JADAVPUR UNIVERSITY
FACULTY OF SCIENCE

WRET for the Ph.D. (Sc) Program

Subject: Chemistry
Duration : 2 Hours
Full marks: 50

Date of Examination: 22.06.2018
Time: 12 Noon

SET-A

1. *Identify the correct answer by putting tick (✔) mark on Question Booklet and return the Booklet at the end of the Examination.*
2. *Answer any **25** questions each from Part-I and Part-II.*
3. *For evaluation, **first 25 answers** in each Part will be considered.*
4. *Do not write your Name or Ref. No. in any portion of Booklet except the Ref. No. in this **Cover Page.***
5. *Calculator and mobile phone are **not** allowed.*

Reference No.

	Number of correct answers	Marks awarded	Total Marks (Out of 50)	Signature of the Examiner
Part-I				
Part-II				

Part-I

Answer any twentyfive (25) questions   1 × 25

1. The molecular weight of polymer obtained by viscosity method lies

a) above $\overline{M_n}$ b) Below $\overline{M_n}$ c) Between $\overline{M_n}$ and $\overline{M_w}$ d) Below $\overline{M_w}$

2. Which of the following is commonly used as the mobile phase in GC-MS?

a) CH_3CN b) Air   c) H_2O d) He

3. The ^{1}H-NMR signals due to the aromatic protons of an unsymmetrical *p*-disubstituted benzene appear at δ7.39 and δ7.22 (measured with 90MHz NMR instrument) with coupling constant 9.0 Hz. The signals will be

a) two well-separated doublets.

b) two well-separated triplets.

c) AB quartet.

d) two sets of multiplets.

4. In case of a particular molecule if a Raman active vibration is normal IR inactive and vice-

versa it indicates

a) the molecule has a centre of symmetry

b) the molecule may or may not have a centre of symmetry

c) the molecule does not have a centre of symmetry

d) Inconclusive.

5. In the ^{1}H NMR spectrum of myrtenal, the two methyl groups are expected to display chemical shift values (δ) in ppm at

 Myrtenal
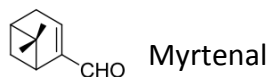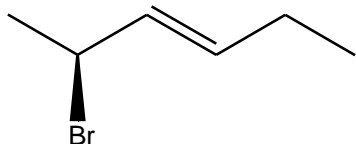
a) 1.33 (s, 6H)   b) 0.74 (s, 6H)

c) 1.35 (s, 3H) and 5.0 (s, 3H)   d) 0.74 (s, 3H) and 1.33 (s, 3H)

6. Calculate the absolute standard deviation of the following

$$y = 0.50 (\pm 0.02) + 4.10 (\pm 0.03) - 1.97 (\pm 0.05)$$

$$= 2.63 (\pm \ ?)$$

a) 0.03   b) 0.06   c) 0.00   d) 0.10

7. The number of 1H NMR signals for the following compound will be:

a) 7   b) 6   c) 5   d) 4

8. The primary analytical method (not using a reference) is

a) inductively coupled plasma emission spectrometry.

b) anodic stripping voltammetry.

c) isotopic dilution mass spectrometry.

d) energy dispersive X-ray fluorescence spectrometry.

9. Which of the following crystal system has four Bravais lattice?

a) Tetragonal   b) Orthorhombic   c) Monoclinic   d) Hexagonal

10. Number of lines and relative intensities of EPR spectrum of the radical anion of benzene, $[C_6H_6^{\bullet}]^-$ are respectively

a) 7 and 1:6:15:20:15:6:1

b) 2 and 1 : 1

c) 5 and 1: 2 : 3 : 2 : 1

d) 7 and 1 : 3 : 6 : 7 : 6 : 3 : 1

11. The nuclear wave function of hydrogen molecules kept in a bottle at normal temperature is given by

$$\frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

How would the NMR spectrum of this H_2 look like?

a) No NMR line.

b) Two NMR peaks each is a doublet.

c) Three NMR peaks with relative intensities 1:2:1.

d) A single NMR peak.
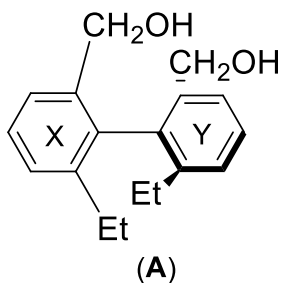
12. In the EI mass spectrum of 1,2-dichloroethane, approximate intensity ratio of peaks at m/z 98, 100, 102 will be

a) 1:2:1   b) 1:1:2   c) 3:1:1   d) 9:6:1

13. Which technique does not assist in Greener synthesis of Chemicals?
a) Derivatization methods

b) Microwave assisted reactions

c) Ultrasound assisted reactions

d) Use of catalytic reagents

14.

(A)

a) In 1H-NMR spectrum, the geminal hydrogens of the CH_2OH group of rings X of compound **A** will appear as a AB-quartet and those of ring Y will appear as a singlet

b) In 1H-NMR spectrum, the geminal hydrogens of the CH_2OH group of rings X of compound **A** will appear as a singlet and those of ring Y will appear as a AB-quartet

c) In 1H-NMR spectrum, the geminal hydrogens of CH_2OH group of both of rings X and Y of compound **A** will appear as a single AB-quartet

d) In 1H-NMR spectrum, the geminal hydrogens of CH_2OH group of both of rings X and Y of compound **A** will appear as a singlet

15. The number of peaks or signals in ^{1}H NMR of N, N-dimethylformamide (DMF) at room temperature is

a) 1   b) 2   c) 3   d) 4

16. The width of the energy gap of a superconductor is zero at

a) 0 K   b) Room temperature   c) Transition temperature   d) 100 °C

17. Column chromatography is based on the principle of

a) adsorption   b) solubility   c) thermal stability   d) molecular size

18. When placed in magnetic field, all the random spins of nuclei

a) stop.

b) reverse direction.

c) align with the magnetic field.

d) rotate to 90 ° away from the induced field.

19. Packing fraction of SC, BCC & FCC in crystalline state are

a) 0.52, 0.68 & 0.74   b) 0.54, 0.68 & 0.74

c) 0.52, 0.62 & 0.74   d) 0.52, 0.64 & 0.74

20. Which of the following transitions is electric-dipole allowed?

a) ^{3}S → ^{3}P   b) ^{3}S → ^{3}D   c) ^{3}S → ^{1}D   d) ^{3}S → ^{1}F

21. Identify the incorrect statement regarding the Absorption spectroscopy.

a) It involves transmission.

b) Scattering is kept minimum.

c) Reflection is kept maximum.

d) Intensity of radiation leaving the substance is an indication of concentration.

22. The bond distance of oxygen molecule can be experimentally determined from

a) microwave spectroscopy

b) IR spectroscopy

c) Raman spectroscopy

d) Fluorescence spectroscopy

23. The HOMO to LUMO electronic transition responsible for the observed colours of halogen gas molecules is

a) $\pi \rightarrow \pi^*$

b) $\pi^* \rightarrow \sigma^*$

c) $\sigma \rightarrow \sigma^*$

d) $\pi \rightarrow \sigma^*$

24. For the gravimetric determination of Ni^{2+} using dimethylglyoxime which of the following is true?

a) Pd^{2+} interferes but Pt^{2+} does not interfere.

b) both Pd^{2+} and Bi^{2+} interfere.

c) Au^{3+} does not interfere.

d) no interference from Pd^{2+}, Bi^{2+}, Bi^{3+}or Au^{3+}.

25. An organic compound exhibited the following ^1H NMR spectra data: d 7.80 (2 H, d, J= 8 Hz) , 6.80 (2 H, d, J= 8 Hz) , 4.10 (2H, q, J =7.2 Hz) , 2.4 (3H, s) ,1.25 (3 H, t, J= 7.2 Hz). The compound is

a)

b)

c)

d)

26. Which one the following spectroscopic techniques takes fastest snapshot of the molecular structure?

a) Mössbauer spectroscopy

b) IR spectroscopy

c) NMR spectroscopy

d) ESR spectroscopy

27. In a voltammetric analysis if a modified form of a redox active compound, for which modification was done away from the redox active group, undergoes reduction at a potential more negative than the original compound it indicates

a) The reducible group in the modified compound is less prone to reduction.

b) The reducible group in the modified compound is more prone to reduction.

c) Inconclusive.

d) Modification does not affect electrochemistry.

28. In cyclic voltammetry (CV), the applied potential is

a) Triangular   b) Linear   c) Rectangular   d) None of the above

29. The number of signals in ^{13}C {^{1}H} NMR spectrum of (R)-4-methyl pentane-2-ol are

a) 6   b) 5   c) 4   d) 3

30. Brown gas is not evolved in qualitative analysis for the reaction of

a) $ZnNO_3$ is heated in a dry test tube
b) $Pb(NO_3)_2$ is heated in a dry test tube
c) $NH_4Cr_2O_7$ is heated in a dry test tube
d) Mixture of KCl and $NH_4Cr_2O_7$ is heated with conc. H_2SO_4


31. ESR spectroscopy is basically an

a) absorption spectroscopy   b) emission spectroscopy

c) nuclear spectroscopy   d) photoelectron spectroscopy

32. In the IR spectrum of an organic compound, a strong and sharp signal at 3320 cm^{-1} along with a signal at 2150 cm^{-1} with medium intensity indicate the occurrence of

a) an alcoholic –OH group.

b) a formyl group.

c) a cyano group.

d) a terminal alkyne moiety.

33. Arrange the increasing order of chemical shift (δ ppm) positions for the protons in the following compound:
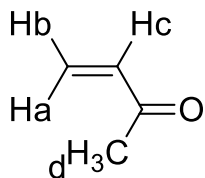
a) Ha < Hb < Hc < Hd

b) Hd < Hb < Hc < Ha

c) Hd < Ha < Hc < Hb

d) Hd < Hc < Hb < Ha

34. The reagent gas used in Chemical Ionization (CI) is

a) Ethane   b) Methane   c) Nitrogen   d) Oxygen

35. In mass spectrometer, the ions are sorted out in which of the following ways?

a) By accelerating them through electric field

b) By accelerating them through magnetic field

c) By accelerating them through electric and magnetic field
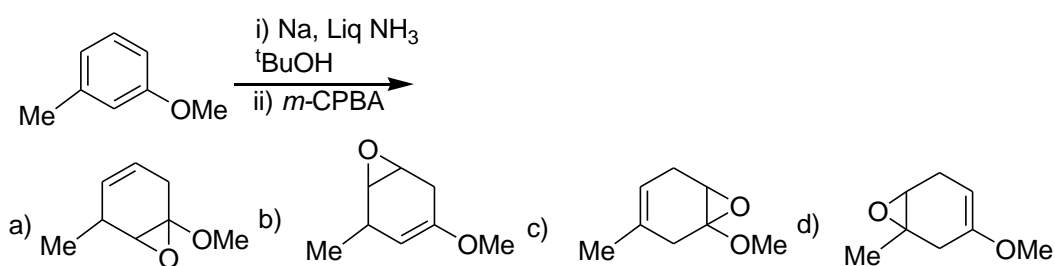
d) By applying a high voltage

FOR ROUGH WORK

Part-II

1. Which pairing of nucleic acid bases between two opposite strands is not found in either DNA or RNA

a) adenine-thymine   b) guanine-cytosine   c) adenine-cytosine   d) adenine-uracil

2. The major product formed in the following reaction sequence is:

3. Stokes shift is defined as

a) difference in wavelength between S_1 and S_2 states;

b) sum of λ(absorption) and λ(emission);

c) difference in wavelength between λ(absorption) and λ(emission)

d) difference in wavelength between λ(phosphorescence) and λ(fluorescence)

4. Colloidal solution of gold prepared by different methods are of different colour because of

a) different diameters of colloidal gold particles.

b) different concentration of gold particles.

c) variable valency of gold.

d) impurities produced by different methods.

5. The transition energy for the electronic transition $\pi_1 \rightarrow \pi_2$ in propenyl radical is 3.2 eV. What would be the transition energy for the transition $\pi_1 \rightarrow \pi_3$ in the framework of Huckel theory?

a) 1.6 eV   b) 3.2 eV   c) 6.4 eV   d) 9.6 eV

6. An enzyme catalyzed reaction is represented as below

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$
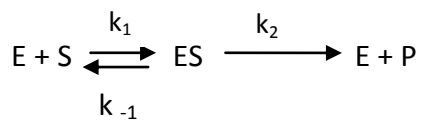
$k_2 = 4.16 \times 10^4 \text{ s}^{-1}$. If $[E]_0 = 10^{-2}$ mol dm^{-3}, the magnitude of maximum velocity and turn over number using Michaelis-Menten kinetics are

a) 4.16×10^6 mol dm^{-3} s^{-1} ; 4.16×10^4 s^{-1} 　　　　b) 4.16×10^2 mol dm^{-3} s^{-1} ; 4.16×10^4 s^{-1}

c) 4.16×10^4 mol dm^{-3} s^{-1} ; 4.16×10^6 s^{-1} 　　　　d) 4.16×10^4 mol dm^{-3} s^{-1} ; 4.16×10^2 s^{-1}

7. Which of the following reactions may occur under thermal condition?

a) [1,3]-sigmatropic shift of hydrogen.

b) [1,3]-sigmatropic shift of alkyl group with retention of configuration.

c) [1,3]-sigmatropic shift of alkyl group with inversion of configuration.

d) none of the above

8. The product of the following reaction is:
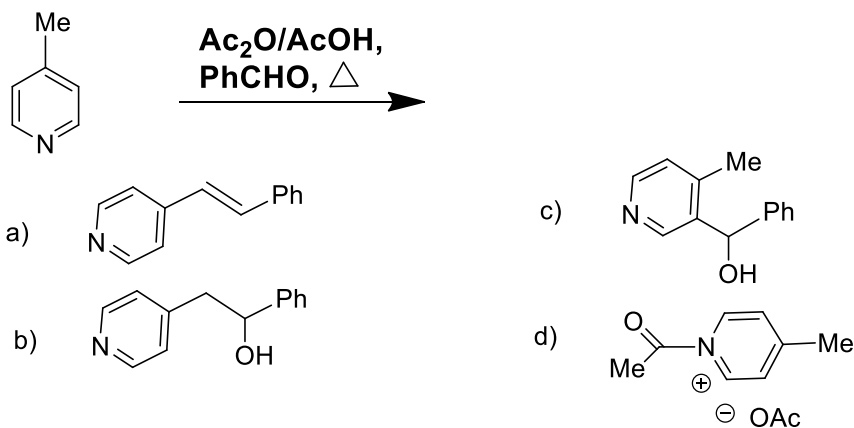
9. L-DOPA is used for the treatment of

a) Cancer 　　　　　b) Tuberculosis 　　　　　c) Parkinson's disease 　　　　　d) Diabetes

10. Identify the high-spin complex amongst the following.

a) $[Co(NH_3)_6]^{3+}$ 　　　　b) $[CoF_6]^{3-}$ 　　　　c) $[Co(CN)_6]^{3+}$ 　　　　d) None of these

11. Identify the incorrect statement.

a) A Slater determinant obeys Pauli Exclusion Principle.

b) A Slater determinant always corresponds to a particular spin state.

c) A many electron wave function should be represented by a Slater determinant.

d) A Slater determinant is an antisymmetrized wave function.

12. Order of K^+ binding constant of the hosts depicted below follows
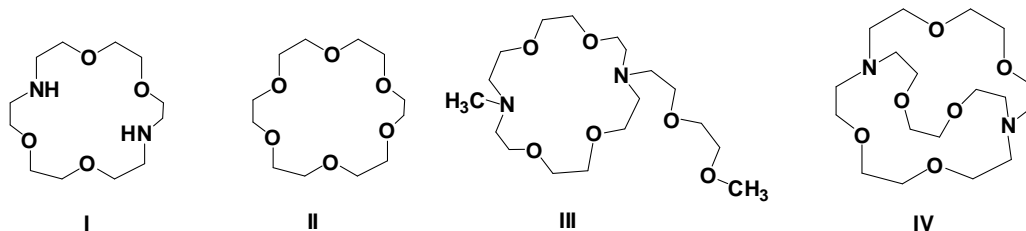
I   II   III   IV

a) I>II>III>IV   b) IV>III>II>I   c) IV>II>III>I   d) IV>III>I>II

13. The conditions 'A' and 'B' required for the following pericyclic reactions are

a) A- Δ ; B – hν

b) A- Δ; B – Δ

c) A- hν; B – hν

d) A- hν; B – Δ
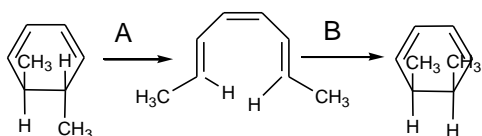
14. Order of reactivity towards borohydride reduction among the carbonyls acetone (I), cyclopentanone (II) and cyclohexanone (III) is

a) I < II < III   b) I > II > III   c) III > I > II   d) II > I > III

15. If a silver strip is immersed in an aqueous solution containing Cu^{2+} ions, what would you expect to happen?

a) Ag would be oxidized.

b) No reaction would occur.

c) Cu^{2+} ions would be reduced.

d) Copper would be deposited on the silver strip.

16. In the following photochemical reaction, identify the major product:

hv, Sensitizer

a)

b)

c)

d)
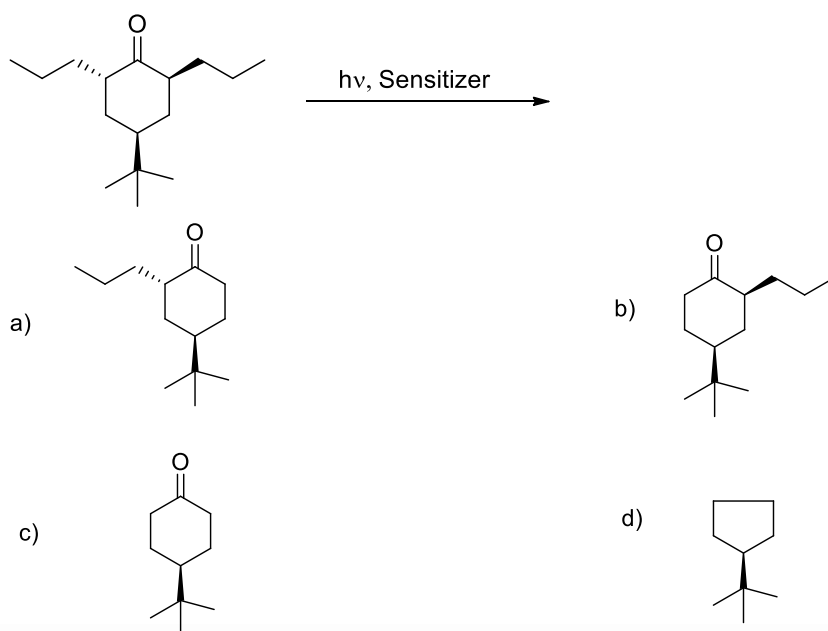
17. Suppose Hamiltonian operator (H) does not commute with a hermitian operator X. Let ϕ_1 is the eigenfunction of X and ϕ_2 is that of H. Which of the following statement is correct regarding the quantum mechanical average value of the commutator [X,H]?

a) $\langle \phi_1 |[X,H]| \phi_1 \rangle = 0$ but $\langle \phi_2 |[X,H]| \phi_2 \rangle \neq 0$

b) $\langle \phi_1 |[X,H]| \phi_1 \rangle = 0$ and $\langle \phi_2 |[X,H]| \phi_2 \rangle = 0$

c) $\langle \phi_1 |[X,H]| \phi_1 \rangle \neq 0$ but $\langle \phi_2 |[X,H]| \phi_2 \rangle = 0$

d) $\langle \phi_1 |[X,H]| \phi_1 \rangle \neq 0$ and $\langle \phi_2 |[X,H]| \phi_2 \rangle \neq 0$

18. In grand canonical ensemble the walls of the individual assembly are

a) Permeable   b) Rigid
c) Diathermic   d) Rigid, permeable and diathermic

19. Ground state of transition metal ion with d^2 electronic configuration in ML_6 complex splits as $^3T_{1g}+{}^3T_{2g}+{}^3A_{2g}$. Which is true in the energy ordering scheme?

a) $^3T_{1g} > {}^3T_{2g} > {}^3A_{2g}$

b) $^3T_{2g} > {}^3T_{1g} > {}^3A_{2g}$

c) $^3A_{2g} > {}^3T_{2g} > {}^3T_{1g}$

d) $^3A_{2g} > {}^3T_{1g} > {}^3T_{2g}$

20. Point-group symmetries of **fac-MX₃Y₃** and **mer- MX₃Y₃** [X and Y are mono dentate ligands] are respectively

a) C_{2v} and T_d b) O_h and O_h c) C_{3v} and C_{2v} d) C_{2v} and C_{3v}

21. The major product **B** formed in the following reaction is

$$C_4H_9-C\equiv C-H \xrightarrow{(C_6H_{11})_2BH} A \xrightarrow{I_2,\ NaOH} B$$

(a) C_4H_9 C_6H_{11} (b) C_4H_9 / C_6H_{11} (c) C_4H_9 / I (d) C_4H_9 / I

22. The reaction: 2 N_2O_5 (g) → 4 NO_2 (g) + O_2 (g), has the rate constant, k = 2.10 × 10^{14} exp (-103.14 kJ mol^{-1}/ RT) s^{-1}. The half-life period of the reaction at 300 K is

a) 50.00 min   b) 50.02 min   c) 50.03 min   d) 50.05 min

23. A constant shift of energy levels of a system changes its Partition function. Which of the following properties do not change?

a) Heat capacity and average energy.

b) Heat capacity and entropy.

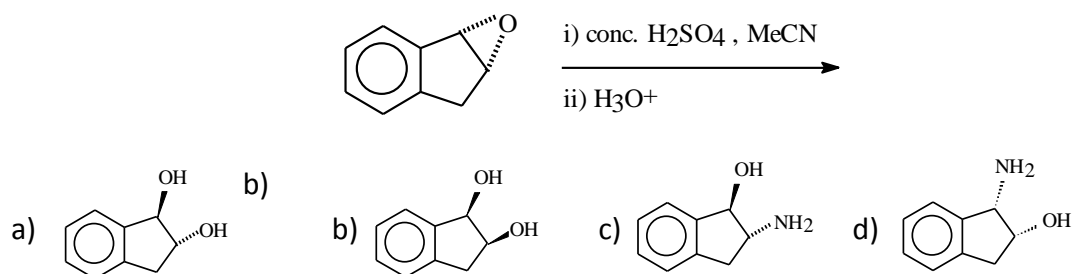c) Average energy, heat capacity and entropy.

d) Average energy and entropy.

24. An organometallic fragment that is isolobal to CH_2 fragment is

a) $Fe(CO)_4$ b) $Ni(CO)_4$ c) $Co(CO)_4$ d) $Mn(CO)_4$

25. The styx number of B_5H_9

a) 4120   b) 4102   c) 4012   d) 4210
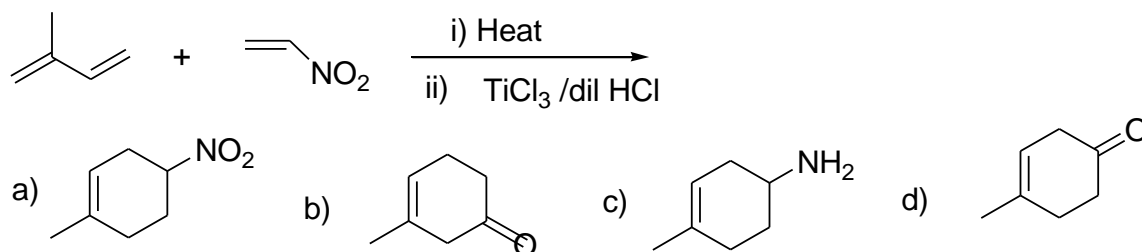
26. The product of the following reaction is

i) conc. H_2SO_4 , MeCN

ii) H_3O^+

a)   b)   b)   c)   d)

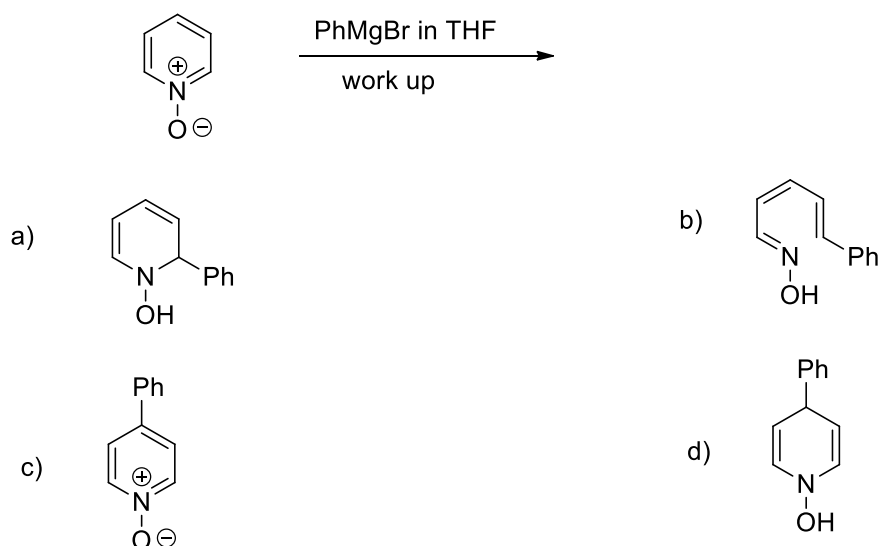27. Write down the major product of the following reaction.

Δ

a)   b)   (c)   d)
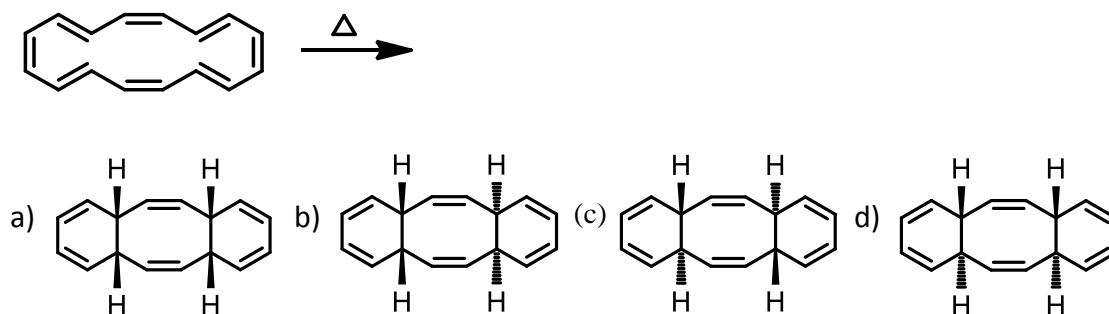
28. Among n-π* and π-π* transitions of a molecular system

a) the former is weaker

b) the latter is weaker

c) both are similar in intensity

d) intensity depends on the polarity of the solvent

29. The Major product in the following reaction is

30. Indicate the major product in the following reaction:

31. The anticancer drug Oxaliplatin is

a) Potassium *cis* dichloro oxalatoplatinate(II)

b) diaminocyclohexane oxalatoplatinum

c) Potassium *trans* dichloro oxalatoplatinate(II)

d) Potassium bis(oxalato)platinate(II)dehydrate

32. Which of isotope of Pu is used as a nuclear fuel in fast breeder reactor?

a) ^{242}Pu   b) ^{241}Pu   c) ^{240}Pu   d) ^{239}Pu

33. The biosynthetic precursor of abietic acid is

a) Cinnamic acid   b) Shikimic acid   c) Mevalonic acid   d) Chorismic acid

34. An aqueous solution of Fe^{2+} reacts instantaneously with thiocyanate because

a) thiocyanate is a powerful oxidizing agent
b) as thiocyanate is unstable in aqueous media, so it quickly reacts with Fe^{2+}
c) spin state of Fe^{2+} changes in this reaction
d) d^5 high-spin Fe^{2+} is kinetically labile

35. Enantioselective reduction of unsymmetrical ketone with CBS reagent involves

a) activation by Lewis acidic centre only

b) activation by Lewis basic centre only

c) dual activation by both the Lewis acidic and Lewis basic centres

d) no activation of any of the above three kinds.

FOR ROUGH WORK