2017

CHEMISTRY

(Major)

Paper : 5.3

(Organic Chemistry)

Full Marks: 60

Time: 3 hours

The figures in the margin indicate full marks for the questions

- 1. Answer the following questions (any seven): 1×7=7
 - (a) Write 'aciform' structure of nitromethane.
 - (b) How is Lindlar's catalyst prepared?
 - (c) Write IUPAC name of



- (d) What is a thiolation reaction? Give example.
- (e) Define 'frontier orbital' with appropriate example.
- (f) Define 'betaine' with example.
- (g) What is a Schiff's base?
- (h) When is a rearrangement reaction said 'anchimerically assisted'?
- 2. Answer the following questions (any four): 2×4=8
 - (a) Give Fittig's synthesis to confirm the fused ring structure of naphthalene.
 - (b) Give one appropriate example to prove that no cross product is formed in Claisen rearrangement reaction.

(c) Write migratory aptitude of alkyl or aryl group in the following reaction and give product with appropriate explanation:

- (d) Write Strecker reaction for preparation of methylsulphonic acid.
- (e) Why does pyridine undergo electrophilic substitution reaction slowly than benzene?
- 3. Answer the following questions [any one from (a) and (b) and two from (c), (d) and (e)]: 5+(5×2)=15
 - (a) How does optically active α-phenyl propionamide undergo Hofmann degradation reaction? Give mechanism of the reaction. Justify configuration of product produced.

1+3+1=5

- (b) How does phenylacetate undergo intramolecular rearrangement reaction in presence of AlCl₃? Give mechanism of this reaction. What are the factors on which relative amount of product depends? 1+3+1=5
- (c) How can (i) alanine and (ii) cinnamic acid be prepared from diethyl malonate? Give reactions. 2½+2½=5
- (d) (i) Why are diazonium salts seldom separated? How do you get benzene from benzene diazonium chloride (give reaction)?
 - (ii) Show with mechanism that carbonyl carbon (C¹³) of (A) is same carbonyl carbon (C¹³) of (B) in following reaction: (1+1)+3=5

- (e) Explain sigmatropic migration of carbon in cope rearrangement reaction.
- 4. Answer the following questions:

Either

- (a) (i) In pericyclic reaction, what are endo-addition and exo-addition?
 - (ii) Why is NaBH₄ generally used in protic solvent?
 - (iii) Identify A and B in the following reactions (give structures and names):

(1)
$$(C_2H_5)_3CH \xrightarrow{CrO_3} A$$

$$(2) \qquad \stackrel{\text{SeO}_2}{\longrightarrow} B$$

(iv) Prove that, the following reaction is stereoselective:

$$CH_3$$
 $C=N-OH \xrightarrow{H^+} \dot{C}H_3-C-NHC_6H_5$
 C_6H_5

8A/271

(Turn Over)

5

3

1

2

2

(v) How does a diazonium ion undergo a structural change in alkaline solution?

Or

- (b) (i) What happens when 2,2-dimethyl propanol is treated with conc. H₂SO₄. Give reaction and its mechanism. What are the driving forces for this reaction? 1+2+2=5
 - (ii) Why LiAlH₄ cannot be used in protic solvent?
 - (iii) Identify A and B in the following reactions (give structure and name):

$$B \stackrel{\text{Pt}}{\longleftarrow} H_2 \stackrel{\text{O}}{\longleftarrow} CHC_6H_5 \xrightarrow{H_2\text{-Pd}} A$$

(iv) Explain why furan is less reactive than pyrrole. 2

Either

- (c) (i) Give explanations of the following products in reactions (1) and (2):
 - (1) $CH_3CH_2NO_2 + Br_2 \xrightarrow{NaOH} CH_3C(Br)_2NO_2$
 - (2) $CH_3CHNO_2 + Br_2 \xrightarrow{NaOH} CH_3 C(Br)NO_2$ $CH_3 \qquad CH_3 \qquad CH_3$
 - (ii) What is Fries rule on structure of polynuclear hydrocarbon?
 - (iii) Write mechanism of the following reaction: 2

$$OCH_3$$
 Li-C₂H₅OH OCH_3

(iv) Write the products and the names for the reactions given below: 1×5=5

$$(1) \xrightarrow{OH} \xrightarrow{PCC} ?$$

8A/271

2

2

1

(2) $CH=CH-CH_2OH$ $Pb(OAc)_4$ Pyridine/RT

(3) $(CH_3CH_2)_2S \xrightarrow{KMnO_4}$?

(4) $CH_2=CH_2+CH_2N_2 \longrightarrow ?$

Or

- (d) (i) How does ethanoic acid react with hydrazoic acid in presence of conc. H₂SO₄? Give the reaction with mechanism.
 - (ii) Give explanations of forming the following products in reactions 1, 2 and 3:

(Continued)

3

3

(2)
$$\bigcirc \stackrel{NO_2}{\longrightarrow} \stackrel{SO_3}{\longrightarrow} \stackrel{NO_2}{\longrightarrow} \stackrel{NO_2}{\longrightarrow}$$

$$SO_3H$$

(3)
$$NO_2$$
 NO_2 OH

- (iii) What is peri-hydrogen interaction in sulphonation of naphthalene?
- (iv) Write the structure of peridinium chlorochromate. 1

2

3

(v) What is Sarett's reagent? 1

Either

- (e) (i) Why does pyridine react under vigorous condition with electrophilic reagents? Explain with appropriate example.
 - (ii) How does thiol undergo desulphurization reaction? Give example.

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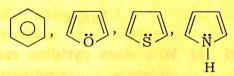
8A/271

- (iii) Write about Gabriel synthesis.
- (iv) How can diazomethane be converted to methyl hydrazine?
 Give reaction.
- (v) Prepare

from acetoacetic ester.

Or

(f) (i) Write relative reactivity towards electrophilic aromatic substitution of



(ii) Why is indole less reactive than pyrrole? What happens when indole reacts with H₂+Raney Ni?

2

1

3

1

(iii) Identify A and B in following reactions (give names and structures): 1+1=2

(1)
$$\langle \bigcirc \rangle$$
 NO₂ + Zn + H₂O $\xrightarrow{NH_4Cl}$ A

(2)
$$Na/heat \rightarrow B$$
 Isopentanol

- (iv) What is the driving force to form alkene in Wittig reaction?
- (v) What happens when anthracene reacts with Na₂Cr₂O₇ + H₂SO₄? Give product name and structure.
- (vi) Prepare CH₃CH₂COOH from cyanoacetic ester.
- (vii) What is a suprafacial process? 1

(Continued)

3 (Sem-5) CHM M 3

1

2