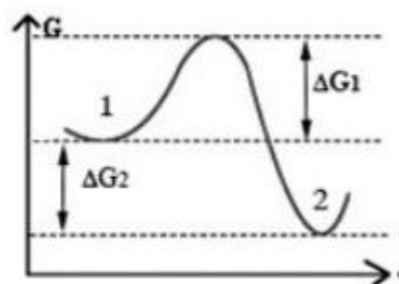


# DU PhD in Chemistry

Topic:- CHEM PHD

1) With reference to the figure below, which represents the Gibbs free energy along a reaction path for a single phase transformation from state 1 to state 2,



[Question ID = 51]

1. rate =  $C \exp(-\Delta G_1/RT)$

[Option ID = 201]

2. rate =  $C \exp(-\Delta G_2/RT)$

[Option ID = 202]

3. rate =  $C \exp(-\{\Delta G_1 + \Delta G_2\}/RT)$

[Option ID = 203]

4. rate =  $C \exp(-\{\Delta G_1 - \Delta G_2\}/RT)$

[Option ID = 204]

2) The degeneracy of a particle in a cubic box having energy three times that of the lowest energy state is [Question ID = 52]

1. 1 [Option ID = 205]

2. 2 [Option ID = 206]

3. 3 [Option ID = 207]

4. 4 [Option ID = 208]

3) Which of the following functions is an eigenfunction of the operator  $d/dx$ ?  $k$  is a constant.

[Question ID = 53]

1.  $\exp(ikx)$

[Option ID = 209]

2.  $kx^2$

[Option ID = 210]

3.  $\sin kx$

[Option ID = 211]

4.  $\exp(kx^2)$

[Option ID = 212]

4) Three non-interacting particles, each with spin  $\frac{1}{2}$ , are moving in a one dimensional box of length  $L$ . The energy of the lowest energy state of the system is

[Question ID = 54]

1.  $\frac{h^2}{4mL^2}$

[Option ID = 213]

2.  $\frac{h^2}{2mL^2}$

[Option ID = 214]

3.  $\frac{3h^2}{4mL^2}$

[Option ID = 215]

4.  $\frac{5h^2}{4mL^2}$

[Option ID = 216]

5) The order of the N-O bond strengths in NO, NO<sup>+</sup>, and NO<sup>-</sup> is [Question ID = 55]

1. NO > NO<sup>+</sup> > NO<sup>-</sup> [Option ID = 217]

2.  $\text{NO}^+ > \text{NO} > \text{NO}^-$  [Option ID = 218]
3.  $\text{NO}^+ > \text{NO}^- > \text{NO}$  [Option ID = 219]
4.  $\text{NO}^- > \text{NO} > \text{NO}^+$  [Option ID = 220]

6) If the energy of a particle can be either 1, 2, 3, 4 or 5 units with probability 1/15, 2/15, 3/15/ 4/15 and 5/15, respectively, the average energy of the particle is[Question ID = 56]

1. 0.5 [Option ID = 221]
2. 3.0 [Option ID = 222]
3. 3.7 [Option ID = 223]
4. 4.3 [Option ID = 224]

7) In terms of the partition function Z of a system of particles, the average energy  $\langle E \rangle$  is expressed as

[Question ID = 57]

1.  $\langle E \rangle = \frac{\partial Z}{\partial \beta}$

[Option ID = 225]

2.  $\langle E \rangle = -\frac{\partial Z}{\partial \beta}$

[Option ID = 226]

3.  $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$

[Option ID = 227]

4.  $\langle E \rangle = \frac{\partial \ln Z}{\partial \beta}$

[Option ID = 228]

8) State which of the following statements about Bose-Einstein (BE) statistics is FALSE[Question ID = 58]

1. BE statistics is for particles with integral spin. [Option ID = 229]
2. BE statistics can be applied to photons. [Option ID = 230]
3. Bosons obey Pauli's Exclusion Principle. [Option ID = 231]
4. The wave function of bosons is symmetric. [Option ID = 232]

9) The equation for the evaluation of  $\beta$  in the Maxwell-Boltzmann distribution law is

[Question ID = 59]

1.  $\beta = 1/kT$ .

[Option ID = 233]

2.  $\beta = -1/kT$ .

[Option ID = 234]

3.  $\beta = kT$ .

[Option ID = 235]

4.  $\beta = 2/kT$ .

[Option ID = 236]

10) According to the Debye-Hückel limiting law, if the concentration of a dilute aqueous solution of KCl is increased 4-fold, the value of  $\log \gamma_{\pm}$  will

[Question ID = 60]

1. decrease by a factor of 2

[Option ID = 237]

2. increase by a factor of 2

[Option ID = 238]

3. decrease by a factor of 4

[Option ID = 239]

4. increase by a factor of 4

[Option ID = 240]

11) In the first excited state,  $S_1$ , acetylene has a *trans* bent configuration compared to its linear  $S_0$  ground state, and its CC bond length also increases from 1.21 Å to 1.34 Å. The  $S_1 \leftarrow S_0$  absorption spectrum will show

[Question ID = 61]

1. no vibrational coarse structure.

[Option ID = 241]

2. a sharp peak.

[Option ID = 242]

3. a continuum.

[Option ID = 243]

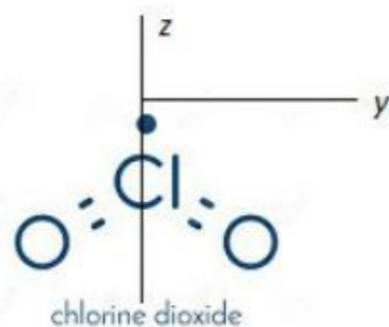
4. a broad vibrational progression.

[Option ID = 244]

12)  $\text{ClO}_2$  molecule was trapped in a solid. Its ground electronic state is known to be  $B_1$ . Light polarized parallel to the y-axis excited the molecule to an upper state. The upper state is

Character table for  $C_{2v}$  point group

	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	linear, rotations	quadratic
$A_1$	1	1	1	1	z	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	xy
$B_1$	1	-1	1	-1	x, $R_y$	xz
$B_2$	1	-1	-1	1	y, $R_x$	yz



[Question ID = 62]

1.  $A_1$

[Option ID = 245]

2.  $A_2$

[Option ID = 246]

3.  $B_1$

[Option ID = 247]

4.  $B_2$

[Option ID = 248]

13) The term symbol for the ground state of  $B_2^+$  is  $^2\Sigma_g^+$ . The total spin and total orbital angular momentum are, respectively,

[Question ID = 63]

1.  $\frac{1}{2}, 0$

[Option ID = 249]

2.  $\frac{3}{4}, 0$

[Option ID = 250]

3.  $\sqrt{3}/2, 0$

[Option ID = 251]

4. 2, 1

[Option ID = 252]

14) Interpret the observed IR and Raman frequencies for an  $\text{XY}_2$  molecule

$\text{V}/\text{CM}^{-1}$	IR	Raman
2224	vs, PR	s, depol
1285	vs, PR	vs, pol
568	s, PQR	-

The structure is

[Question ID = 64]

1. linear  $\text{XYY}$

[Option ID = 253]

2. linear  $\text{YXY}$

[Option ID = 254]

3. bent  $\text{XYY}$

[Option ID = 255]

4. bent  $\text{YXY}$

[Option ID = 256]

15) Assuming that the force constants of double and triple bonds are roughly two and three times, respectively, that of single bonds, the ratio of the stretching frequencies of the C-C, C=C and  $\text{C}\equiv\text{C}$  bonds is

[Question ID = 65]

1. 1:2:3

[Option ID = 257]

2. 1:1.4:1.7

[Option ID = 258]

3. 3:2:1

[Option ID = 259]

4. 1:4:9

[Option ID = 260]

16) The mean time for the  $2p \rightarrow 1s$  spectral transition is  $1.6 \times 10^{-9}$  s, while the mean time for the  $2s \rightarrow 1s$  transition is 0.14 s. This is because

[Question ID = 66]

1. the  $2p \rightarrow 1s$  transition is forbidden, but  $2s \rightarrow 1s$  is allowed.

[Option ID = 261]

2. the  $2p \rightarrow 1s$  transition is allowed, but  $2s \rightarrow 1s$  is forbidden.

[Option ID = 262]

3. the  $2p \rightarrow 1s$  transition is allowed, and  $2s \rightarrow 1s$  is also allowed.

[Option ID = 263]

4. the  $2p \rightarrow 1s$  transition is forbidden, and the  $2s \rightarrow 1s$  transition is also forbidden.

[Option ID = 264]

17) The vibrations of diatomic molecules are usually modelled by a harmonic potential. If the potential is given by  $x^2$ , the correct statement is:

[Question ID = 67]

1. The force constant is 2 and the force is  $2x$ .

[Option ID = 265]

2. The force constant is 2 and the force is  $-2x$ .

[Option ID = 266]

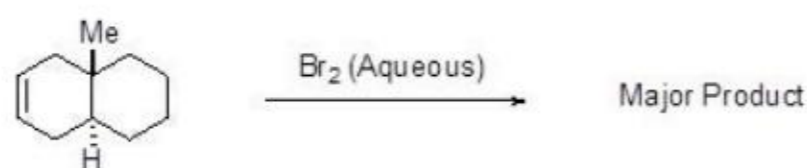
3. The force constant is  $-1$  and the force is  $-2x$ .

[Option ID = 267]

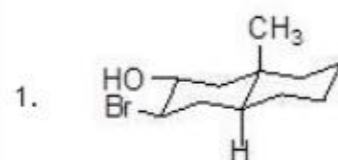
4. The force constant is 1 and the force is  $2x$ .

[Option ID = 268]

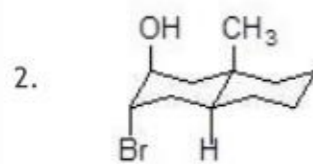
18) Major product of the following reaction is:



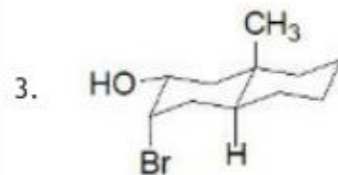
[Question ID = 68]



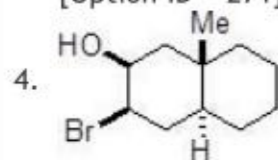
[Option ID = 269]



[Option ID = 270]



[Option ID = 271]



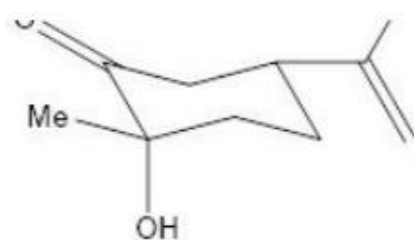
[Option ID = 272]

19) Which of the following conformer(s) will predominate(s) in dimethylsulfoxide (DMSO) solvent?

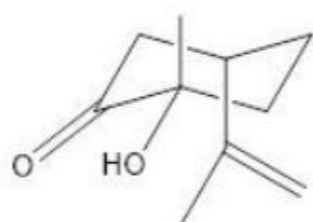
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/

Me



(A)



(B)

[Question ID = 69]

1. (B) only

[Option ID = 273]

2. (A) only

[Option ID = 274]

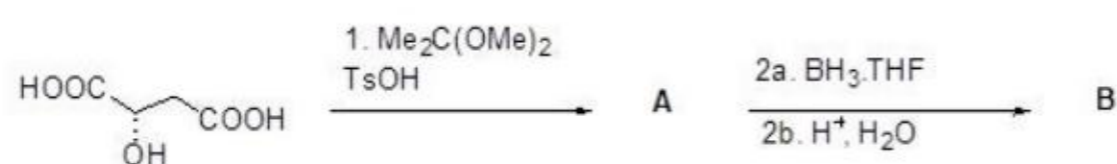
3. (B) is 50% and (A) is 50 %

[Option ID = 275]

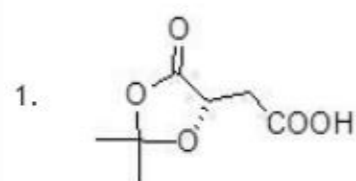
4. (B) is 78% and (A) is 22%

[Option ID = 276]

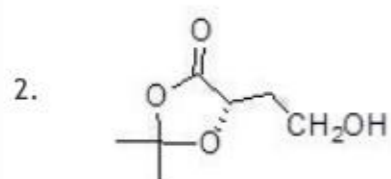
20) Consider the following reaction:



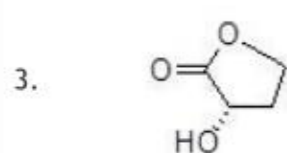
[Question ID = 70]



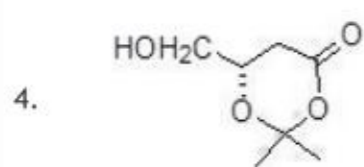
[Option ID = 277]



[Option ID = 278]



[Option ID = 279]



[Option ID = 280]

21) Which one of the following reducing reagents will not give below given product?



[Question ID = 71]

1. 9-Borobicyclo[3,3,1]nonane (9-BBN), THF, 0°C

[Option ID = 281]

2. NaBH<sub>4</sub>, CeCl<sub>3</sub>, MeOH

[Option ID = 282]

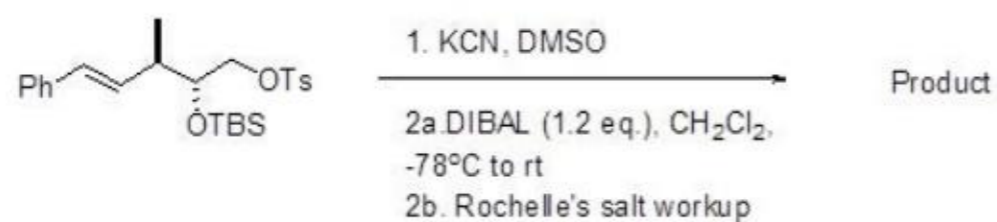
3.  $\text{LiAlH}(\text{OMe})_3$ , THF,  $0^\circ\text{C}$

[Option ID = 283]

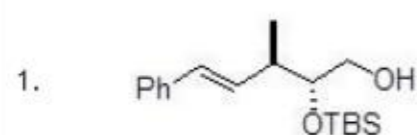
4.  $\text{NaBH}_4$ , EtOH,  $0^\circ\text{C}$

[Option ID = 284]

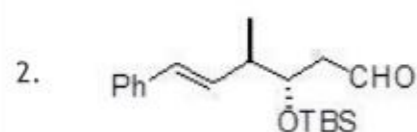
22) The major product formed in the following reaction is:



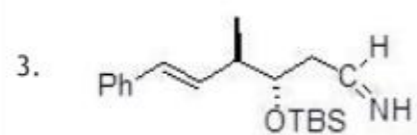
[Question ID = 72]



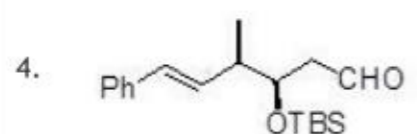
[Option ID = 285]



[Option ID = 286]

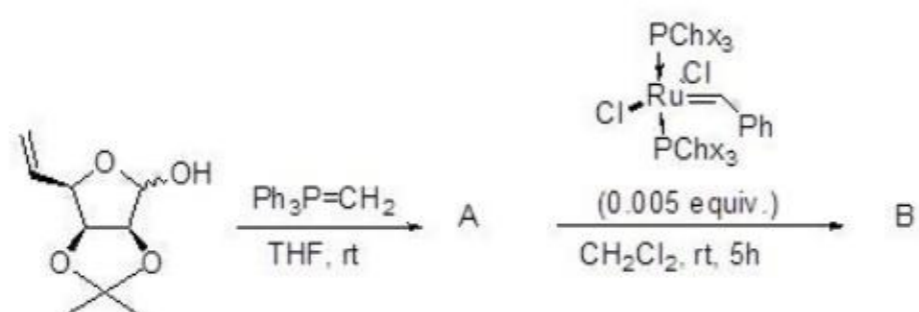


[Option ID = 287]



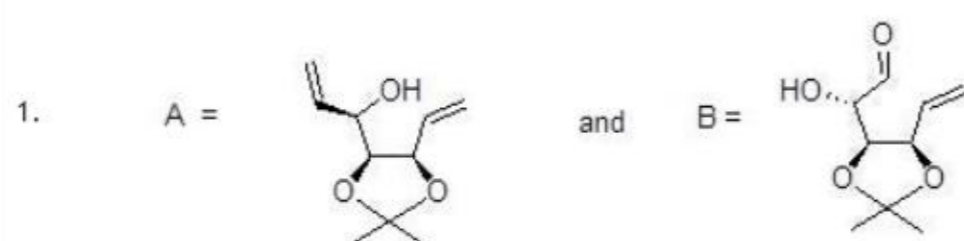
[Option ID = 288]

23) Consider the following reaction

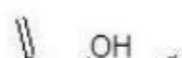


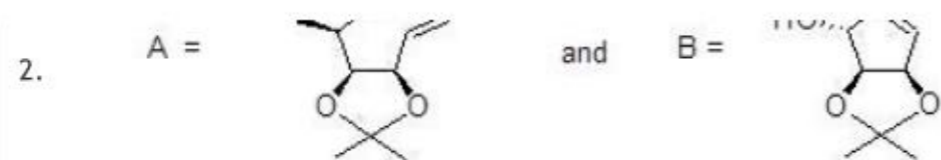
The products A and B are:

[Question ID = 73]

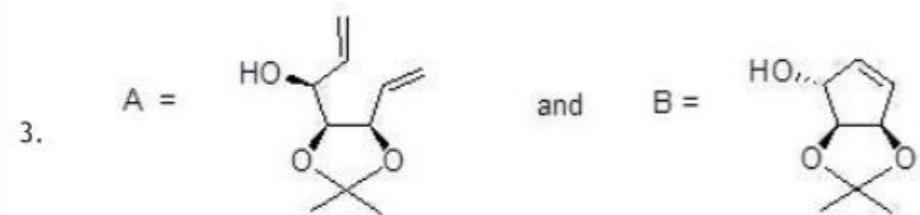


[Option ID = 289]

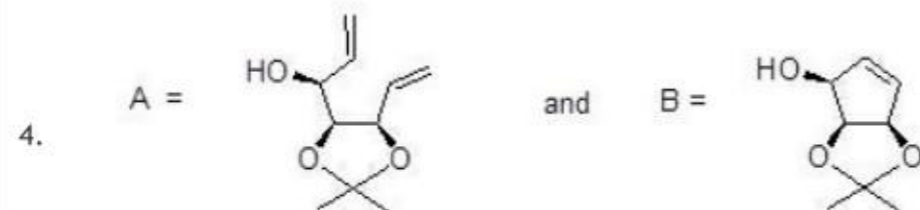




[Option ID = 290]

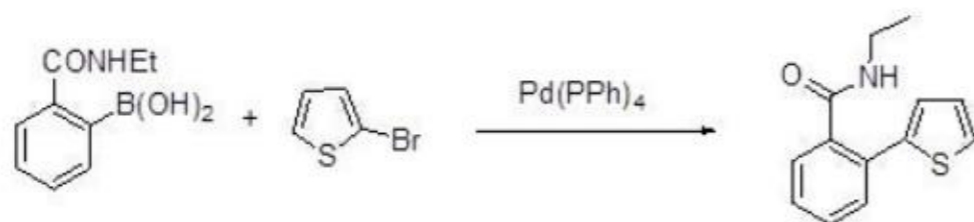


[Option ID = 291]



[Option ID = 292]

24) The following reaction is known as:



[Question ID = 74]

1. Suzuki reaction

[Option ID = 293]

2. Heck reaction

[Option ID = 294]

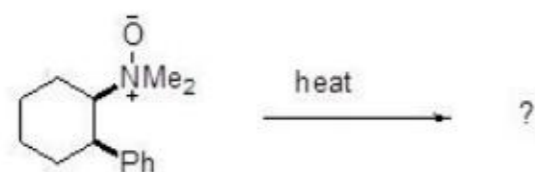
3. Stille coupling

[Option ID = 295]

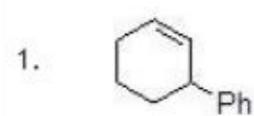
4. Sonogashira coupling

[Option ID = 296]

25) Which one of the following products will be major product in the below given reaction?



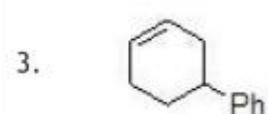
[Question ID = 75]



[Option ID = 297]

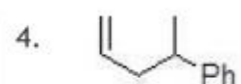


[Option ID = 298]



[Option ID = 299]





[Option ID = 300]

26) Which one of the following is suitable reagent for the below given reaction?



[Question ID = 76]

1.  $t\text{-BuOOH}$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$ , (+)-Diethyl tartrate

[Option ID = 301]

2.  $t\text{-BuOOH}$ , (+)-Diethyl tartrate

[Option ID = 302]

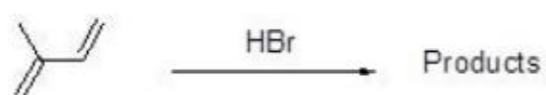
3.  $t\text{-BuOOH}$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$ , (-)-Diethyl tartrate

[Option ID = 303]

4.  $t\text{-BuOOH}$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$

[Option ID = 304]

27) Consider the following addition reaction:



The least favored product is:

[Question ID = 77]

1. 3-Bromo-3-methyl-1-butene

[Option ID = 305]

2. 1-Bromo-3-methyl-2-butene

[Option ID = 306]

3. 3-Bromo-2-methyl-1-butene

[Option ID = 307]

4. 4-Bromo-2-methyl-1-butene

[Option ID = 308]

28) Which one is the correct order of potential effectiveness as leaving group in the nucleophilic substitution reaction?



[Question ID = 78]

1. II > I > III > IV

[Option ID = 309]

2. I > III > II > IV

[Option ID = 310]

3. IV > II > III > I

[Option ID = 311]

4. III > I > II > IV

[Option ID = 312]

29) Nitration of cinnamic acid will give the product(s):

[Question ID = 79]

1. 2-Nitro-cinnamic acid only

[Option ID = 313]

2. 3-Nitro-cinnamic acid only

[Option ID = 314]

3. 4-Nitro-cinnamic acid only



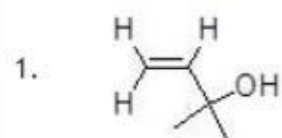
[Option ID = 315]

4. 2-nitro-cinnamic acid and 4-nitro-cinnamic acid formed more than 3-nitro-cinnamic acid

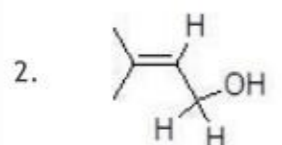
[Option ID = 316]

30) An organic compound having molecular formula  $C_5H_{10}O$  and it shows peak at  $3410\text{ cm}^{-1}$  in FT-IR.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.05$  (dd, 1H),  $5.02$  (dd, 1H),  $4.09$  (dd, 1H),  $2.80$  (s,  $\text{D}_2\text{O}$  exchangeable),  $1.3$  (s, 6H) ppm.  $^{13}\text{C-NMR}$ :  $\delta = 150, 110, 70, 29$  ppm. Dept-135:  $\delta = 150(+), 110(-), 29(+)$ . The structure of the compound will be:

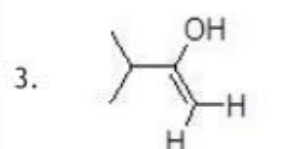
[Question ID = 80]



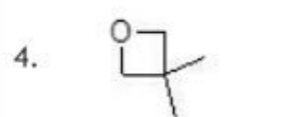
[Option ID = 317]



[Option ID = 318]



[Option ID = 319]



[Option ID = 320]

31) Cyclohexanone and cyclopentanone give one common  $m/z$  base peak. The value of the peak in  $m/z$  is:

[Question ID = 81]

1. 84

[Option ID = 321]

2. 42

[Option ID = 322]

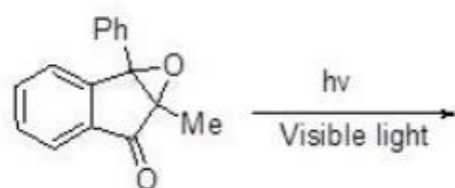
3. 55

[Option ID = 323]

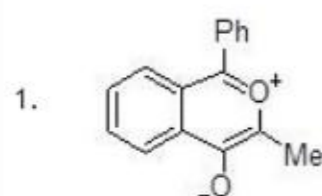
4. 83

[Option ID = 324]

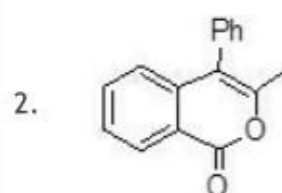
32) The principal product of the following reaction is:



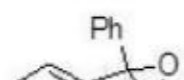
[Question ID = 82]

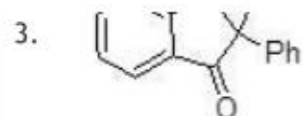


[Option ID = 325]

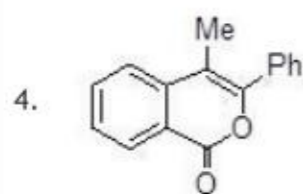


[Option ID = 326]



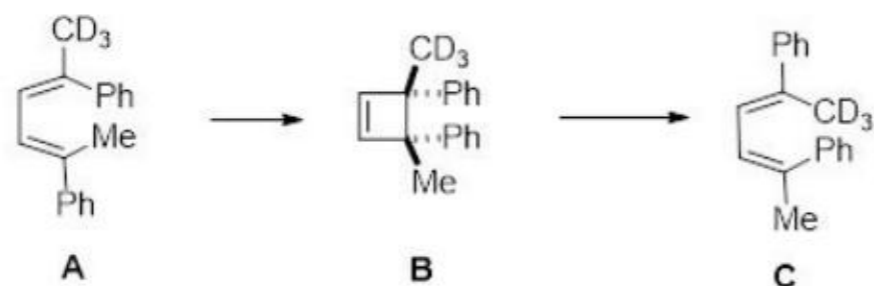


[Option ID = 327]



[Option ID = 328]

33) In the following reaction A and C are interconverted under thermal conditions through cyclobutane B.



[Question ID = 83]

1. Ring closure of A and ring opening of B both will be conrotatory processes

[Option ID = 329]

2. Ring closure of A will be disrotatory process and ring opening of B will be conrotatory process

[Option ID = 330]

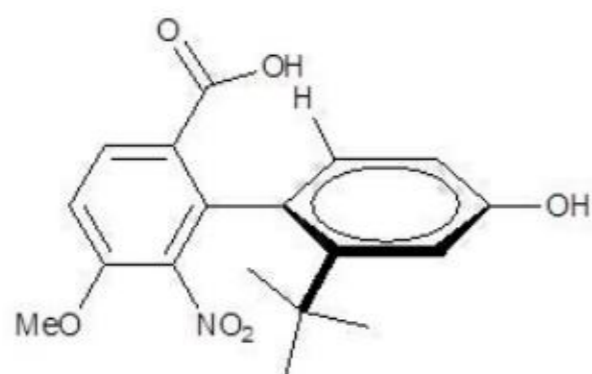
3. Ring closure of A and ring opening of B both will be disrotatory processes

[Option ID = 331]

4. Ring closure of A will be conrotatory process and ring opening of B will be disrotatory process

[Option ID = 332]

34) The absolute configuration of below given compounds will be:



[Question ID = 84]

1. R

[Option ID = 333]

2. S

[Option ID = 334]

3. R, S

[Option ID = 335]

4. S, S

[Option ID = 336]

35) Which ordering correctly shows the variation in rates of water exchange in high spin aqua complexes  $[M(OH_2)_6]$ ?

[Question ID = 85]

1.  $Co^{2+} > Cr^{2+}$

[Option ID = 337]

2.  $V^{2+} > Co^{2+}$

[Option ID = 338]

3.  $Cr^{3+} > Fe^{3+}$

[Option ID = 339]

4.  $Cr^{2+} > Cr^{3+}$

[Option ID = 340]

36) The principal axis  $C_4$  is present in

[Question ID = 86]

1.  $BF_3$

[Option ID = 341]

2.  $SnO_2$

[Option ID = 342]

3.  $BrF_5$

[Option ID = 343]

4.  $C_6H_6$

[Option ID = 344]

37) Which one of the following sentence is false about EDTA?

[Question ID = 87]

1. Alkali medium is required for complexation because EDTA will ionize better in alkali medium.

[Option ID = 345]

2. EDTA form complexes with all metal ions.

[Option ID = 346]

3. Solubility of EDTA is lower than its disodium counterpart.

[Option ID = 347]

4. Alkali medium is required for complexation because EDTA will ionize more in acidic medium.

[Option ID = 348]

38) The non-covalent interaction present in the  $Na^+$  -crown ether complex is due to,

[Question ID = 88]

1. ion-ion

[Option ID = 349]

2. ion-dipole

[Option ID = 350]

3. dipole-dipole

[Option ID = 351]

4. hydrogen bonding

[Option ID = 352]

39) The series identifying the thiophilic heavy metal ions,

[Question ID = 89]

1.  $Cu^{1+}$ ,  $Hg^{2+}$ ,  $Tl^{1+}$

[Option ID = 353]

2.  $Ti^{4+}$ ,  $La^{3+}$ ,  $Si^{4+}$

[Option ID = 354]

3.  $V^{5+}$ ,  $Te^{6+}$ ,  $Y^{3+}$

[Option ID = 355]

4.  $Nb^{5+}$ ,  $Sc^{3+}$ ,  $B^{3+}$

[Option ID = 356]

40) A metal X on heating in nitrogen gas gives Y. Y on treatment with  $H_2O$  gives a colourless gas which when passed through  $CuSO_4$  solution gives blue colour. Y is

[Question ID = 90]

1.  $Mg(NO_3)_2$

[Option ID = 357]

2.  $Mg_3N_2$

[Option ID = 358]

3.  $MgCl_2$

[Option ID = 359]

4.  $MgO$

[Option ID = 360]

41) Which of the following statement is true for the diffraction pattern in the crystal lattice?

[Question ID = 91]

1. Diffraction patterns are linear space.

[Option ID = 361]

2. Diffraction patterns possess a center of symmetry

[Option ID = 362]

3. Diffraction pattern does not have center of symmetry

[Option ID = 363]

4. Diffraction patterns contain  $\alpha$ -rays.

[Option ID = 364]

42) Which is the sequence showing the correct order of increasing intensity for the d-d transition?

[Question ID = 92]

1.  $\text{CoCl}_4^{2-} > [\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{NH}_3)_6]^{2+} > [\text{Co}(\text{H}_2\text{O})_6]^{2+}$

[Option ID = 365]

2.  $[\text{Co}(\text{H}_2\text{O})_6]^{2+} > [\text{Co}(\text{NH}_3)_6]^{3+} > \text{CoCl}_4^{2-} > [\text{Co}(\text{NH}_3)_6]^{2+}$

[Option ID = 366]

3.  $[\text{Co}(\text{NH}_3)_6]^{2+} > [\text{Co}(\text{H}_2\text{O})_6]^{2+} > \text{CoCl}_4^{2-} > [\text{Co}(\text{NH}_3)_6]^{3+}$

[Option ID = 367]

4.  $[\text{Co}(\text{NH}_3)_6]^{3+} > [\text{Co}(\text{NH}_3)_6]^{2+} > \text{CoCl}_4^{2-} > [\text{Co}(\text{H}_2\text{O})_6]^{2+}$

[Option ID = 368]

43) The equilibrium shift towards the products in  $\text{Cr}_2\text{O}_7^{2-} \rightleftharpoons \text{CrO}_4^{2-}$

[Question ID = 93]

1. occurs in acidic medium

[Option ID = 369]

2. occurs in basic medium

[Option ID = 370]

3. occurs in neutral medium

[Option ID = 371]

4. does not exist

[Option ID = 372]

44) Which one of the following ion shows kinetic masking?

[Question ID = 94]

1.  $\text{Co}^{2+}$

[Option ID = 373]

2.  $\text{Cu}^{2+}$

[Option ID = 374]

3.  $\text{Cr}^{3+}$

[Option ID = 375]

4.  $\text{Fe}^{3+}$

[Option ID = 376]

45) The  $p^5$  electronic configuration is equivalent to the term in ground state

[Question ID = 95]

1.  $^3P$

[Option ID = 377]

2.  $^2P$

[Option ID = 378]

3.  $^3F$

[Option ID = 379]

4.  $^4P$

[Option ID = 380]

46) The molecule which has an inversion center and  $S_6$ -axis is

[Question ID = 96]

1. Chlorobenzene

[Option ID = 381]

2. p-dichlorobenzene

[Option ID = 382]

3. 1,3, 5- trichlorobenzene

[Option ID = 383]

4. Chair form of cyclohexane

[Option ID = 384]

47) The type of intermolecular interaction present in the herring bone packing of benzene,

[Question ID = 97]

1. Cation -  $\pi$

[Option ID = 385]

2. anion -  $\pi$

[Option ID = 386]

3. dipole-ion

[Option ID = 387]

4.  $\pi$  -  $\pi$

[Option ID = 388]

48) Which one of the following statement is correct?

[Question ID = 98]

1. A dissociative mechanism is a 2-step mechanism with the leaving group departing in the second step.

[Option ID = 389]

2. An associative mechanism is a 2-step mechanism; the intermediate has a lower coordination number than the starting complex.

[Option ID = 390]

3. In a dissociative interchange mechanism, bond breaking dominates over bond formation

[Option ID = 391]

4. In an associative interchange mechanism, the entering group associates with the substrate after the leaving group has departed.

[Option ID = 392]

49) Which one of the following cannot show linkage isomerism?

[Question ID = 99]

1.  $\text{Cl}^-$

[Option ID = 393]

2.  $\text{SCN}^-$

[Option ID = 394]

3.  $\text{CN}^-$

[Option ID = 395]

4.  $\text{NH}_3$

[Option ID = 396]

50) Match List I with List II based on the molecular symmetry

List I	List II
Molecule	Point group
A. $(\text{Si}_4\text{O}_4)^{4-}$	I. $C_{2v}$
B. $\text{Hg}_2\text{Cl}_2$	II. $C_{3v}$
C. $\text{SeCl}_3^+$	III. $D_{\infty h}$
D. $\text{NO}_2\text{F}$ (N-central metal atom)	IV. $T_d$

Choose the correct answer from the options given below:

[Question ID = 100]

1. A - III, B - I, C - IV, D - II

[Option ID = 397]

2. A - II, B - III, C - I, D - II

[Option ID = 398]

3. A - IV, B - I, C - III, D - II

[Option ID = 399]

4. A - IV, B - III, C - II, D - I

[Option ID = 400]