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Entrance Examination – 2020 (Ph.D. Admissions - January 2021 Session)

Ph.D. Chemistry

ſime	: 2 hours Max. Marks : 70
HA	LL TICKET NUMBER:
1.	Write your HALL TICKET NUMBER in the space provided above and also on the OMR ANSWER SHEET given to you.
2.	Make sure that pages numbered from $1 - 19$ are present (excluding 5 pages assigned for rough work).
3.	There are eighty (80) multiple-choice questions in this paper (20 in Part-A and 60 in Part-B). You are required to answer all questions of Part-A and a maximum of 20 questions of Part-B. If more than the required number of questions are answered in Part-B, only the first 20 questions will be evaluated.
4.	Each question in Part-A and Part-B carries 1.75 marks.
5.	There is no negative marking.
6.	Answers are to be marked on the OMR answer sheet following the instructions provided on it.
7.	Handover the OMR answer sheet to the invigilator at the end of the examination.
8.	In case of a tie, the marks obtained in the first 20 questions (Part-A) will be used to determine the order of merit.
8.	No additional sheets will be provided. Rough work can be done in the space provided at the end of the booklet.
9.	Calculators are allowed. Cell phones are not allowed.
10.	Useful constants are provided just above Part-A in the question paper.
11.	OMR without hall ticket number will not be evaluated and University shall not be held responsible.

Useful Constants:

Rydberg constant = 109737 cm^{-1} ; Faraday constant = 96500 C; Planck constant = $6.625 \times 10^{-34} \text{ J}$ s; Speed of light = $2.998 \times 10^8 \text{ m s}^{-1}$; Boltzmann constant = $1.380 \times 10^{-23} \text{ J} \text{ K}^{-1}$; Gas constant = $8.314 \text{ J} \text{ K}^{-1} \text{ mol}^{-1}$ = 0.082 L atm K⁻¹ mol⁻¹ = $1.987 \text{ cal } \text{K}^{-1} \text{ mol}^{-1}$; Mass of electron = $9.109 \times 10^{-31} \text{ kg}$; Mass of proton = $1.672 \times 10^{-27} \text{ kg}$; Charge of electron = $1.6 \times 10^{-19} \text{ C}$; 1 bar = $10^5 \text{ N} \text{ m}^{-2}$; RT/F (at 298.15 K) = 0.0257 V; Avogadro number = 6.022×10^{23}

Part-A

- 1. The crystal system with lowest symmetry among the following is:
 - [A] Cubic[B] triclinic[C] Monoclinic[D] orthorhombic
- 2. With increase in temperature, the electrical conductivities of metals and semiconductors will:

[A] d	lecrease and	increase respectively	[B]	increase
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[C] increase and decrease respectively [D] decrease

3. Excitons that give rise to electroluminescence are created by:

[A]	Photoexcitation	[B]	thermal annealing
[C]	application of an electric field	[D]	electron beam irradiation

- 4. X-ray diffraction peaks for a specific Miller plane of a crystal appear at the angles θ_1 and θ_2 for incident X-ray wavelengths of λ_1 and λ_2 , respectively. If $\lambda_2 = 2\lambda_1$, then:
 - [A] $\theta_2 = 2\theta_1$ [B] $\sin\theta_1 = 2\sin\theta_2$ [C] $\sin\theta_2 = 2\sin\theta_1$ [D] $\sin\theta_2 = \sin2\theta_1$
- 5. Critical temperature and pressure of a van der Waals gas are -122 °C and 48 atm, respectively. The radius of the gas atom is close to:

[A]	2.5 Å	[B]	1.5 Å
[C]	1.05 Å	[D]	3.1 Å

6. The ligand that forms sigma, pi, delta and phi bonds with actinides is:

[A]	[C ₅ H ₅] ⁻	[B]	[C ₈ H ₈] ²⁻
[C]	[C ₆ H ₆] ⁻	[D]	[C ₈ H ₈] ⁻

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- 7. The space and spin parts of the valence bond wave function of H₂ molecule, in its ground state respectively, are:
 - [A] symmetric and antisymmetric [B] symmetric
 - [C] antisymmetric and antisymmetric
- [B] symmetric and symmetric

[D] antisymmetric and symmetric

8. A constant current of 0.8 ampere is used for 15.2 minutes to deposit copper (at wt. 63.55) at the cathode from the electrolyte containing Cu²⁺ in water and oxygen evolution at the anode of an electrolytic cell. The amounts of oxygen and copper deposited at the anode and the cathode, respectively, are:

[A]	0.0096 and 0.1008 g	[B]	0.1238 and 0.0408 g
[C]	0.5203 and 0.3232 g	[D]	0.0605 and 0.2403 g

9. Effective magnetic moment for a f^{10} ion is:

[A]	10.60 BM	[B]	9.72 BM
[C]	9.59 BM	[D]	7.94 BM

10. The number of lines shown by $[VO(acetylacetonate)_2]$ in the EPR spectrum at 25 °C $[I = 7/2 \text{ for } {}^{51}V]$ is:

[A]	6	[B]	7
[C]	8	[D]	1.

11. The chemical shift (δ) in ppm for a proton that resonates at 130 Hz downfield from TMS on a spectrometer operating at 60 MHz is:

ζ,

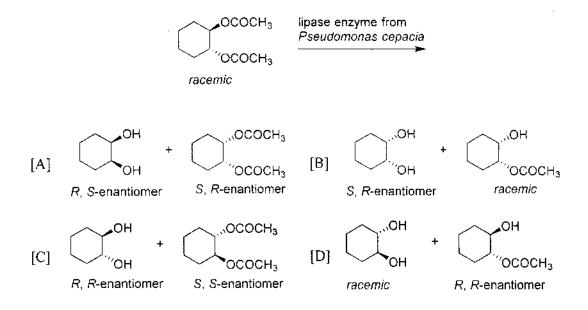
[A]	0.46	[B]	2.16
[C]	1.96	[D]	2.26

- 12. The origin of the yellow-orange colour of $[Co(en)_3]Cl_3$ is due to:
 - [A] ligand-to-metal charge transfer transition
 - [B] metal-to-ligand charge transfer transition
 - [C] ligand-to-ligand charge transfer transition
 - [D] ligand field transition

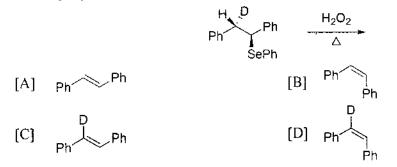
13. Ferredoxin is a Fe-S protein, where the oxidation state of iron varies between:

[A]	0 and 2	[B]	2 and 4
[C]	2 and 3	[D]	3 and 5

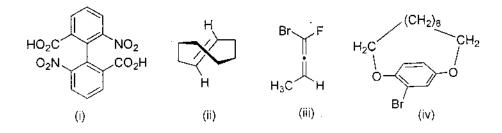
- 14. Identify the set of terpenes which contains mono-, di- and triterpenes respectively, from the following:
 - [A] Camphor, Retinol, and Geraniol
 - [B] Menthol, Rubber, and Phytol
 - [C] Camphor, Retinol, and β -Carotene
 - [D] Menthol, Phytol, and Eucalyptol
- 15. The products obtained in the given biotransformation are:



16. The major product obtained in the following reaction is:



17. Identify the compounds which exhibit axial chirality from the following:



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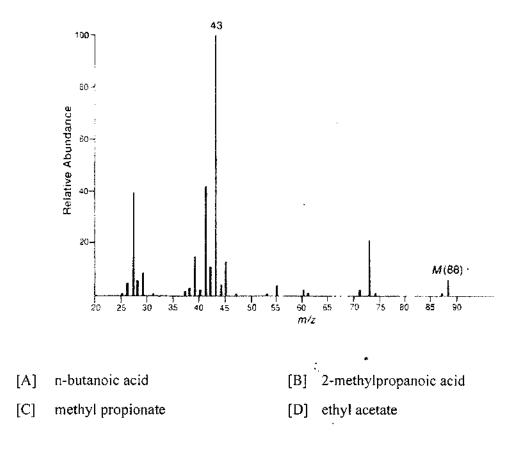
[A]	(i), (ii)	[B]	(i), (iii)
[C]	(ii), (iii)	[D]	(i), (iv)

18. Identify the most appropriate method for N-terminal sequencing of peptides:

[A]	Bergmann degradation	[B]	Edman degradation
[C]	Hoffmann degradation	[D]	Weerman degradation

19. Identify the set of alkaloids from the following:

- [A] caryophyllene and α -ocimene
- [B] cortisone and diosgenin
- [C] cephalin and lecithin [D] mescaline and vinblastine
- 20. The IR spectrum of an unknown compound shows a very strong, broad peak in the range of 2500-3400 cm⁻¹ and a strong, broadened peak at 1710 cm⁻¹. The electron impact mass spectrum of the compound is given below. The compound is:



<u>Part-B</u>

- 21. The number of stereoisomers possible for [Co(en)(NH₃)₂ClBr] (en = 1,2-diaminoethane) is:
 - [A] 3 [B] 4 [C] 5 [D] 6
- 22. The concentration of H^+ in a solution of NaOH having pOH of 11.30 is:
 - [A] 2.0×10^{-3} M [C] 4.0×10^{-8} M [D] 5.0×10^{-10} M

23. 0.3542 g of pure Na₂CO₃ (MW = 106 g/mol) is dissolved in water in a conical flask and titrated with aqueous HCl solution. 30.23 mL of HCl is required to neutralise the solution. The strength of the HCl solution is:

[A]	1.0 N	[B]	0.33 N
[C]	0.22 N	[D]	0.09 N

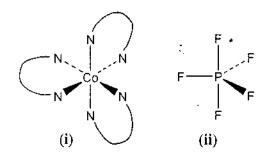
24. The most preferred cation for valinomycin is:

[A]	$\mathrm{NH_4}^+$	[B]	K^+
[C]	Cs ⁺	[D]	Na^+

25. Compared to ground state, photoexcited chlorophyll acts as:

- [A] A better oxidizing agent only
- [B] A better reducing agent only
- [C] Both inferior oxidizing and reducing agent
 - [D] Both superior oxidizing and reducing agent

26. The point groups of the following molecules are :



- [A] (i) D_3 and (ii) C_{5h}
- [C] (i) D_3 and (ii) D_{3h}

- [B] (i) D_{∞} and (ii) $D_{\infty h}$
- [D] (i) D_{6h} and (ii) C_{5h}

27. In sandwich-type ferrocene, the orbitals involved in bonding are:

[A]	Only d_{xz} and $p\pi$	[B]	$d_{\mathrm{xv}},d_{\mathrm{yz}}andp\pi$
[C]	d_{xz} , d_{yz} and $p\pi$	{D]	Only d_{yz} and $p\pi$

28. The product of the reaction of sodium with a (2.2.2)-cryptand is:

[A]	[Na(2.2.2.)] ⁺ Na ⁻	[B]	[Na ₂ (2.2.2.)]
[C]	[Na(2.2.2.)] ⁺ e ⁻	[D]	[Na(2.2.2.)] ⁻ Na ⁺

29. Anhydrous AlCl₃ and GaCl₃ are covalent in character, but form metal ions in solution, because:

- [A] they do not react with water
- [B] the ions are hydrated and the amount of ionization energy exceeds the hydration energy
- [C] the ions are not hydrated and the amount of hydration energy released exceeds the ionization energy
- [D] the ions are hydrated and the amount of hydration energy released exceeds the ionization energy.
- 30. The correct statements from the following is/are:

(i) $Co^{3+}(aq)$ is a powerful oxidizing agent.

(ii) $[Co(NH_3)_6]^{2+}$ is less labile than $[Co(NH_3)_6]^{3+}$.

(iii) Overall formation constant of $[Co(NH_3)_6]^{3+}$ is much higher than that of $[Co(NH_3)_6]^{2+}$.

[A] (i) and (ii)	[B]	(i) and (iii)
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[C] (ii) and (iii) [D] (i) only

31. The product of the reaction of XeF₂ with AsF₅ is:

[A]	$[XeF]^{+}[AsF_6]^{-}$	[B]	$[AsF_4]^{+}[XeF_3]^{-}$
[C]	$[Xe]^{*}[AsF_{7}]^{2-}$	[D]	[AsF ₆] [*] [XeF] ⁻

32. The correct statements regarding the substitution reactions of octahedral complexes via associative pathway are:

- (i) a large negative value of ΔS^{\neq}
- (ii) a large positive value of ΔV^{\neq}
- (iii) a large positive value of ΔS^{\neq}

(iv) a large negative value of ΔV^{\neq}

[A]	(i) and (ii)	[B]	(ii) and (iv)
[C]	(i) and (iv)	[D]	(ii) and (iii)

33. The products of the reaction between Cp_3Ln and $FeCl_2$ are:

[A]	Cp ₃ Fe and LnCl ₃	[B]	Cp_2Fe and $LnCl_2$
[C]	Cp ₂ Fe and LnCl ₃	[D]	CpFeCl and LnCl ₃

34. The incorrect statement regarding beryllocene is:

- [A] Be is coordinated to two η^{-5} cp ligands
- [B] Distance between Be and two cp-rings are not equal
- [C] It has a slipped sandwich structure
- [D] It does not obey 18-e rule

35. *A-D* in the following reactions are:

Fe₃O₄ + A \rightarrow FeO FeO + B \rightarrow Fe + CO₂ Fe + CO \rightarrow C C + D \rightarrow [Fe(CO)₄]²⁻ [A] A = O₂; B = CO; C = Fe(CO)₅; D = KOH [B] A = CO; B = CO; C = Fe(CO)₅; D = KOH [C] A = CO; B = CO; C = [Fe(CO)₃]⁴; D = H⁺

[D] $A = O_2$; B = CO; $C = [Fe(CO)_3]^{4+}$; $D = H^{+}$

36. The oxidation states of iron in hemoglobin, myoglobin, transferrin and ferritin, are respectively.

[A]	+2, +2, +2 and +2	[B]	+2, +3, +2 and +3
[C]	+3, +2, +2 and +3	[D]	+2, +2, +3 and +3

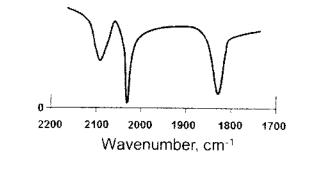
37. The number of electrons donated by an alkyne ligand bridging two metal centers is:

			۰.
[A]	0	[B]	2
[C]	3	[D]	4

38. The structure of $N_2B_4H_6$ as per polyhedral skeleton electron pair theory is:

[A]	closo	[B]	nido
[C]	arachno	[D]	hypo

39. The following type of IR-spectrum is not shown by:



[A]	$Rh_6(CO)_{16}$	(B)	$Fe_3(CO)_{12}$
[C]	Co ₄ (CO) ₁₂	[D]	$Ir_4(CO)_{12}$

40. The complex ion expected to exhibit both spin and orbital magnetic moments is:

[A]	[TiCl₄] [−]	[B]	$[Cr(H_2O)_6]^{3+}$
[C]	$[Fe(CN)_6]^{4-}$	[D]	[CuCl₄] ²⁻

41. The difference in potential between the fixed part of the double layer and bulk solution in the electrical double layer model is called:

[A]	Zeta potential	[B]	Double layer potential
[C]	Sedimentation potential	[D]	Chemical potential

42. At constant pressure, the heat capacity of a one mole perfect gas varies with temperature as C_p (J K⁻¹) = 20.17 +0.47. The change in internal energy when the temperature is raised from 0 to 100 °C is close to:

[A]	7.45 kJ	[B]	7.05 kJ
[C]	15.9 kJ	[D]	14.1 kJ

43. At 25 °C and 1.00 bar, a perfect gas in a container of volume 0.50 dm³ is allowed to expand to 1.00 dm³ and is simultaneously heated to 100 °C. The entropy change for this process is close to:

[A]	— 0.17 J K ⁻¹	[B]	0.17 J K ⁻¹
[C]	1.17 J K ⁻¹	[D]	-1.17 J K^{-1}

44. $\left(\frac{\partial s}{\partial v}\right)_T$ is equal to (α is the thermal expansion coefficient and κ_T is isothermal compressibility):

[A]	$\alpha \kappa_T$	[B]	α
[C]	$\frac{\alpha}{\kappa_T}$	[D]	κ_T

45. The equilibrium constant of a reaction is found to follow the expression $lnK = -2.04 - (1176/T) + (2.1 \times 10^7/T^3)$. The standard reaction enthalpy for this reaction at 450 K is close to:

[A]	3.5 kJ mol ⁻¹	[B]	22.2 kJ mol ⁻¹
[C]	7.2 kJ mol ⁻¹	[D]	10.8 kJ mol ⁻¹

46. Two polymers, one having $M = 62 \text{ kg mol}^{-1}$ and the other with $M = 78 \text{ kg mol}^{-1}$, are mixed in the mole ratio of 3:2. The average molar mass of the mixture is:

[A]	59 kg mol ^{-t}	[B]	68 kg mol ⁻¹
[C]	65 kg mol ⁻¹	[D]	75 kg mol ⁻¹

47. Which of the following molecules among H_2 , HCl, CH₄ and H_2O can show a rotational Raman spectrum?

[A]	H ₂ and HCl only	[B]	H_2 and CH_4 only
[C]	HCI and H ₂ O only	[D]	H_2 , HCl and H_2O only

48. The ground state term symbol for carbon atom is:

•	[A]	$^{1}\mathbf{D}$	[B]	¹ P
	[C]	³ D	[D]	^{3}P

49. $\hat{C}_3^2 \hat{C}_2 \hat{C}_3$ is equivalent to (all rotations are through a common axis):

[A]	Ê	[B]	\hat{C}_3^{-1}	
[C]	$\hat{\sigma}_h$	[D]	\hat{C}_2	*

50. The function that is not well-behaved among the following is:

[A]	$e^{- x }$	[B]	sin x
[C]	$e^{- x^2 }$	[D]	sin 2x

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51. The normalized wavefunction of a particle moving along x axis is given by

 $\Psi(x) = A e^{-ax^2}$ ($-\infty \le x \le \infty$). The constant A is equal to:

 $\begin{array}{ll} [A] & \left(\frac{\pi}{2a}\right)^{1/2} & [B] & \left(\frac{2a}{\pi}\right)^{1/2} \\ [C] & \left(\frac{\pi}{2a}\right)^{1/4} & [D] & \left(\frac{2a}{\pi}\right)^{1/4} \end{array}$

52. The point group of 1,2-dichlorobenzene is:

[A]	D _{2h}	[B]	D_{6h}
[C]	C_{2y}	[D]	D_2

53. The magnetic field at which a proton would resonate at a frequency of 150 MHz is ($\beta_N = 5.05 \times 10^{-27} \text{ JT}^{-1}$, g = 5.6):

[A]	1.7 T	[B]	3.5 T
[C]	5.3 T	[D]	7.0 T

54. What is the enthalpy of a reaction for which the equilibrium constant is doubled when the temperature is raised from 27 $^{\circ}$ C to 37 $^{\circ}$ C? (R= 8.314 J K⁻¹ mol⁻¹)

[A]	15.3 kJ mol ⁻¹	[B]	33.5 kJ mol ⁻¹
[C]	53.8 kJ mol ⁻¹	[D]	73.3 kJ mot ⁻¹

55. According to the transition state theory, a reaction between two molecules is slower than that between two atoms by a factor of (Given, q_v and q_r represent vibrational and rotational partition function respectively, per degrees of freedom):

	[A]	$(q_v/q_t)^3$	[B]	$(q_v/q_r)^5$
•	[C]	$(q_v/q_r)^2$	[D]	(q_v/q_r)

56. The characters of a particular reducible representation Γ_R under $C_{3\nu}$ point group are given below. The correct coefficients of the irreducible representations A_1 and A_2 in Γ_R are (Character table of $C_{3\nu}$ point group is also given below):

C _{3v}	E	2C3	3σ _v
Γ _R	12	0	2
·			
C _{3v}	Ľ.E	$2C_3$	3σ _ν
A ₁	1	1]
A ₂	1	1	-1
E	2	-1	0

[A]	1,3	[B]	1,2
[C]	2,1	[D]	3,1

57. If the zero-point energy difference of RH and RD is 4.5 kJ mol⁻¹ at 25°C, the kinetic isotope effect (k_H/k_D) for the reaction, R-H + R' \rightarrow R + H-R' is expected to be;

[A]	4.5	[B]	2.3
[C]	7.9	[D]	6.1

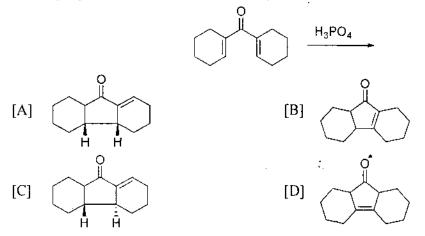
58. At 300 K, the molecular partition function of a system is 1×10^{30} . If the internal energy is 3740 J mol⁻¹, then molar entropy of the system is nearly equal to (in J K⁻¹ mol⁻¹):

[A]	262	[B]	587
[C]	374	[D]	453

59. The rate constant of a reaction is found to decrease with increase in temperature indicating that it is a:

[A]	diffusion controlled reaction	[B]	exothermic reaction
[C]	complex reaction	[D]	ultrafast reaction

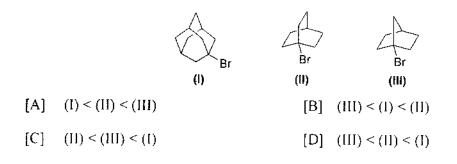
- 60. The mechanism which causes intersystem crossing is:
 - [A] hyperfine coupling [B] spin-orbit coupling
 - [C] vibronic coupling [D] electronic coupling
- 61. The major product formed in the following reaction is:



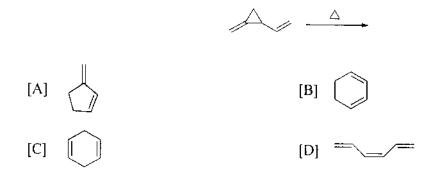
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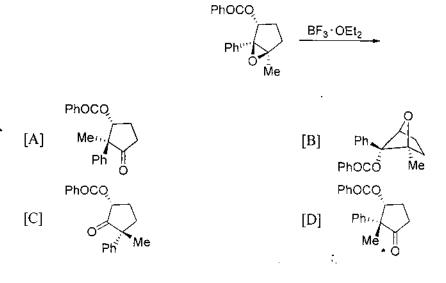
62. The order of increasing rate of solvolysis of the following compounds in ethanol is:

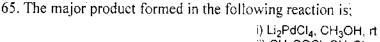


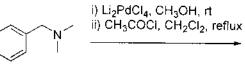
63. The major product formed in the following reaction is:



64. The major product formed in the following reaction is:

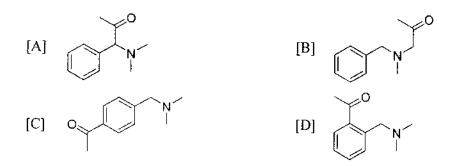




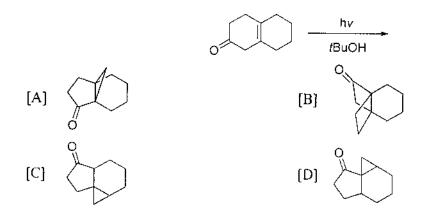


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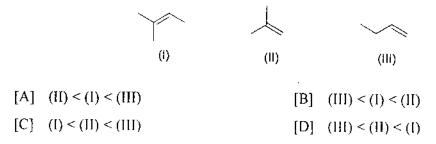
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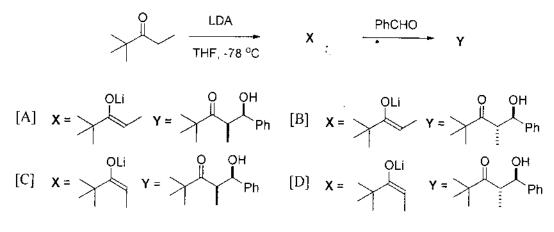
66. The major product formed in the following reaction is:



67. Order of increasing rates of bromination using Br₂ in methanol of the following alkenes is:

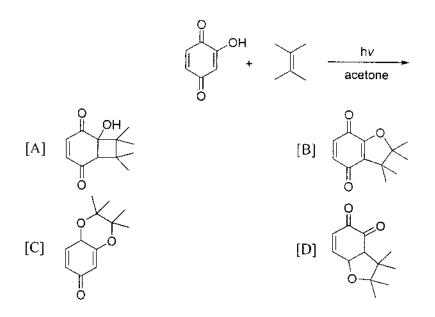


68. The major products X and Y formed in the following transformations, respectively, are:

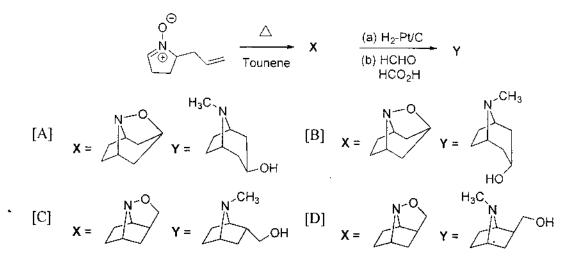


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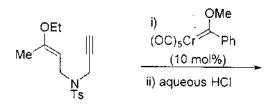
69. The major product formed in the following reaction is:



70. Identify the products X and Y in the following reaction sequence:

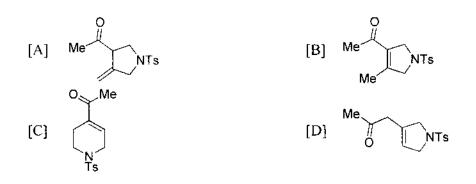


71. The major product obtained in the following reaction is:

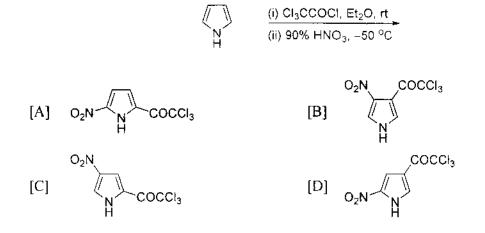


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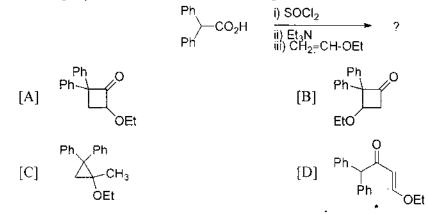
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72. The major product obtained in the following transformation is:



73. The major product formed in the following reaction is:



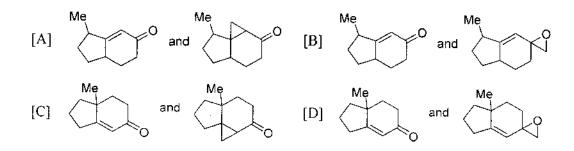
74. The major products X and Y formed in the following transformations, respectively, are:

•

Me
$$(i)$$
 pyrrolidine, cat. H⁺, C₆H₆
 (i) $(CH_3)_2S^+-CH_2^-$
 (i) $(CH_3)_2S^+-CH_2^-$
 (i) $($

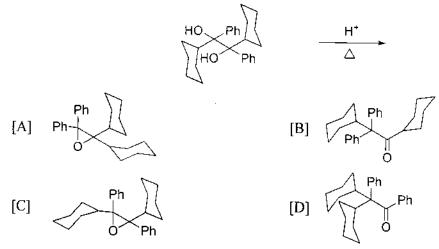
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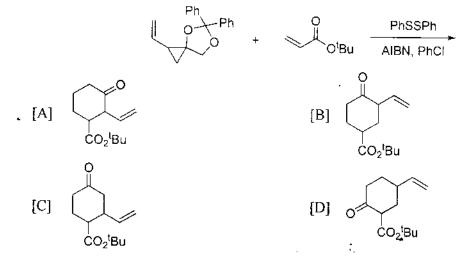


75. The major product obtained in the following reaction is:

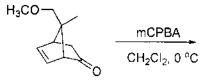
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76. The major product obtained in the following reaction is:



77. The major product formed in the following reaction is:

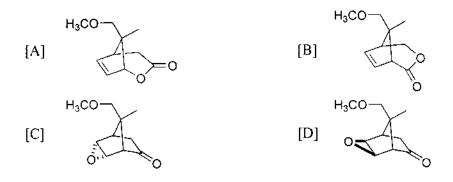


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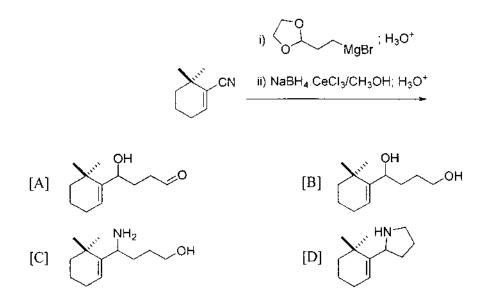
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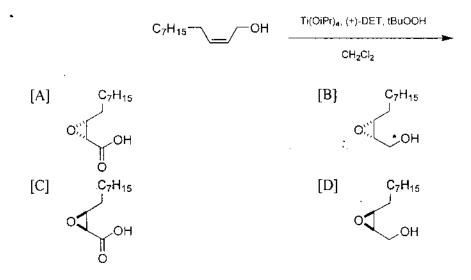
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78. The major product obtained in the following reaction is:



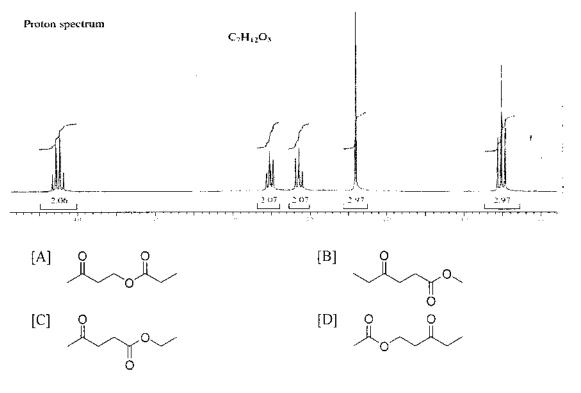
79. Identify the most appropriate product in the following transformation:



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80. The compound with molecular formula $C_7H_{12}O_3$ that will show the following ¹H NMR spectrum is:



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: School of Chemistry : Ph.D. Chemistry

Q.No.	Answer	Q.No.	Answer	Q.No.	Answer	Q.No.	Answer
1	В	26	С	51	D	76	С
2	А	27	С	52	С	77	A
3	С	28	А	53	В	78	A
4	С	29	D	54	С	79	B
5	Β.	30	В	55	В	80	C
6	В	31	А	56	D	81	· · · •
7	A	32	С	57	D	82	
8	D	33	С	58	В	83	
9	А	34	A	59	С	84	
10	С	35	В	60	В	85	
11	В	36	D	61	С	86	
12	D	37	D	62	D	87	
13	С	38	В	63	A	88	
14	· C	39	D	64	D	89	
15	C	40	D	65	D	90	
16	С	41	A	66	А	91	
17	В	42	D	67	D	92	
18	В	43	В	68	А	93	
19	D	44	C	69	В	94	•••
20	В	45	С	70	A	95	
21	D	46	В	71	D	96	
22	A	47	D	72	Α	97	
23	С	48	D	.73	• B	98	
24	В	49	D	74	В	99	
25	D	50	Α	75	D	100	

Note/Remarks :

K.M. 28/1/2021 Signature

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