

Sl. No.

741

D-VSF-L-PUB

CHEMISTRY

Paper II

Time Allowed : Three Hours

Maximum Marks : 200

INSTRUCTIONS

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

All questions carry equal marks.

Marks for each part/subpart of a question are indicated against each.

*Answers must be written in **ENGLISH** only.*

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

Unless otherwise indicated, symbols and notations have their usual meanings.

(Contd.)

Section 'A'

1. Attempt any *four* of the following : $4 \times 10 = 40$

(a) (i) Which one of the following chemical species is aromatic? Justify with reasoning.

1. Cycloheptatrienyl radical

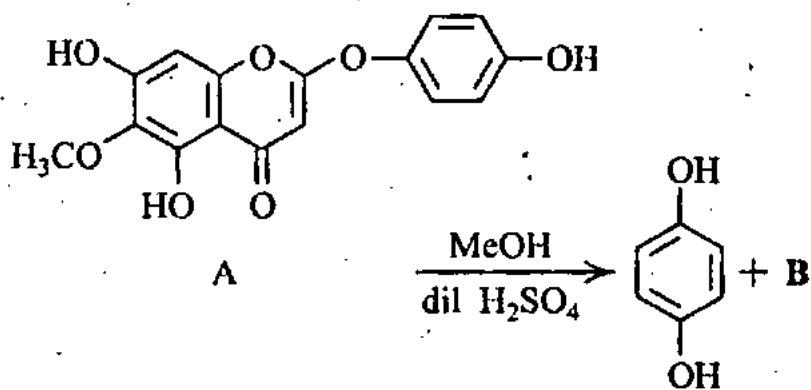
2. Cycloheptatrienyl cation

3. Cycloheptatrienyl anion and

4. Cyclopentadienyl radical 5

(ii) What are nitrenes? How is nitrene generated by thermal decomposition of acyl azide? 5

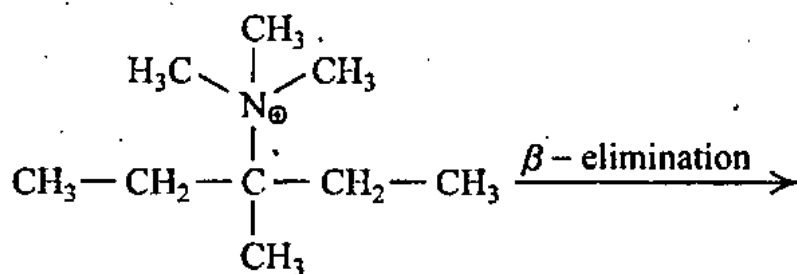
(b) (i) Identify B in the following reaction and explain the result by mechanism.



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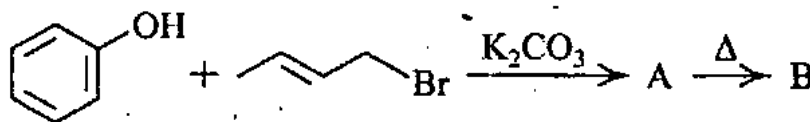
(ii) The reaction of *t*-butyl bromide is faster through $S_N1/E1$ pathway in the presence of Ag^+ ion. Explain the reason. 5

(c) (i) Identify the major product in the following reaction. Justify its regioselectivity.



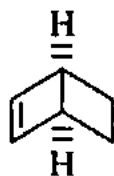
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(ii) Give structure of A and B in the following sequence and offer mechanistic explanation for conversion of A to B.



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- (d) (i) Which one of the two cyclobutenes A and B undergoes ring opening under thermal conditions under concerted process? Explain while writing structure of the products.



A

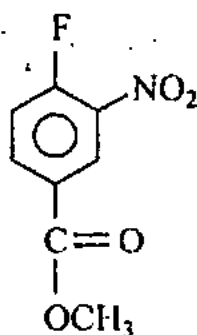


B

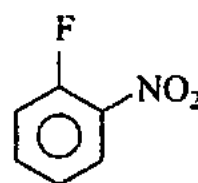
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- (ii) Which of the compound in each set given below reacts more readily in nucleophilic aromatic substitution with $\text{CH}_3\text{O}^-\text{Na}^+$ in CH_3OH ? Explain your answer.

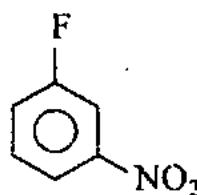
1.



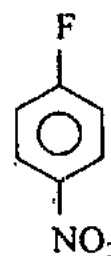
or



2.



or



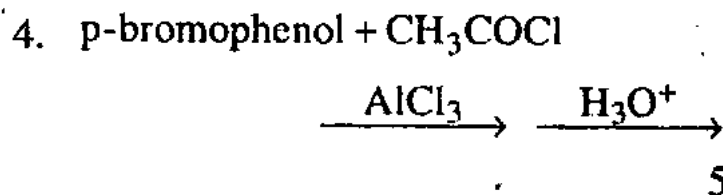
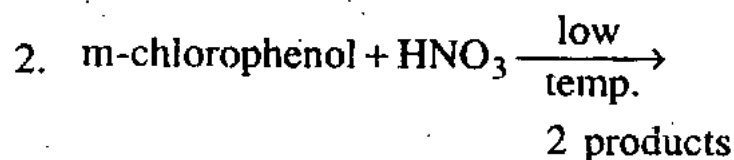
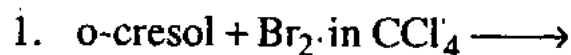
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- (e) (i) The elevation in boiling point of a 2% aqueous solution of a polymer is 0.0021 K. Calculate the molecular weight of the polymer.

Given: The molal elevation in boiling point of water is $K_b = 0.52 \text{ k/m}$.

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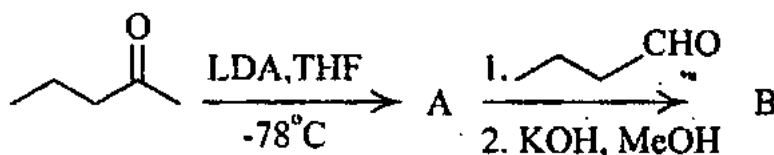
- (ii) Write the major product formed in each of the following reactions.



2. (a) How do pyrrole aromaticity established based on the basis of orbital theory? 10

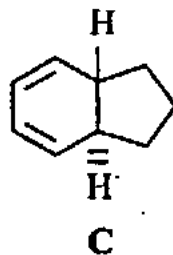
- (b) Identify the addition products from the reaction of 1,3-butadiene with HCl at 0°C and at 30°C. Explain which one of them is kinetic and thermodynamic. 10

- (c) Write the structure of A and B in the following synthetic scheme. Discuss regiochemistry of A



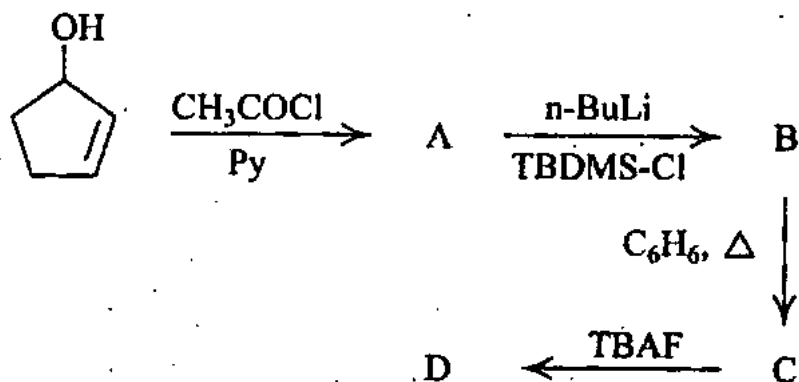
LDA = Lithium diisopropylamide. 10

- (d) An organic compound A of MF : $\text{C}_6\text{H}_{12}\text{O}$ forms 2,4-DNP derivative. It does not reduce Tollen's reagent but undergoes iodoform reaction. Its mass spectrum has m/z 43 (base peak), 72, 100 (Molecular ion peak, M^+). Deduce its structure. 10
3. (a) A hydrocarbon A of MF : C_9H_{12} absorbs two moles of hydrogen. On photolysis in methanol at -20°C A isomerises to B. B absorbs three moles of hydrogen to form cyclononane. In its UV spectrum B exhibits λ_{max} at 290 nm. On warming to 30°C B isomerises to C whose structure is given below. Write structure of A and B and explain each step.



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- (b) Write the structure of A–D in the following synthetic sequence and explain the conversion of B to C with appropriate mechanism.



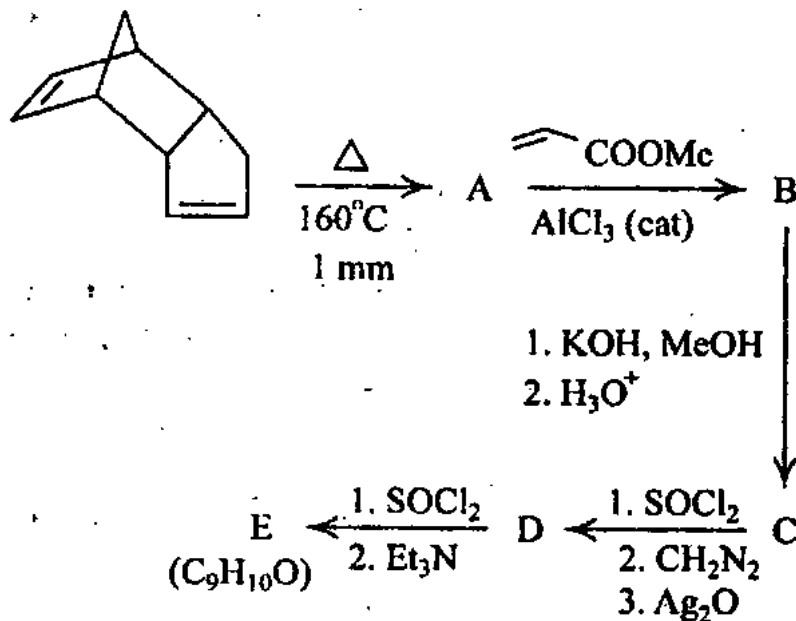
TBDMS-Cl = *t*-Butyl dimethylsilyl chloride

TBAF = tetra-*n*-butylammonium fluoride

Py = Pyridine

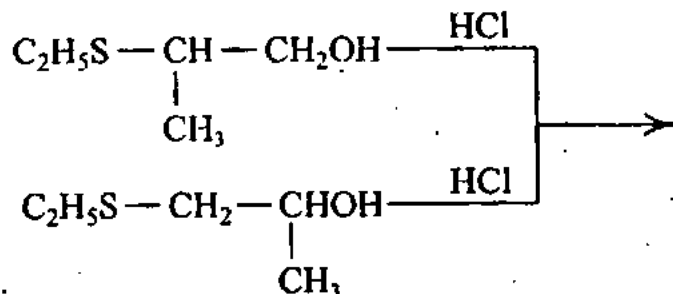
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- (c) Write the structures for A–E in the following synthetic sequence and explain.



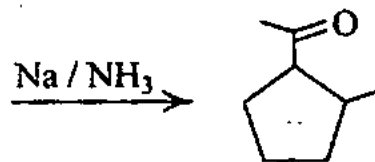
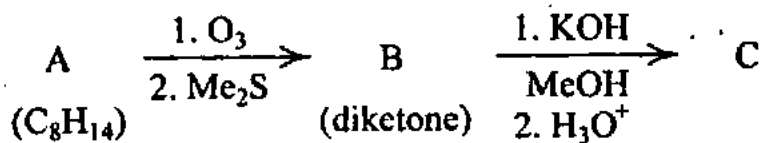
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- (d) Why the following two alcohols each react with HCl to give the same alkyl halide ?



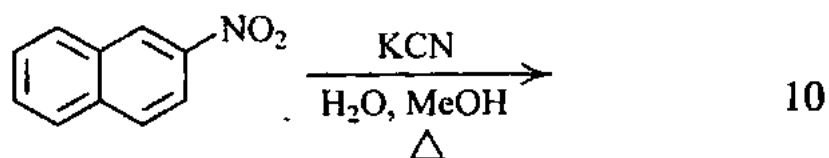
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4. (a) A mixture of 3-Methoxyaniline, methyl vinyl ketone were heated in nitrobenzene in presence of H_2SO_4 (cat), $\text{Fe}(\text{II})\text{SO}_4$ (cat). Write the structure of the major product and offer mechanistic explanation. Indicate the name reaction. 10
- (b) Write structures for A, B and C in the following synthetic sequence and give mechanism for conversion of B to C.

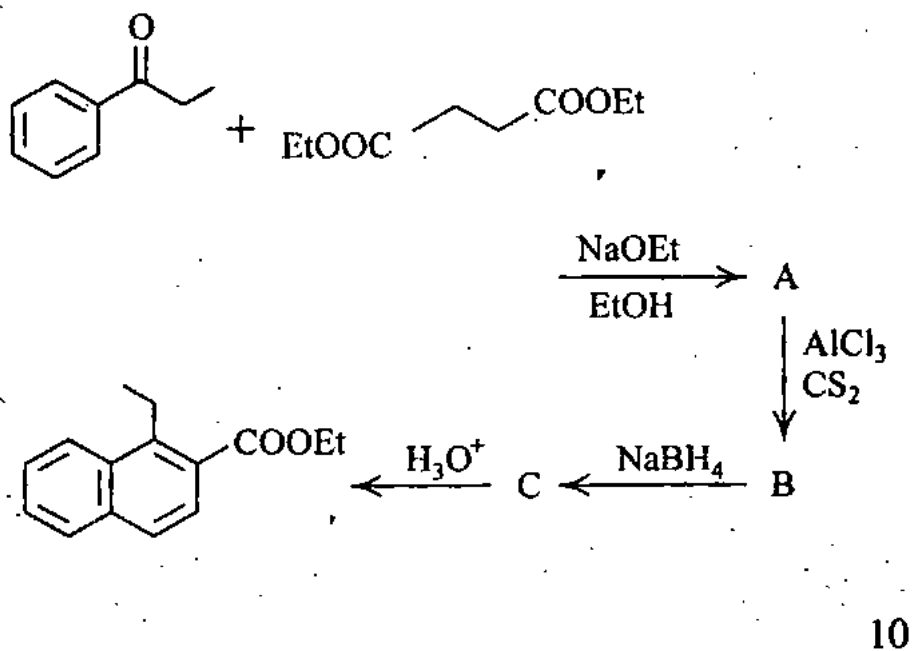


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- (c) Write the structure of the product formed in the following reaction and give mechanism.



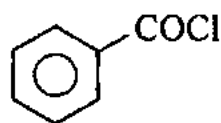
- (d) Identify synthetic intermediates A–C and give mechanism for formation of A.



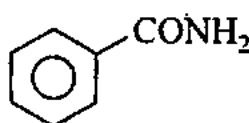
Section 'B'

5. Attempt any *four* of the following : $4 \times 10 = 40$

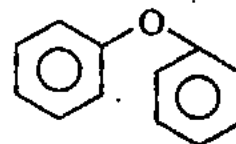
- (a) (i) Starting from benzene and ethylene enumerate industrial synthesis of polystyrene. 5
- (ii) What are silicones? Give the method for their synthesis from chlorosilanes. 5
- (b) (i) Explain the salient features of the structure of zeolites useful for water softening. 5
- (ii) Distinguish the following compounds by IR spectroscopy.



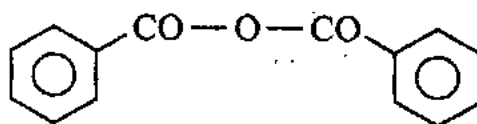
A



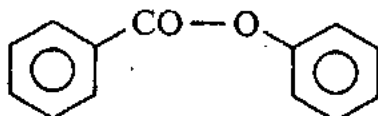
B



C



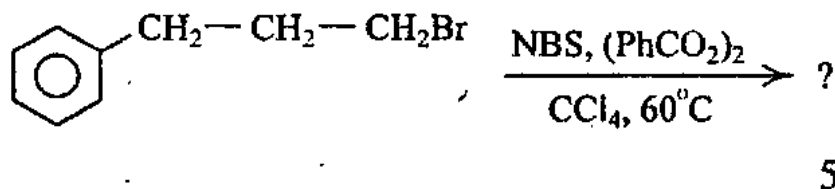
D



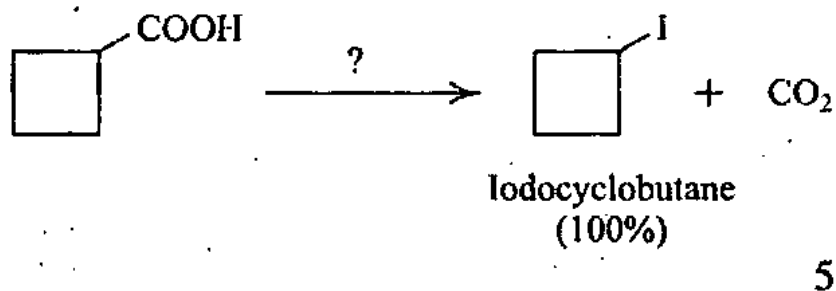
E

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- (c) (i) Write the products of the following reaction. Propose a suitable mechanism to account for the product.



- (ii) What are the reagents used to effect the following reaction to proceed to completion? What is the name of this reaction?



- (d) (i) Two isomeric ketones A and B MF : $\text{C}_6\text{H}_{10}\text{O}$ show following spectral data :

A : UV : λ_{max} 220, 311 nm.

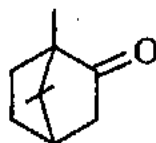
^1H NMR : a doublet for 1H at δ 6.4 ppm. $J = 15$ Hz

B : UV : λ_{max} 236, 314 nm.

^1H NMR : a singlet for 1H at 6.4 ppm.

Work out structures for A and B. 5

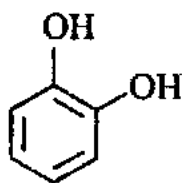
- (ii) When *n*-heptane solution of camphor was irradiated with UV light it isomerizes to an aldehyde. Write its structure and give mechanism.



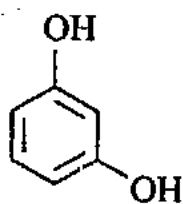
Camphor

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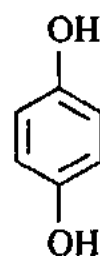
- (e) (i) Explain how to differentiate between dihydroxy benzenes A-C by ^1H decoupled ^{13}C NMR spectroscopy.



A



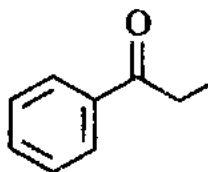
B



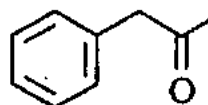
C

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- (ii) Differentiate following ketones by mass spectrometry.



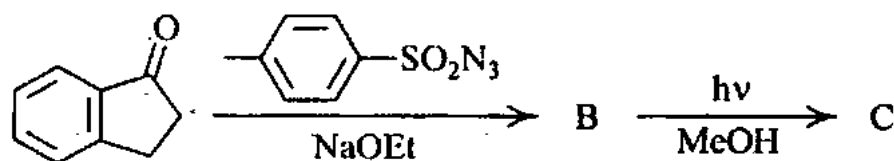
A



B

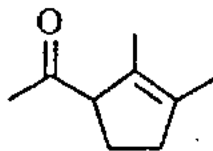
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6. (a) Explain why Grignard reagent, MeMgI, does not add to 1,3-cyclohexane dione but it adds to cyclohexanone. 10
- (b) Write the structure of the monomer of natural rubber. Explain why it is elastic. How to reduce its elastic property by chemical processes? 10
- (c) Why does bromination of cyclohexene with NBS in CCl₄ occur exclusively at allylic position rather than at one of the other positions? 10
- (d) How to determine the weight average molecular weight of PVC by light scattering technique? 10
7. (a) Write the structure of the intermediate B and final product C in the following sequence. C shows strong IR band at 1740 cm⁻¹, ¹H NMR spectral signal at 3.8 ppm and ¹³C NMR spectral signal at 170 ppm. Assign the spectral data for C.



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- (b) Direct photolysis of ketone A leads to its isomer B whereas photolysis in presence of sensitizer leads to another isomer C. Identify B and C and explain with mechanism.



A

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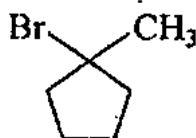
- (c) Photolysis of dimethyl acetylenedicarboxylate in benzene provides dimethyl 1,3,5,7-cyclo-octatetraenedicarboxylate. Explain the result by identifying the intermediate. 10
- (d) Discuss the nature of bonding and structures of phosphonitric halides. 10
8. (a) Deduce the structures of compounds A and B based on the following data :

A (MF : $C_7H_7NO_3$) exhibits strong IR bands at 1530 and 1350 cm^{-1} . A can be reduced to B (MF : $C_7H_9NO_3$) by reaction with Sn/HCl (aq). B exhibits following signals in its ^1H NMR spectrum.

δ 6.4 (d, $J = 8\text{ Hz}$, 2H), 6.3 (d, $J = 8\text{ Hz}$, 2H), 3.5 (s, 3H), 3.2 (br s, 2H).

The signal at 3.2 disappears on shaking NMR solution with D_2O . 10

- (b) Differentiate methyl benzoate and phenyl acetate by IR and ^1H NMR spectroscopy. 10
- (c) Show the splitting of the gaseous ion degeneracy of V^{3+} , of the ground state by the crystal field, spin-orbit coupling and magnetic field. 10
- (d) (i) The compound given below can be prepared by the addition of HBr to either of two alkenes. Write the structures of the two alkenes.



- (ii) What are the products formed if the same two alkenes each react with DBr? 10
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