C.S.E. (MAIN)

CHEMISTRY - 2005

PAPER - I

Time Allowed : Three Hours *Maximum Marks : 300*

Candidates should attempt Questions 1 *and* 5 *which are compulsory, and any* THREE *of the remaining questions selecting at least* ONE *question from each Section.*

Assume suitable data if considered necessary and indicate the same clearly.

SECTION-A

1. Answer any *three* of the following : 20 × 3 = 60

(a) What do you understand by orthogonal wave function ?

Normalise the wave function, $\psi_n(x) = A \sin \frac{n\pi x}{a}$ for a particle in a one-dimensional box of size 'a'.

(b) Explain why CO_2 has a linear structure whereas SO_2 is a bent molecule.

(c) Mention the temperature and pressure at which water has a triple point where it can exist as solid ice, liquid and vapour. Apply phase rule to this triple point.

(d) Half life of a first order may be determined from its rate constant. If rate constant of a first order reaction is 4.5×10^{-5} min^{-1} then calculate its half life.

2. (a) Explain following :

(i) Ion selective electrodes
(ii) Quantum yield
(iii) Nernst heat theorem
(iv) Fuel cells
(v) Langmuir isotherm 30

(b) Benzaldehyde undergoes transfromation in presence of CN^- as :

$$2C_6H_5CHO\,(aq) \xrightarrow{CN^-} C_6C_5CH(OH)COC_6H_5(aq)$$

where following kinetic data were obtained :

Initial concn. (mol dm^{-3})		Initial reaction rate (mol $dm^{-3} s^{-1}$)
C_6H_5CHO (aq)	CN^-(aq)	
0·50	0·50	$1·00 \times 10^{-4}$
1·00	0·50	$4·01 \times 10^{-4}$
1·00	1·00	$7·96 \times 10^{-4}$

Calculate overall order of reaction and its rate constant. 20

(c) Prove that entropy is a state function. 10

3. (a) Justify that s-orbitals are non-directional whereas p- and d-orbitals have directional character. Derive wave functions of sp^3 hybridized orbitals. 20

(b) What are seven crystal systems and 14 Bravais lattices ? Discuss the structures of CsCl and ZnS. 20

(c) What are the factors that decide the percent ionic character in polar compounds ? 20

4. (a) Explain crystal fields stabilization energy (CFSE). What are the various factors which affect its magnitude ? Calculate CFSE and magneitc moments (μ_{eff}) in cases of $FeCl_3 . 6H_2O$ and $K_4Fe(CN)_6$. 25

(b) Derive Clausius-Clapeyron equation for the variation of vapour pressure with temperature. Calculate the equilibrium pressure for the conversion of graphite to diamond at 25°C assuming their densities to be 2·25 and 3·51 g cm^{-3} and ΔG° = 2900 J mol^{-1}. 25

(c) Explain the role of metal ions in biological systems and their role in ion transport across the cell membrane. 10

SECTION-B

5. Answer any *three* of the following : 20 × 3 = 60

(a) Define Frenkel and Schottky defects in a crystal with a suitable example for each.

(b) Explain the intense blue colour of aqueous permanganate solution. What happens to it when the solution is left in sunlight for a day ?

(c) Heme acts as carrier of O_2 in the system whereas toxic effects of CO can be explained by replacement reaction. Explain.

(d) Draw the nature of a typical polarogram and explain diffusion current, limiting current and residual current. Show that $E_{1/2}$ is independent of concentration.

6. (a) Name all the lanthanides and show how its common oxidation state is +3 though some of these exhibit other oxidation states as well. Explain why ionic radii decreases from La^{3+} to Lu^{3+} even though atomic number increases by 14. 30

(b) Explain the nature of metal-carbonyl bond in carbonyls. Draw the structures of $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Mn_2(CO)_{10}$ and $Ni(CO)_4$. In what respects terminal CO group is different than bridging CO in such complexes? 20

(c) Discuss the role of photosynthesis in ferrodoxin molecule and describe its structural features. 10

7. (a) What are metallocenes and their characteristic structural features? Discuss the structure of ferrocene with MO diagram. 20

(b) Explain 'trans effect' and dicuss its theories. Describe substitution in square planar complexes with sutiable examples. 20

(c) Describe the construction and functioning of lithium batteries and its advantages over conventional batteries. 20

8. (a) Define molecular partition function and explain its importance. Show that heat capacity of an ideal gas is $\frac{3}{2}R$. 20

(b) Derive an expression for the entropy of mixing of two ideal gases at the same temperature and pressure. 20

(c) Explain homogenous and heterogeneous catalysis with a suitable example for each. Derive and expression for the rate of a surface catalyzed reaction. 20

C.S.E. Chemistry (MAIN) - 2005

PAPER - II - 2005

Time Allowed : Three Hours *Maximum Marks : 300*

Candidates should attempt Questions 1 *and* 5 *which are compulsory, and any* THREE *of the remaining questions selecting at least* ONE *question from each Section.*

The number of marks carried by each question is indic ated at the end of the question.

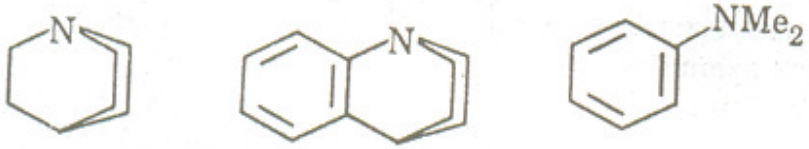
All questions carry equal marks.

SECTION-A

1. Answer any *three* of the following : 20×3=60

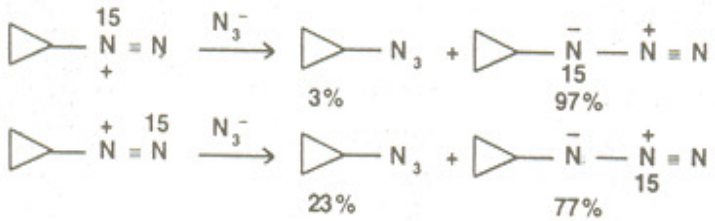
(a) The stereochemistry of nucleophilic substitution by the $S_{RN}1$ mechanism is almost always racemization. However the stereochemistry of substitution of A by thiophenoxide ion is dependent upon the concentration of nucleophile. When it is low, the product is almost racemic but when it is high, the product is of retained stereochemistry. Explain.

(b) Explain the mentioned pKa of the following compounds :



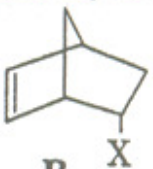
(i) pKa 10·58 (ii) 7·79 (iii) 5·06

(c) Explain the following observations with respect ot yields of products :

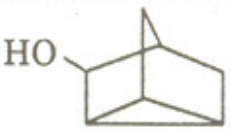


(d) Halide **A** solvolyzes ten times faster than halide **B**. Both give **C** as the product of solvolysis in aqueous ethanol. Explain.

A

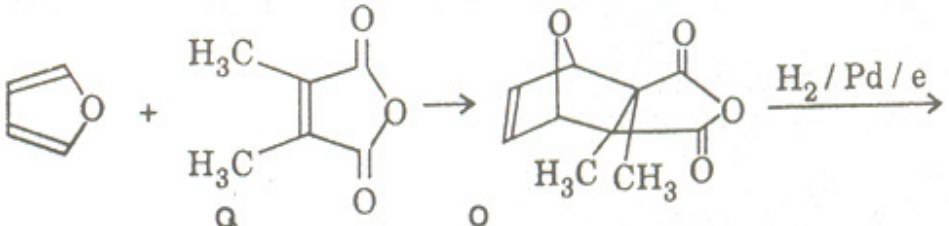


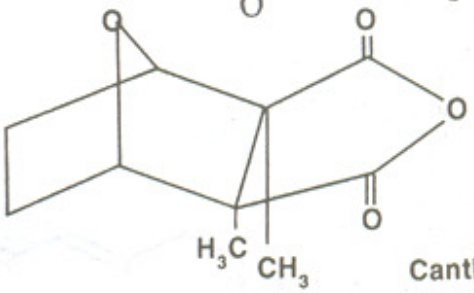
B



C

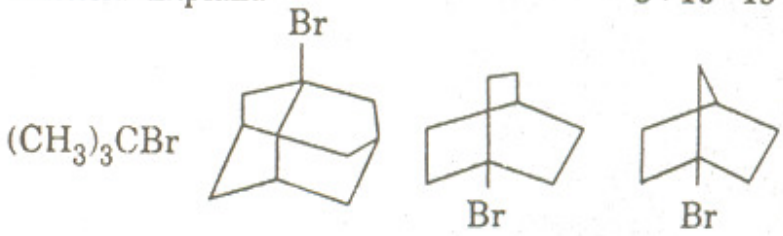
2. (a) (i) Explain why the following 4 + 2 cycloaddition reaction does not occur to produce cantharidin isolated from dried beetles (*Cantharis vesicatoria*)





Cantharidin

(ii) The order of reactivity of the following to solvolysis in 80% ethanol decreases in the same as they are written. Explain. **5+10=15**



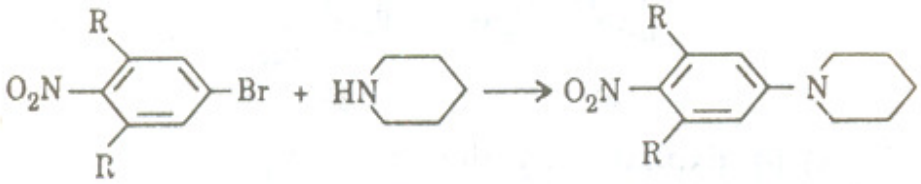
(i) (ii) (iii) (iv)

(b) Explain the following observations : **5×3=15**

(i) Methyl vinyl ketone reacts more rapidly with cyclopentadiene than with 1, 3-butadiene in the cycloaddition reaction.

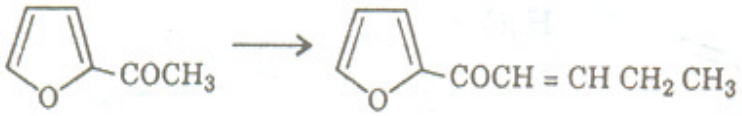
(ii) Bromine reacts about 165 times faster with PhCH = CHPh than with PhCH = CHBr.

(iii) The following reaction proceeds 35 times less rapidly when R = CH_3 than when R = H :

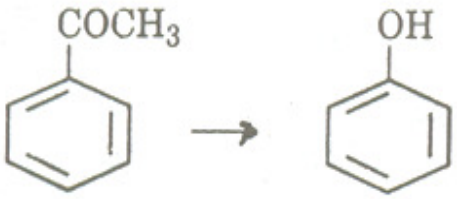


(c) Indicate the steps by means of which you will effect the following conversions in good yields : 20

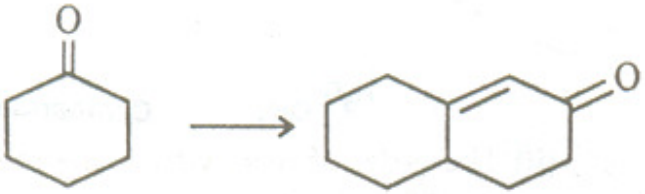
(i)



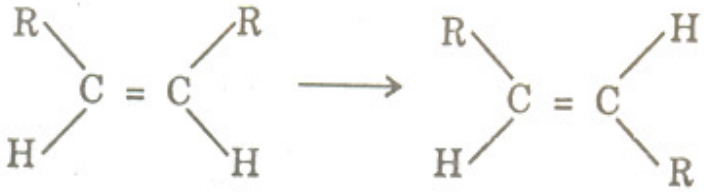
(ii)



(iii)



(iv)

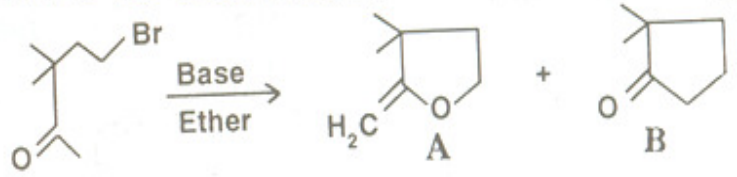


The only reagents available are m-chloroperbenzonic acid and triphenyl phosphine.

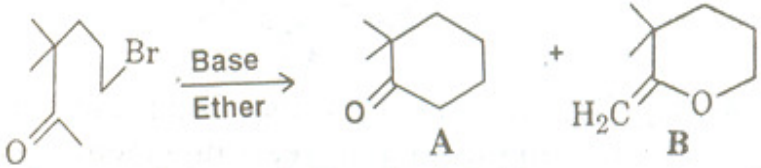
(d) Benzaldehyde on reaction with alcoholic $CN^{\ominus}$ gives benzoin but acetaldehyde under the same conditions does not give acetion. Why ? If you were to get acetoin, how will you proceed to synthesize it ? 10

3. (a) In the following reactions (i) and (ii), the major product of the reaction is **A** with very little amount of **B**. Rationalize the observations : 15

(i)

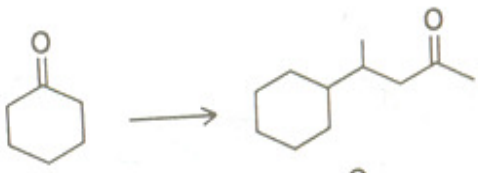


(ii)

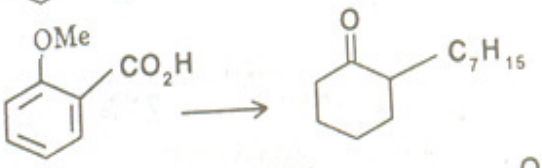


(b) Give steps and reagents involved in the conversion of compounds written on the left hand side of the arrow to compounds written on the right hand side of the arrow : 20

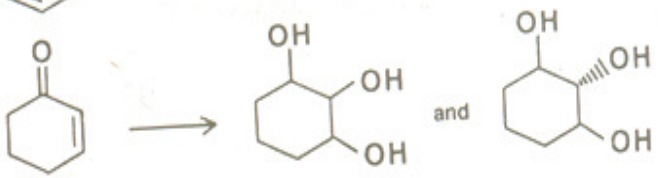
(i)



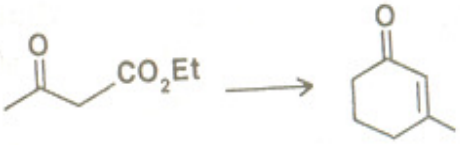
(ii)



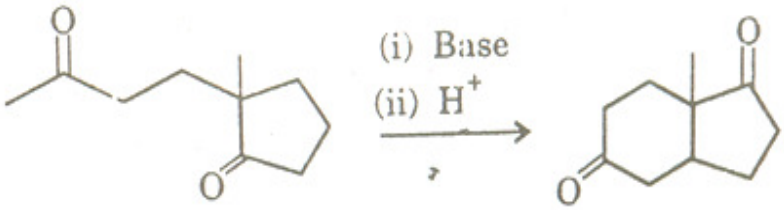
(iii)



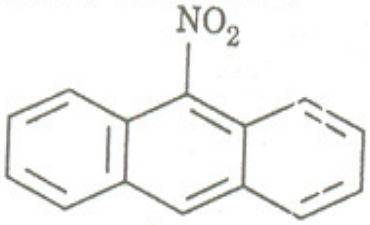
(iv)



(c) Comment on the selectivity shown in the following reaction : 15



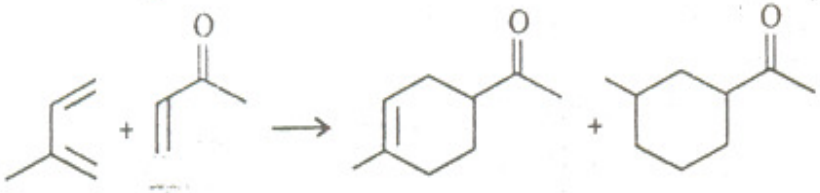
(d) On heating A in toluene in the presence of SbF_5 and HF, one gets over 95% yields of p-nitro toluene. Explain the mechanism of the reaction. **10**



A

4. (a) How will you prove that Beckmann rearrangement is an intermolecular rearrangement? Take suitable examples to illustrate your answer. **10**

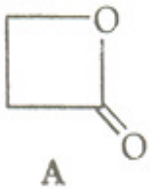
(b) Give the mechanism of the reaction that explains the following observations :



(i) Heat in a sealed tube at 120°C	71%	29%
(ii) Keep in contact with $SnCl_4 . 5H_2O$ at 0°C	93%	7%

Explain your answer. **15**

(c) Explain why A reacts with sodium ethoxide to give B, but with sodium acetate and sodium phenoxide, it gives C and D respectively. **10**



A

$\bar{O}CH_2CH_2CO_2C_2H_5$

B

$CH_3COOCH_2CH_2CO_2^-$

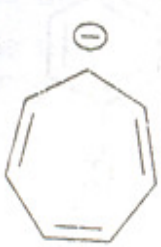
C

$PhOCH_2CH_2CO_2^-$

D

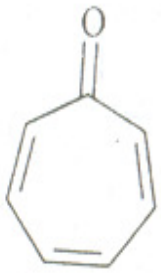
(d) (i) How do you explain the concepts of aromaticity, anti-aromaticity and homo-aromaticity ?

(ii) Which of the following compounds are aromatic and why ? 10 + 15 = 25

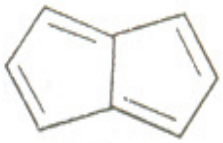


A

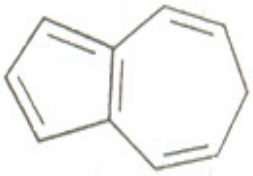
B



C



D



E

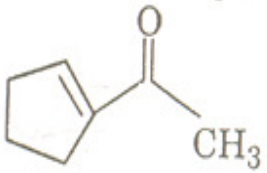
SECTION-B

5. Answer any *three* of the following : 20 × 3 = 60

(a) Normal O - H stretch comes at about 3600 cm^{-1}. What is the reduced mass for O - H ? What happens to the reduced mass when atomic mass of each atom is doubled in turn; i.e., when O - H is converted to O - D and S - H ? In fact both O - D and S - H stretch come at about 2500 cm^{-1}. Why ?

(b) Indicate how IR spectrum can be used to distinguish :

(i)



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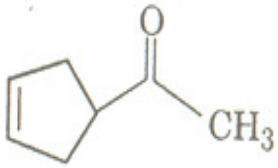
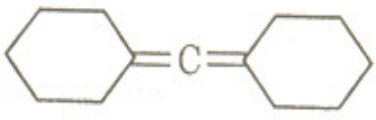


(ii)



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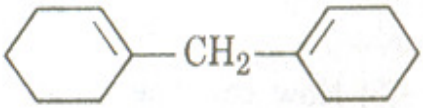
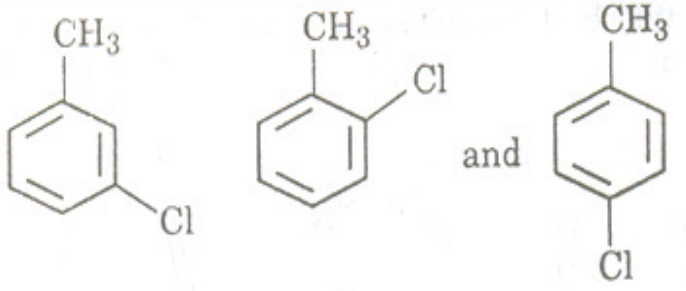
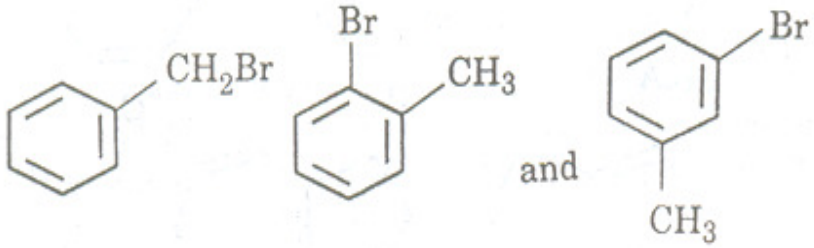
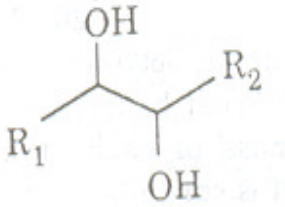


(c) Indicate how NMR can be used to distinguish

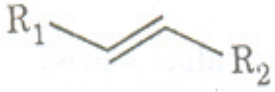
(i) 

(ii) 

(d) Syn diol A can be converted to trans olefin B in good yields. Write all the steps involved in such a conversion. Give reasons for your choice of method or the reagents.

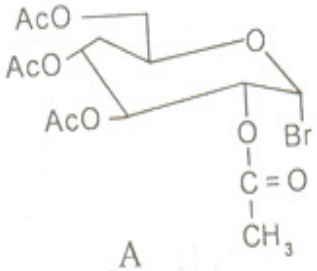


A

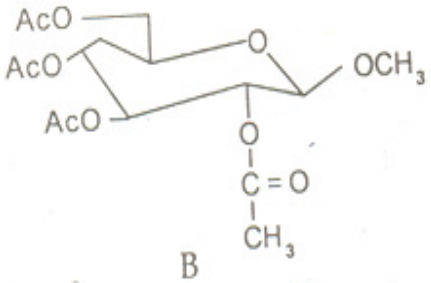


B

6. (a) Explain how can A be converted to B on treatment with silver perchlorate in methanol.



A



B

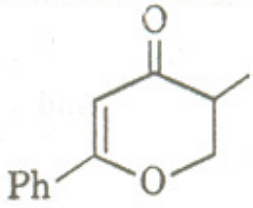
(b) How can one identify from the inspection of mass spectrum of the compound that it contains 20

(i) one nitrogen atom (ii) one chlorine atoms

(iii) two chlorine atoms (iv) one bromine atom

(c) Outline the synthesis of 100% cis-poly(isoprene). Discuss reasons for the choice of reagents or catalysts and the mechanism of polymerization. 20

7. (a) The natural product bullatenone was isolated in the 1950s and assigned the structure A. When compound A was synthesized, it was not identical with the natural sample. Predict the expected ^{1}H NMR spectrum of A. Given the full spectroscopic data available nowadays, but not in 1950s, say why A was wrong and suggest a better structure for bullatenone.



A

Alleged bullatenone

Spectra of bullatenone :

Mass spectrum : m/z 188 (10%),
Mol. formula : ($C_{12}H_{22}O_2$),
105 (20%), 102 (100%), 77 (20%)

IR spectrum : 1604 and 1705 cm^{-1}

^{1}H NMR spectrum : 1·45(6H, s), 5·82(1H, s)
7·35(3H, m), 7·68(2H, m)

(b) (i) Sketch the high resolution H NMR spectrum of ethyl acetoacetate.

(ii) Indicate main stretch frequencies for functional groups present in acetyl acetone. What would happen to the spectrum if a small amount of organic base is added to it ? 10 × 2 = 20

(c) Illustrate Woodward-Fieser Rules to calculate the expected λ_{max} of enones in the uv-spectrum. 10

8. (a) Give the steps involved in the synthesis of the following

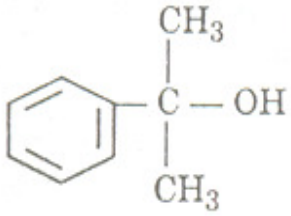
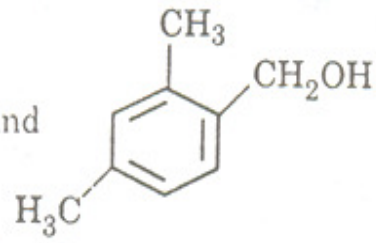
compounds from indicated materials : 15

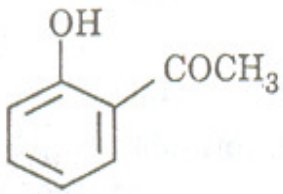
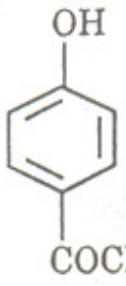
(i) Phenolphthalein form phenol, phthalic anhydride and sulphuric acid.

(ii) α-methyl cinnamic acid from benzaldehyde, base and propanoic anhydride.

(b) Using chemical and/or spectral methods (as indicated), show how the following can be differentiated : 15

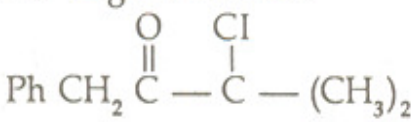
(i) $HC \equiv CCH_2CH_2OH$ and $CH_3C \equiv CCH_2OH$
(Chemical methods only)

(ii)  and 
(Chemical and spectral methods)

(iii)  and 
(Spectral methods only)

(c) Illustrate different types of pericyclic reactions by taking at least one example for each type. Explain why some of these reactions are also occasionally referred to as 'no reagent' reactions. 15

(d) There are two possible products from Favorskii rearrangement that occur. when A reacts with sodium methoxide. What are the products and which will be formed in larger amount ? 15



A

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