भारतीय वन सेवा परीक्षा 2011
Indian Forest Services Examination

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.

Section 'A'

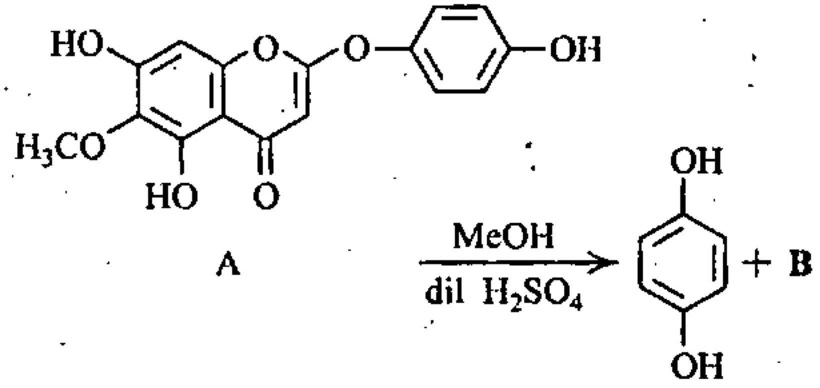
1. Attempt any *four* of the following : 4×10=40

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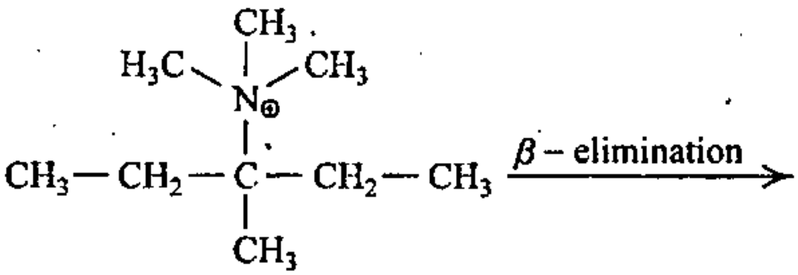
(ii) The reaction of *t*-butyl bromide is faster through $S_N1/E1$ pathway in the presence of Ag^+ ion. Explain the reason. 5

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



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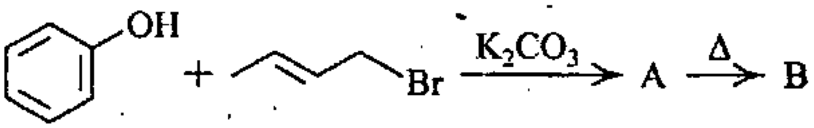
(ii) Give structure of A and B in the following sequence and offer mechanistic explanation for conversion of A to B.



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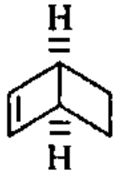
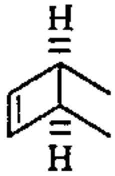
(d) (i) Which one of the two cyclobutenes A and B undergoes ring opening under thermal conditions under concerted process ? Explain while writing structure of the products.



A



B

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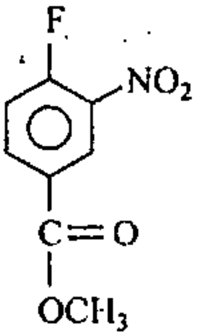
(ii) Which of the compound in each set given below reacts more readily in nucleophilic aromatic substitution with $CH_3O^-Na^+$ in CH_3OH ? Explain your answer.

1.



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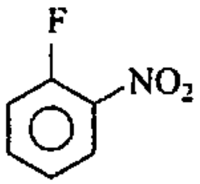
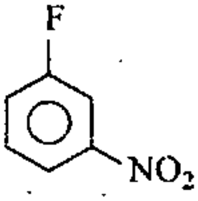


2.



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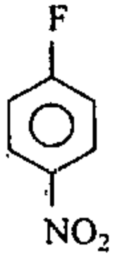

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(e) (i) The elevation in boiling point of a 2% aqueous solution of a polymer is 0·0021 K. Calculate the molecular weight of the polymer.

Given : The molal elevation in boiling point of water is $K_b = 0{\cdot}52$ k/m.

5

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

1. o-cresol + Br_2 in $CCl_4 \longrightarrow$

2. m-chlorophenol + $HNO_3 \xrightarrow[\text{temp.}]{\text{low}}$ 2 products

3. p-cresol + Br_2 in $H_2O \longrightarrow$

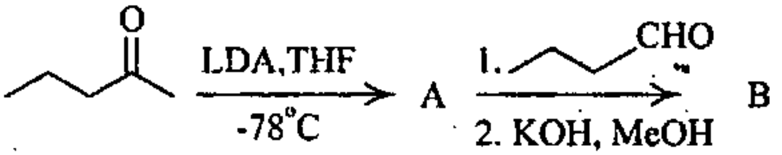
4. p-bromophenol + $CH_3COCl \xrightarrow{AlCl_3} \xrightarrow{H_3O^+}$

5

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

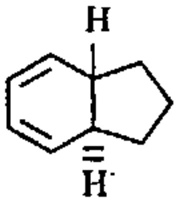
(c) Write the structure of A and B in the following synthetic scheme. Discuss regiochemistry of **A**



LDA = Lithium diisopropylamide. 10

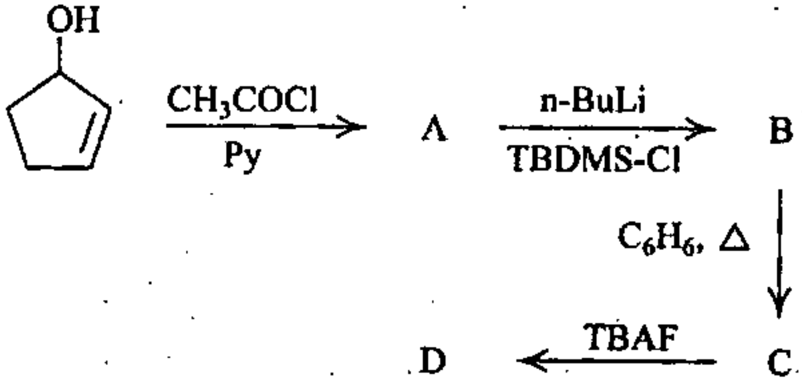
(d) An organic compound A of MF : $C_6H_{12}O$ forms 2,4-DNP derivative. It does not reduce Tollen's reagent but undergoes iodoform reaction. Its mass spectrum has m/z 43 (base peak), 72, 100 (Molecular ion peak, M^+). Deduce its structure. 10

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.



C 10

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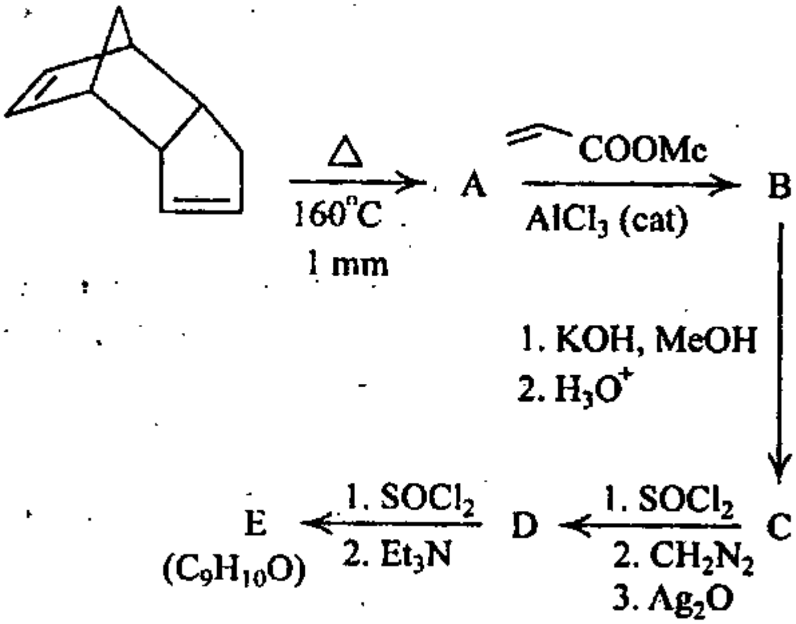
(c) Write the structures for A–E in the following synthetic sequence and explain.



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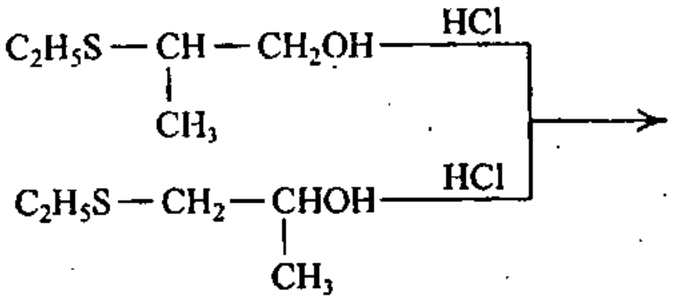
(d) Why the following two alcohols each react with HCl to give the same alkyl halide ?



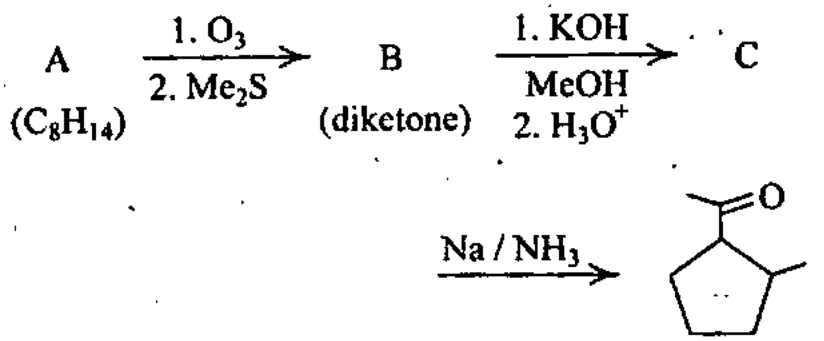
$$C_2H_5S-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH \xrightarrow{HCl}$$

$$C_2H_5S-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CHOH}} \xrightarrow{HCl}$$

10

4. (a) A mixture of 3-Methoxyaniline, methyl vinyl ketone were heated in nitrobenzene in presence of H_2SO_4 (cat), Fe(II)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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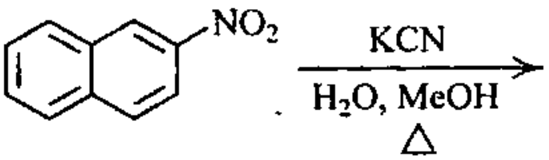
(c) Write the structure of the product formed in the following reaction and give mechanism.



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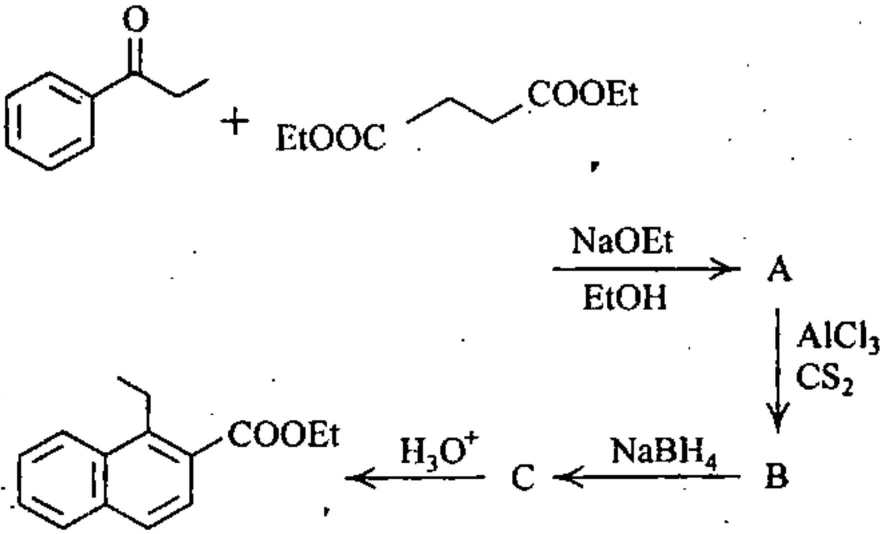
(d) Identify synthetic intermediates A–C and give mechanism for formation of A.



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Section 'B'

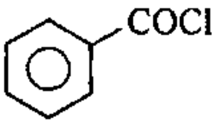
5. Attempt any *four* of the following : 4×10=40

(a) (i) Starting from benzene and ethylene enumerate industrial synthesis of polystyrene. 5

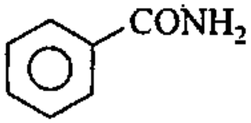
(ii) What are silicones ? Give the method for their synthesis from chlorosilanes. 5

(b) (i) Explain the salient features of the structure of zeolites useful for water softening. 5

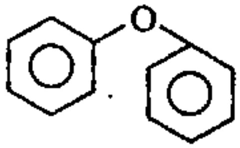
(ii) Distinguish the following compounds by IR spectroscopy.



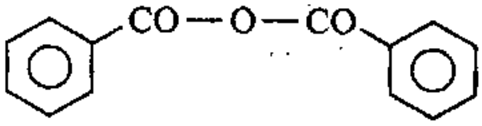
A



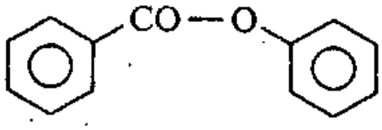
B



C



D



E

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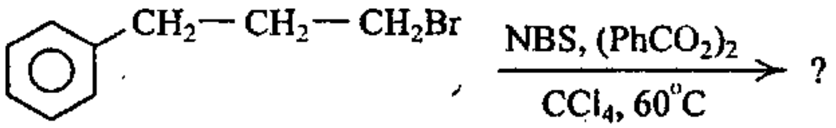
(c) (i) Write the products of the following reaction. Propose a suitable mechanism to account for the product.



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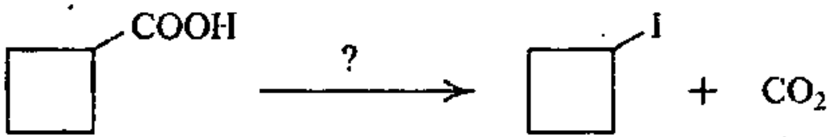
(ii) What are the reagents used to effect the following reaction to proceed to completion ? What is the name of this reaction ?



Iodocyclobutane
(100%)

5

(d) (i) Two isomeric ketones A and B MF : $C_6H_{10}O$ show following spectral data :

A : UV : λ_{max} 220, 311 nm.

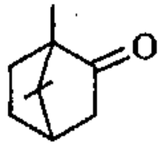
^{1}H NMR : a doublet for 1H at δ 6·4 ppm. J = 15 Hz

B : UV : λ_{max} 236, 314 nm.

^{1}H NMR : a singlet for 1H at 6·4 ppm.

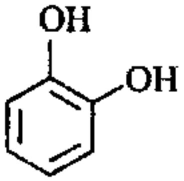
Work out structures for A and B. 5

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

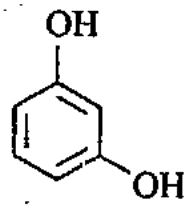


Camphor 5

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



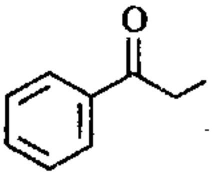
A



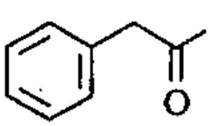
B

C 5

(ii) Differentiate following ketones by mass spectrometry.



A



B 5

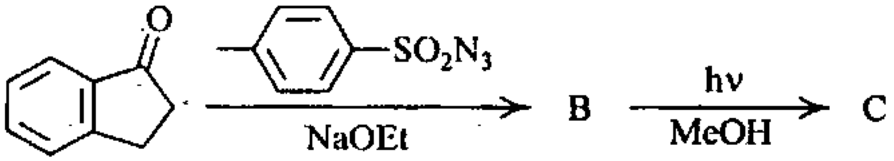
6\. (a) Explain why Grignard reagent, MeMgI, does not add to 1,3-cyclohexane dione but it adds to cyclohexanone. 10

(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 CCl_4 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 ^{13}C NMR spectral signal at 170 ppm. Assign the spectral data for C.



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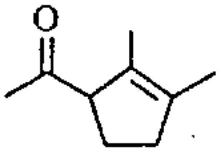
(b) Direct photolysis of ketone A leads to its isomer B whereas photolysis in presence of sensitizer leads to another isomer C. Identify B and C and explain with mechanism.



A

10

(c) Photolysis of dimethyl acetylenedicarboxylate in benzene provides dimethyl 1,3,5,7-cyclooctatetraenedicarboxylate. Explain the result by identifying the intermediate. 10

(d) Discuss the nature of bonding and structures of phosphonitrillic 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.

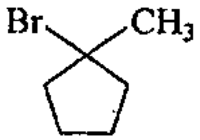
δ 6·4 (d, J = 8 Hz, 2H), 6·3 (d, J = 8 Hz, 2H), 3·5 (s, 3H), 3·2 (br s, 2H).

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