophene is
- (iii) The two electrons in a singlet carbene have spin.
- (iv) The addition of HCN to a ketone is an example of
- (v) Nitration of benzene and hexadeuterobenzene proceeds at rates.
- (vi) Claisen rearrangement can also be classified as

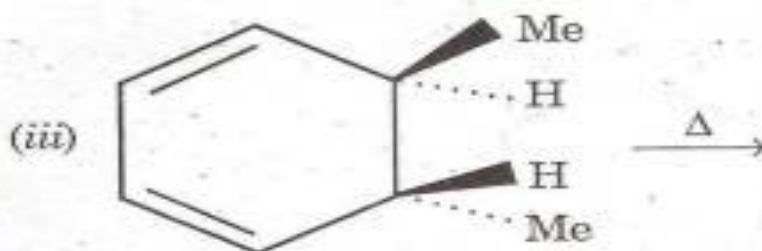
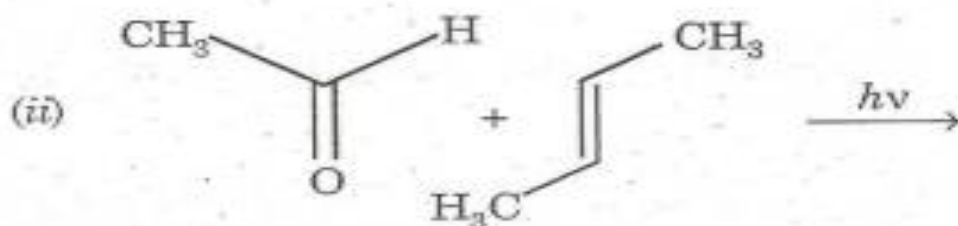
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- (b) Explain kinetic Vs. thermodynamic control for generation of enolates using 2-methyl cyclohexanone as an example. Which conditions favour thermodynamic control ?
- (c) Explain what is combinatorial chemistry ? What are its advantages and its applications ?
- (d) Outline mechanism for the following reaction :



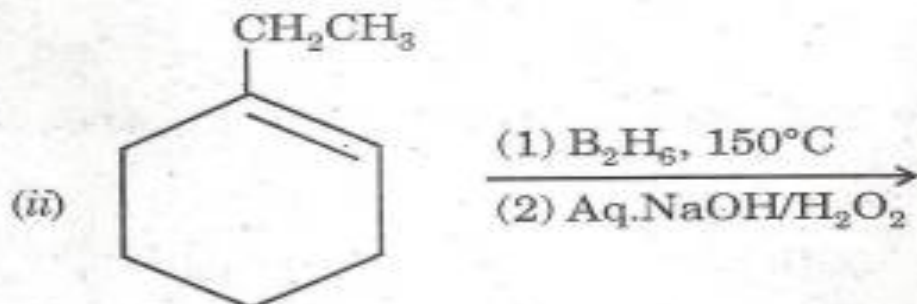
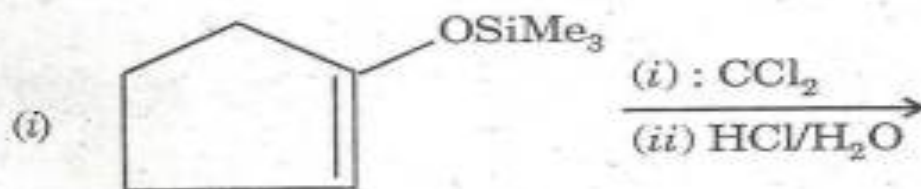
- (e) Write the product and classify the reaction :

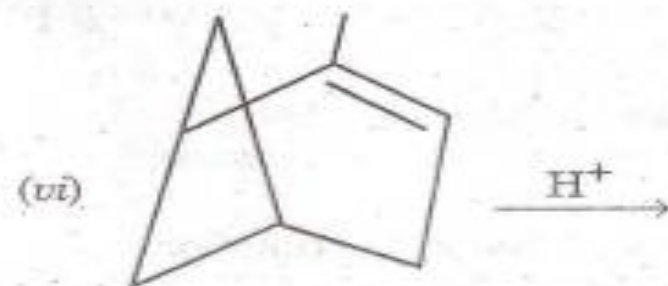
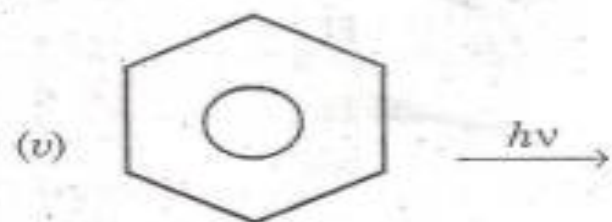
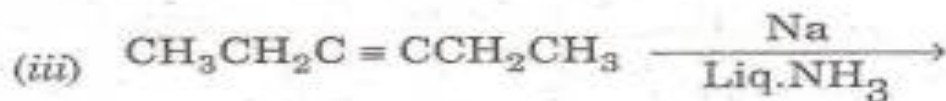




6. (a) Explain Franck-Condon principle and its applications in photochemistry.

(b) Complete the following reactions :



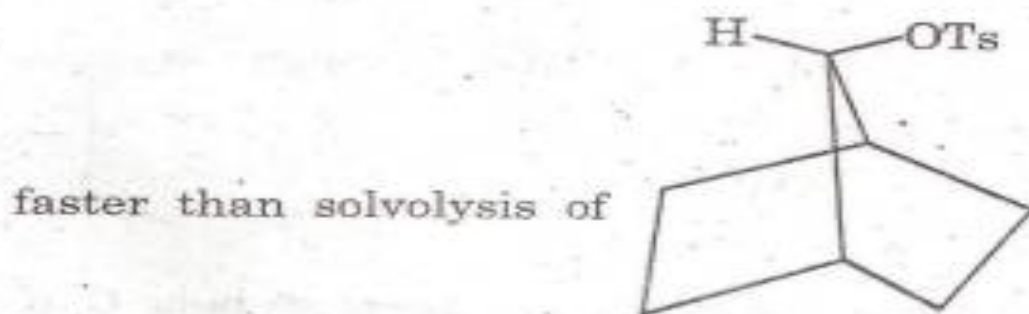
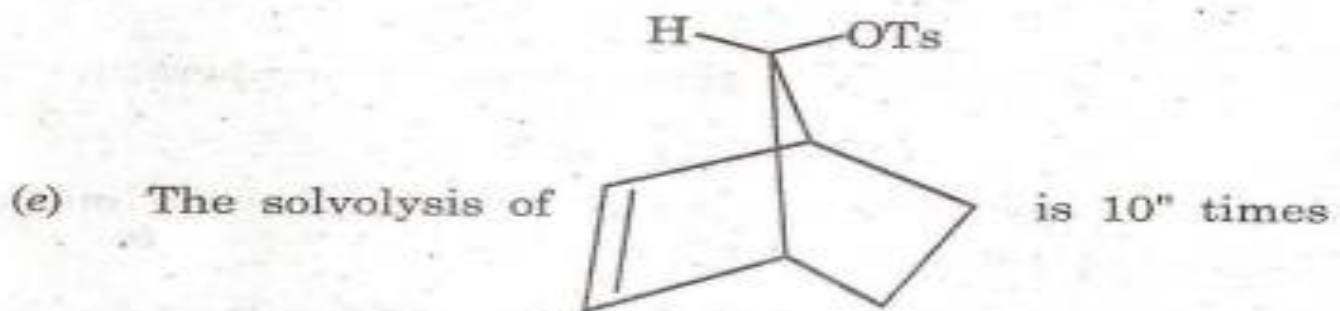


- (c) Explain the role of BuN^+X^- as phase transfer catalyst in the reaction :



Outline the mechanism of phase transfer catalysis and its advantages.

- (d) What are conducting polymers ? Explain with a suitable example. What are different applications of conducting polymers ?

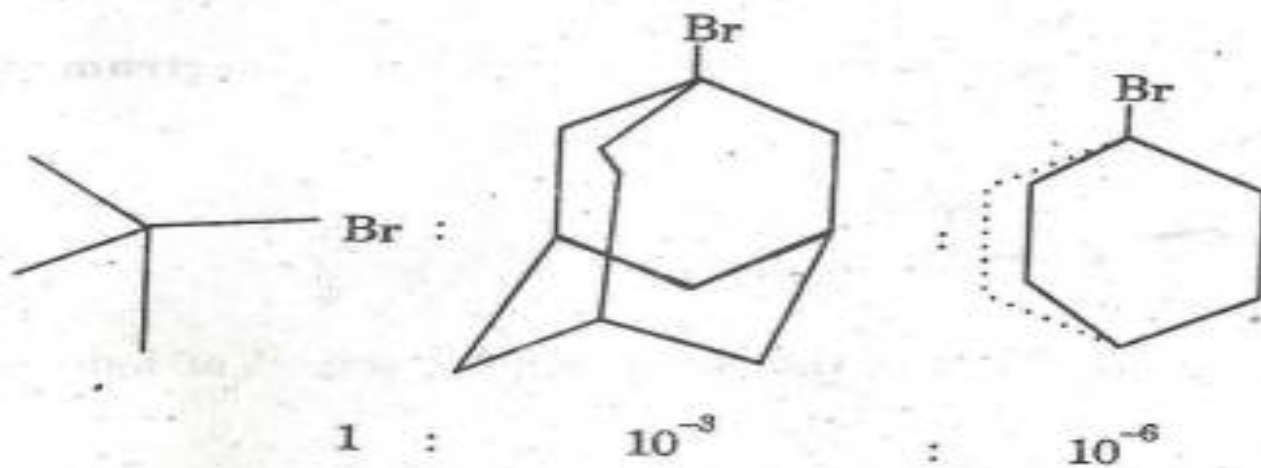


Give the mechanism and justify your answer.

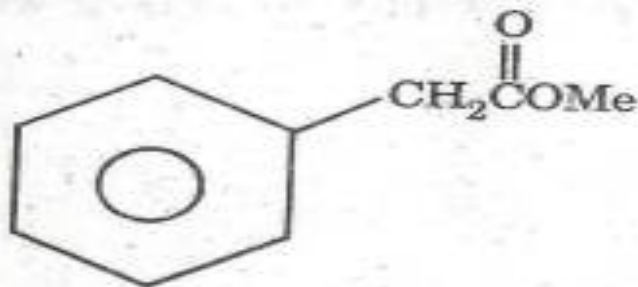
What is the phenomenon called ?

7. (a) Complete the following as directed :
- (i) Give the structure of polymer used in Bullet proof vests.
 - (ii) Give structure of a biodegradable polymer.
 - (iii) What is glass transition temperature ?
 - (iv) Polystyrene has a number average molecular weight of 1,00,000 and a polydispersity of 5. What is its weight average molecular weight ?
 - (v) Among *cis*- and *trans*-stilbene ($\text{PhCH}=\text{CHPh}$), which one has a higher λ_{max} and higher ϵ ?
 - (vi) What is nitrogen rule in mass spectroscopy ?

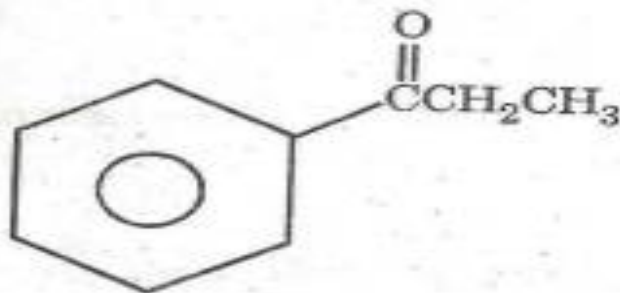
(b) Explain the relative reactivities of :



(c) (i) How can you distinguish between



and



by IR spectroscopy ?

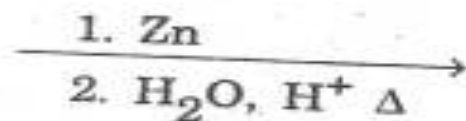
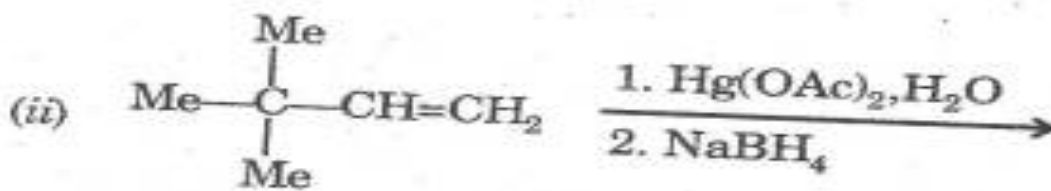
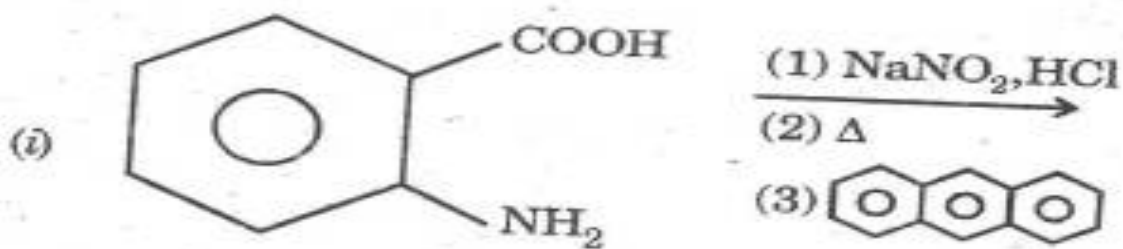
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- (ii) Give the structure of ion responsible for $m/z = 99$ peak in the mass spectrum of 2-heptanone.
- (iii) What is the wave number (cm^{-1}) of light of 2.5 micron wavelength ?
- (d) Explain catenanes and rotaxanes with suitable examples.
- (e) (i) Give *one* example of S_Ni reaction.
- (ii) Give *one* example of sharpless epoxidation.
- (iii) Give *one* example each of polymer supported reagent and polymer supported catalyst.

8. (a) Why does an aprotic solvent favour O-alkylation while a protic solvent favours C-alkylation of ethyl acetoacetate ? Write the reaction also.

(b) Identify a compound with molecular formula $C_4H_{10}O_2$ which shows two singlets with an area ratio of 2 : 3. Predict their δ value.

(c) Complete the following reactions :



P.T.O.

(d) Describe the stability of singlet and triplet carbenes. Write the products of singlet and triplet carbene ($:\text{CH}_2$) with *cis*- and *trans*-2-butene.

(e) (i) Give an example of ambident nucleophile and its reactions.

(ii) Calculate how much faster *p*-bromobenzyl chloride will solvolyze in water than *p*-nitrobenzyl chloride.

$$\sigma_{p\text{-Br}} = 0.2, \sigma_{p\text{-NO}_2} = 0.78 \text{ and}$$

$$\rho_{\text{Cl}} = -1.31.$$