

ENTRANCE EXAMINATIONS – 2022

B-6

Ph.D. Chemistry

TIME: 2 HOURS

MAXIMUM MARKS: 70

HALL 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 - 26** are present (excluding **4** 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** for both Part-A and Part-B.
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.
9. No additional sheets will be provided. Rough work can be done in the space provided at the end of the booklet.
10. Calculators are allowed. Cell phones are not allowed.
11. Useful constants are provided just above Part-A in the question paper.
12. OMR without hall ticket number will not be evaluated and University shall not be held responsible.

**Useful Constants:**

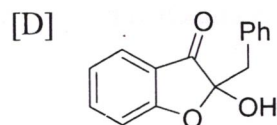
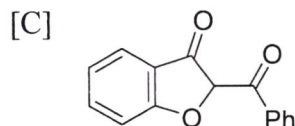
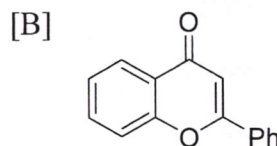
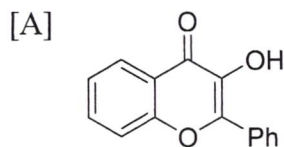
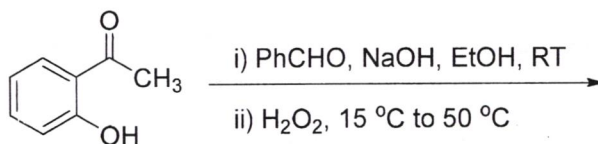
Rydberg constant =  $109737 \text{ cm}^{-1}$ ; Faraday constant =  $96500 \text{ C}$ ; Planck constant =  $6.625 \times 10^{-34} \text{ J s}$ ; Speed of light =  $2.998 \times 10^8 \text{ m s}^{-1}$ ; Boltzmann constant =  $1.380 \times 10^{-23} \text{ J K}^{-1}$ ; Gas constant =  $8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ ; Mass of electron =  $9.109 \times 10^{-31} \text{ kg}$ ; Mass of proton =  $1.672 \times 10^{-27} \text{ kg}$ ; Charge of electron =  $1.6 \times 10^{-19} \text{ C}$ ;  $1 \text{ bar} = 10^5 \text{ N m}^{-2}$ ;  $RT/F$  (at  $298.15 \text{ K}$ ) =  $0.0257 \text{ V}$ ; Avogadro number =  $6.022 \times 10^{23}$ ; amu =  $1.674 \times 10^{-27} \text{ kg}$ .

**PART-A**

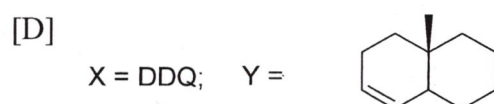
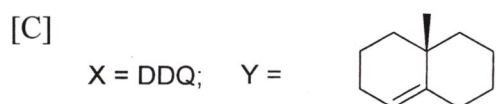
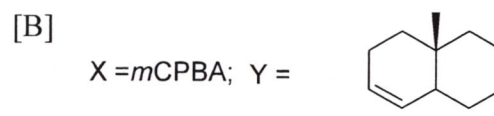
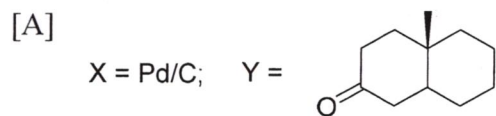
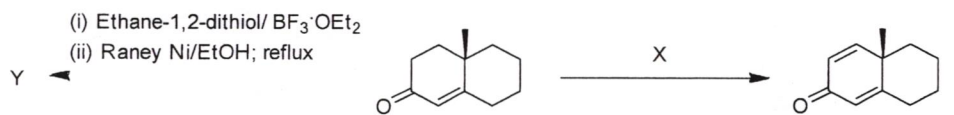
1. Identify the most appropriate name reactions for conversion of (i) benzaldehyde into styrene and (ii) phenol into salicylaldehyde

- |   |   |
|---|---|
| [A] (i) Wittig reaction<br>(ii) Prins reaction          | [B] (i) Wittig reaction<br>(ii) Reimer-Tiemann reaction |
| [C] (i) Reimer-Tiemann reaction<br>(ii) Wittig reaction | [D] (i) Reimer-Tiemann reaction<br>(ii) Prins reaction  |

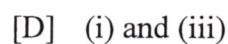
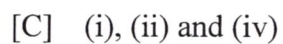
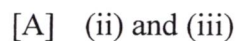
2. The major product obtained in the following reaction is:



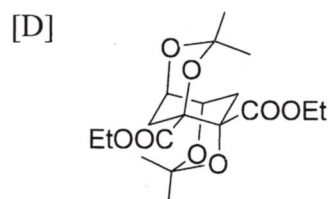
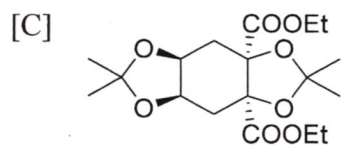
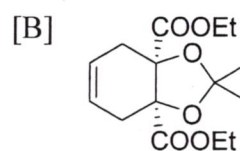
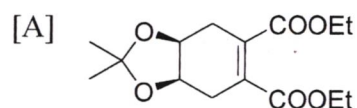
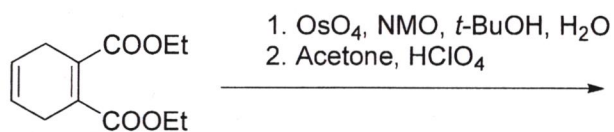
3. Identify the most appropriate reagent (X) and the product (Y) in the following reactions:



4. Identify the species that can act as a 1,3-dipole in cycloadditions:



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





9. Hypophosphorous acid molecule has

- [A] 4 lone pairs, 1  $\pi$  bond and 5  $\sigma$  bonds.
- [B] 5 lone pairs and 5  $\sigma$  bonds.
- [C] 6 lone pairs, 1  $\pi$  bond and 6  $\sigma$  bonds.
- [D] 7 lone pairs and 6  $\sigma$  bonds.

10. The compound *isolobal* to  $\text{Ni}(\text{CO})_2$  is:

- [A]  $[\text{Co}(\text{CO})_4]^+$
- [B]  $\text{Fe}(\text{CO})_4$
- [C]  $[\text{Ni}(\text{CO})_3]^+$
- [D]  $[\text{Cu}(\text{CO})_2]^+$

11. The lowest formal oxidation state of iron is found in

- [A]  $[\text{CpFe}(\text{CO})_2]_2$
- [B]  $\text{K}_4[\text{Fe}(\text{CN})_6]$
- [C]  $\text{Na}_2[\text{Fe}(\text{CO})_4]$
- [D]  $\text{Fe}(\text{CO})_5$

12. Coulometry refers to:

- [A] Determination of quantity of analyte using Faraday's law when the reaction proceeds at 100% current efficiency.
- [B] Determination of quantity of analyte using half-wave potential.
- [C] Qualitative determination of elements using half-wave potential.
- [D] Quantitative determination of metals deposited on electrodes in an electrolytic process.

13. The metalloprotein oxyhemocyanin contains

- [A]  $\text{Co}(\text{II})$  and  $\text{O}_2^{2-}$
- [B]  $\text{Cu}(\text{II})$  and  $\text{O}_2^{2-}$
- [C]  $\text{Co}(\text{IV})$  and  $\text{O}_2^-$
- [D]  $\text{Fe}(\text{III})$  and  $\text{O}_2^{2-}$

14. The most appropriate statement about valinomycin is:

- [A] It is an acyclic oligopeptide capable of binding  $K^+$
- [B] It is a cyclic oligopeptide capable of binding  $K^+$
- [C] It is an acyclic oligopeptide capable of binding  $Cl^-$
- [D] It is a cyclic oligopeptide capable of binding  $Cl^-$

15. Among  $N_2$ ,  $H_2O$ ,  $CH_3CH_3$  and  $CH_2Cl_2$ , pure vibrational spectrum will be shown by

- [A]  $N_2$ ,  $H_2O$  and  $CH_2Cl_2$
- [B]  $H_2O$  and  $CH_2Cl_2$
- [C]  $H_2O$ ,  $CH_3CH_3$  and  $CH_2Cl_2$
- [D]  $H_2O$

16. The commutator  $2\pi[x, p_x]$  equals to

- [A]  $i\hbar$
- [B]  $-i\hbar$
- [C]  $ih$
- [D]  $-\hbar$

17. For a first-order reaction,  $2A \rightarrow \text{Products}$ , the expression for  $[A]$  is:

(Here,  $k$ : rate constant,  $t$ : time,  $[A]_0$ : initial concentration)

- [A]  $[A] = [A]_0 \exp(-kt/2)$
- [B]  $[A] = 2[A]_0 \exp(-kt)$
- [C]  $[A] = 2[A]_0 \exp(-2kt)$
- [D]  $[A] = [A]_0 \exp(-2kt)$

18. The value of the rotational partition function for a structureless particle is:

- [A] 0
- [B] 1
- [C]  $\ln 2$
- [D] Infinite

19. The single equivalent symmetry operation for  $S_6^3$  is:

[A]  $C_3$

[B]  $\sigma_h$

[C]  $E$

[D]  $i$

20. The rotational symmetry number for water is:

[A] 0

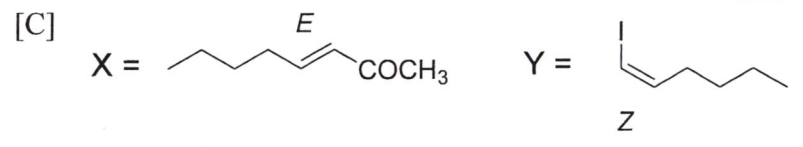
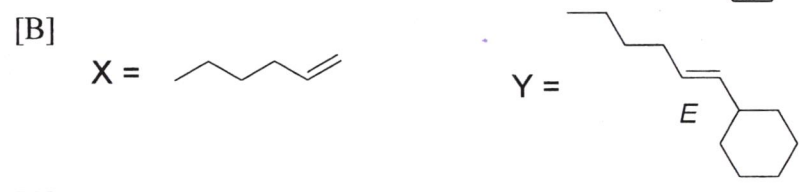
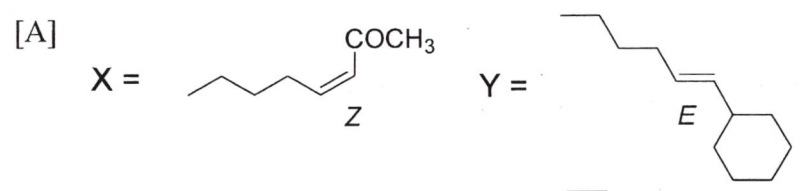
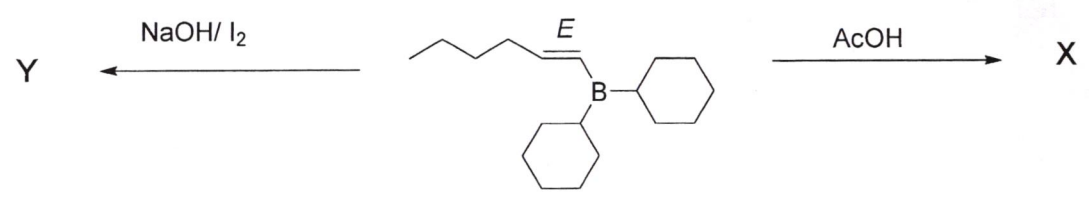
[B] 1

[C] 2

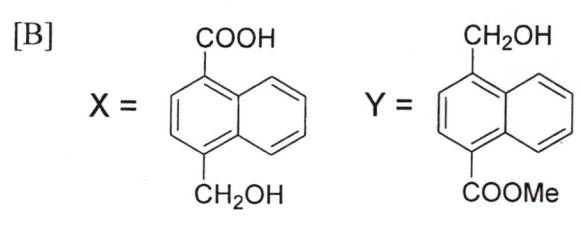
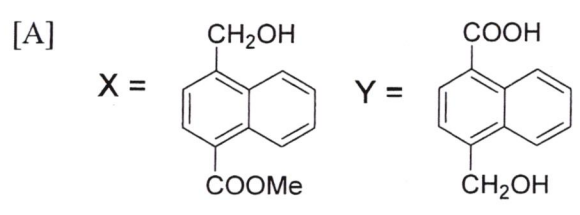
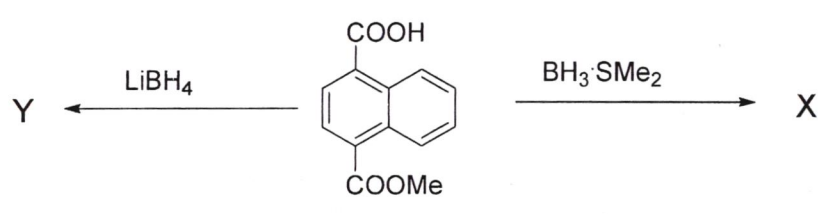
[D] 3

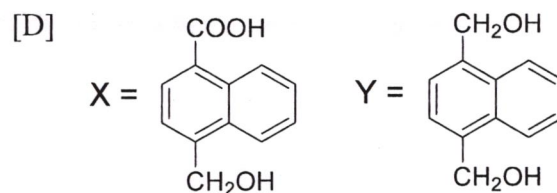
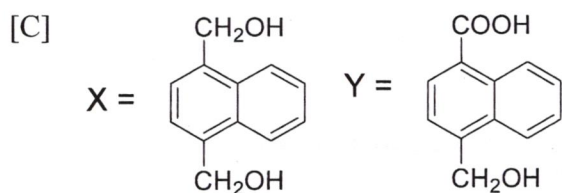
**PART - B**

21. Identify X and Y in the following reactions

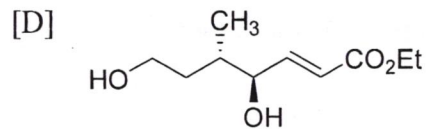
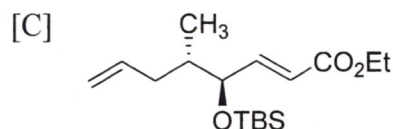
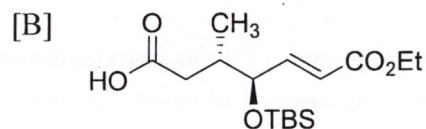
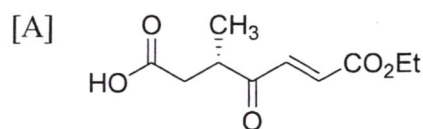
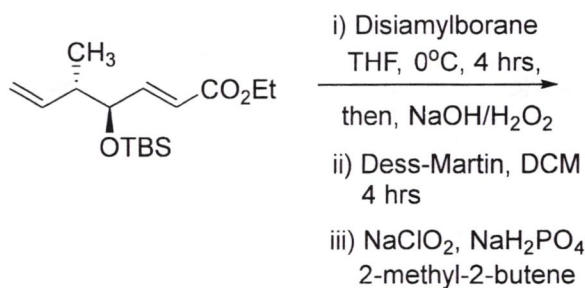


22. Identify X and Y in the following reactions

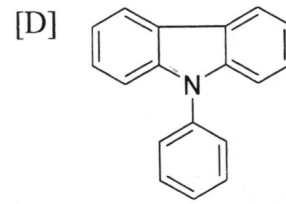
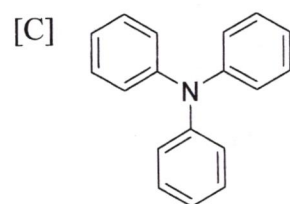
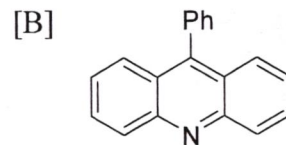
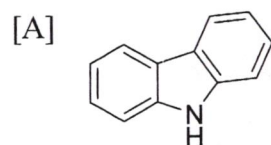




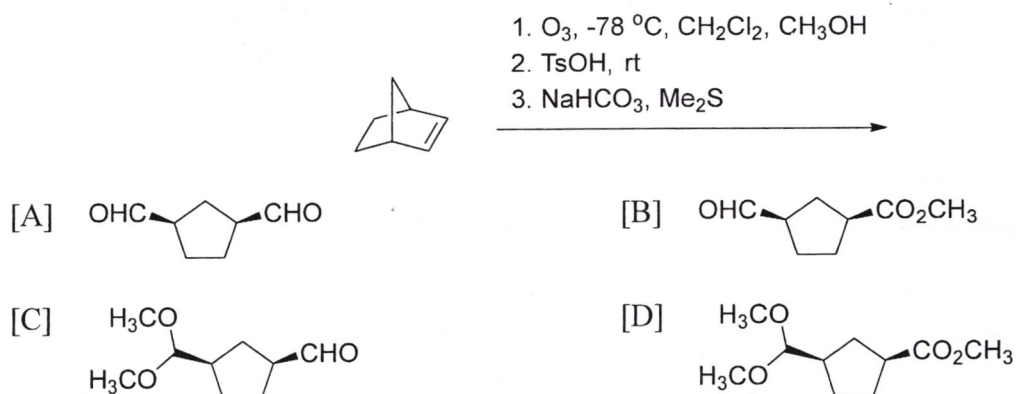
23. The major product formed in the following reaction is:



24. The major product obtained by the reaction of diphenylamine with benzoic acid in the presence of  $\text{ZnCl}_2$  at  $230^\circ\text{C}$  is:



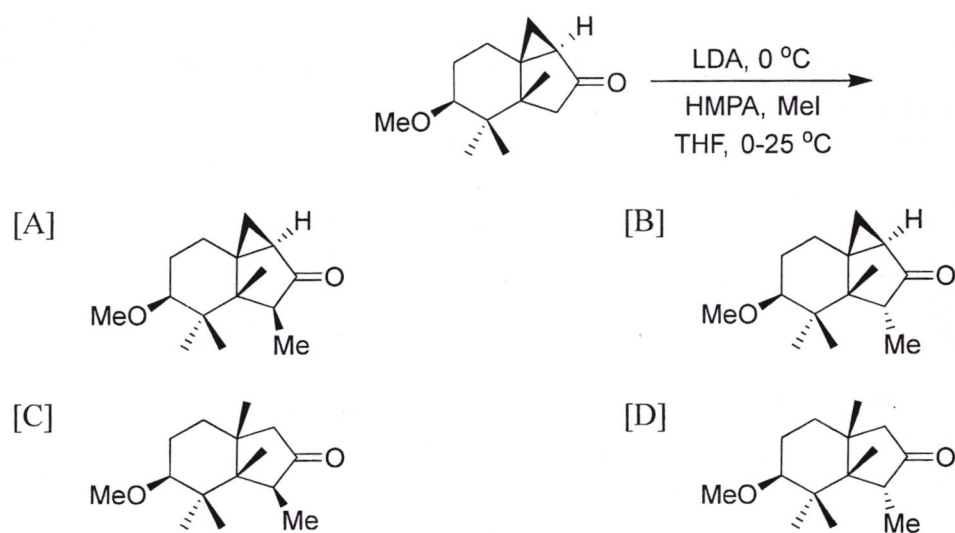
25. The major product formed in the following reaction is:



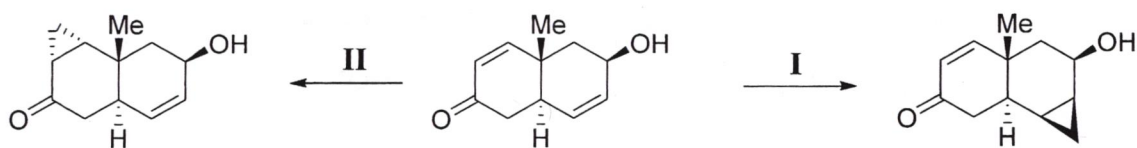
26. The biosynthetic precursor for the hormone serotonin and natural camphor respectively are:

- [A] tryptophan and linaloyl pyrophosphate
- [B] phenylalanine and neryl pyrophosphate
- [C] glycine and chrysanthemyl pyrophosphate
- [D] dopamine and farnesyl pyrophosphate

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

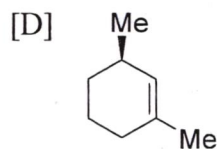
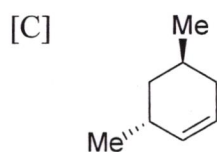
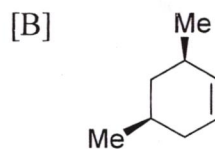
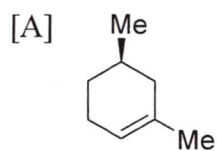
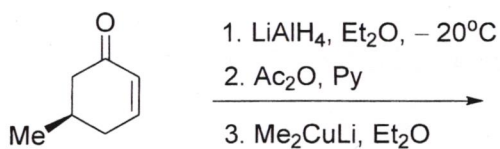


28. The reagents I and II in the following reactions are

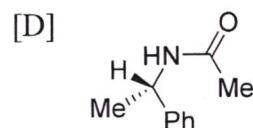
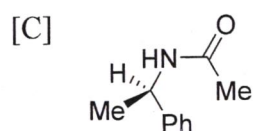
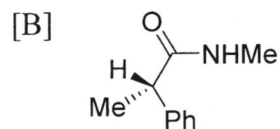
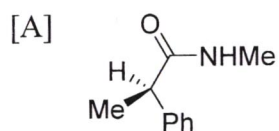
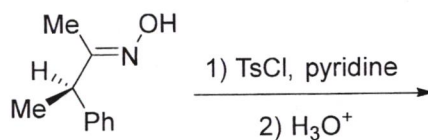


- [A] I =  $\text{CH}_2\text{I}_2$ , Zn-Cu; II =  $\text{Me}_3\text{S}^+\text{I}^-$ , NaH  
 [B] I =  $\text{CH}_2\text{I}_2$ , Zn-Cu; II =  $\text{Me}_3\text{S}^+(\text{O})\text{I}^-$ , NaH  
 [C] I =  $\text{Me}_3\text{S}^+(\text{O})\text{I}^-$ , NaH; II =  $\text{Me}_3\text{S}^+\text{I}^-$ , NaH  
 [D] I =  $\text{Me}_3\text{S}^+(\text{O})\text{I}^-$ , NaH; II =  $\text{CH}_2\text{I}_2$ , Zn-Cu

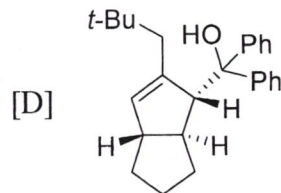
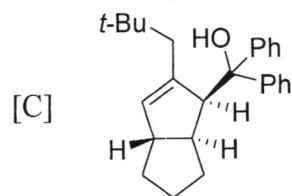
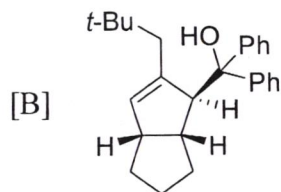
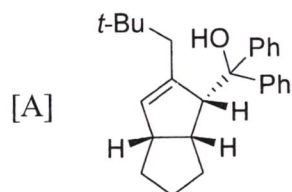
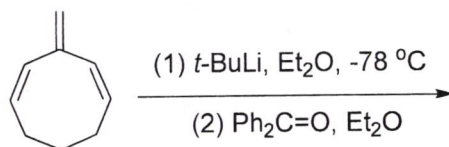
29. The major product formed in the following reaction is:



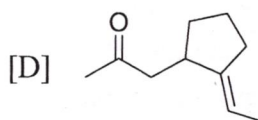
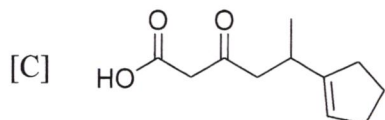
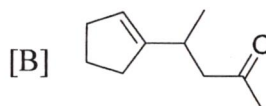
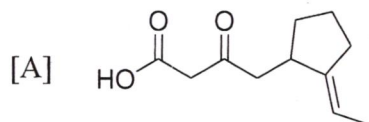
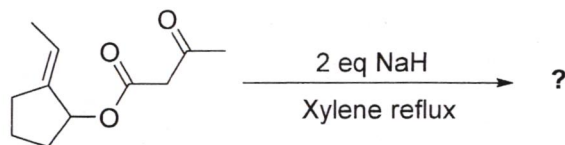
30. The major product formed in the following reaction is:



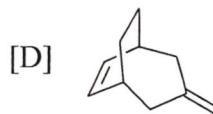
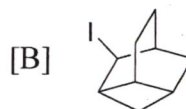
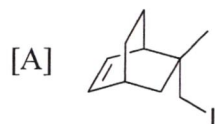
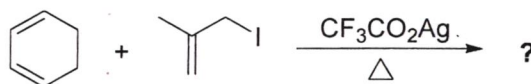
31. The major product formed in the following reaction is:



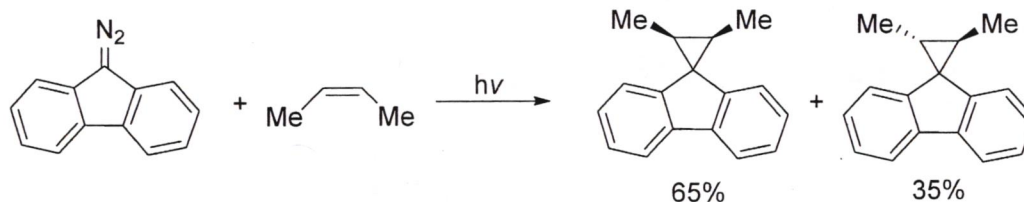
32. The major product formed in the following reaction is:



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

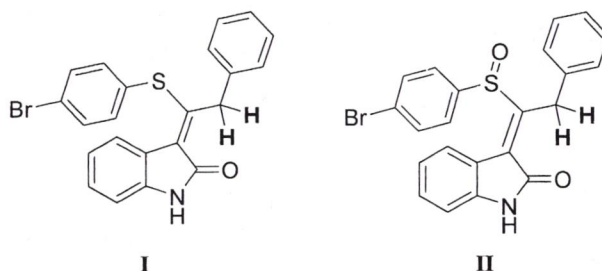


34. The reaction intermediate involved in the following reaction is a



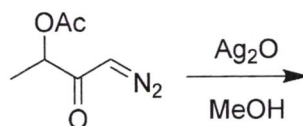
- [A] singlet carbene  
 [B] radical  
 [C] carbanion  
 [D] triplet carbene

35. The relation between the benzylic protons (marked bold) in the following compounds I and II are respectively:



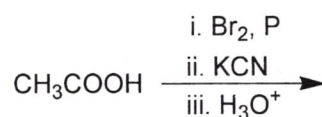
- [A] homotopic and enantiotopic  
 [B] enantiotopic and enantiotopic  
 [C] enantiotopic and diastereotopic  
 [D] diastereotopic and enantiotopic

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



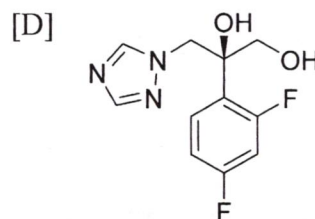
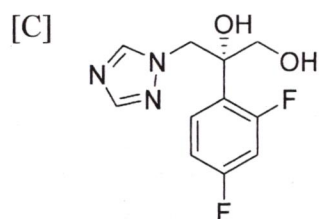
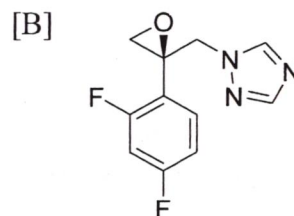
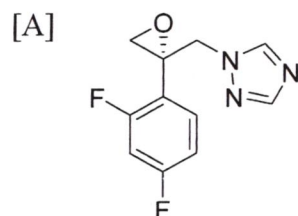
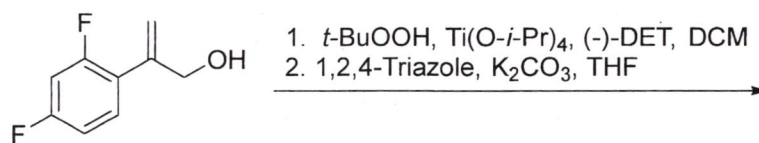
- [A] [B]   
 [C] [D]

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

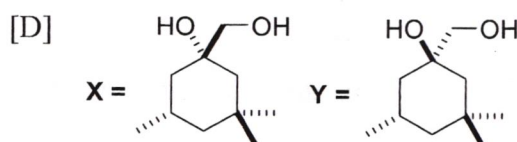
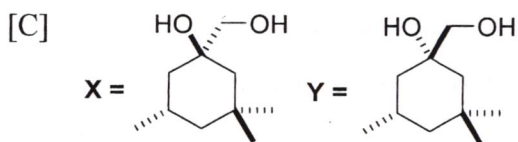
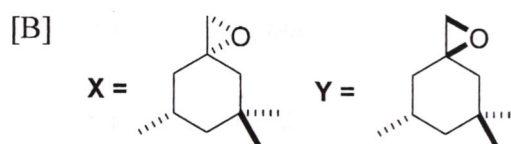
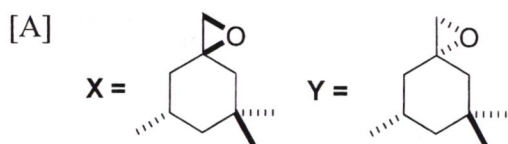
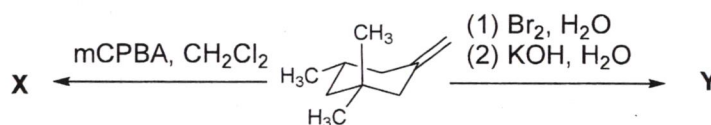


- [A] Succinic acid [B] Malonic acid  
 [C] Glycolic acid [D]  $\alpha$ -Hydroxypropionic acid

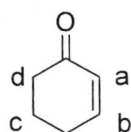
38. The major product formed in the following reaction sequence is:



39. The major products X and Y formed in the following reactions are:



40. Identify the most appropriate chemical shifts (i to iv) to the labelled carbons (a to d) of the given compound from the following list:



- (i)  $\delta$  25.7
- (ii)  $\delta$  38.1
- (iii)  $\delta$  129.8
- (iv)  $\delta$  150.9

- [A] a – (iv); b – (iii); c – (ii); d – (i)
- [B] a – (iii); b – (iv); c – (ii); d – (i)
- [C] a – (iv); b – (iii); c – (i); d – (ii)
- [D] a – (iii); b – (iv); c – (i); d – (ii)

41. The experimental hydration energies of  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  were plotted against atomic numbers. A straight line passing through these points gave a value of  $-716$  kcal/mol as the hydration energy of  $\text{Ni}^{2+}$ . If the  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$  transition for  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  occurs at  $8650$   $\text{cm}^{-1}$ , calculate the expected hydration energy of  $\text{Ni}^{2+}$  [ $1$  kcal/mol =  $350$   $\text{cm}^{-1}$ ].

- [A]  $-666$  kcal/mol
- [B]  $-686$  kcal/mol
- [C]  $-746$  kcal/mol
- [D]  $-766$  kcal/mol

42. Trigonal-bipyramidal complex of formula  $[\text{M}(\text{A}-\text{A})\text{B}_2\text{X}]$  (A–A represents a symmetrical bidentate ligand and B and C represent two different monodentate ligands) can have

- [A] 3 geometrical isomers and one of them will be optically active.
- [B] 4 geometrical isomers and 2 of them will be optically active.
- [C] 3 geometrical isomers and 2 of them will be optically active.
- [D] 4 geometrical isomers and one of them will be optically active.