

CSM – 17/20
Chemistry
Paper – II

Time : 3 hours

Full Marks : 300

The figures in the right-hand margin indicate marks.

*Candidates should attempt Q. No. 1 from Section – A and Q. No. 5 from Section – B which are compulsory and any **three** of the remaining questions, selecting at least **one** from each Section.*

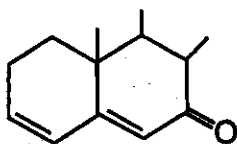
SECTION – A

1. Answer any **three** questions of the following :

20×3 = 60

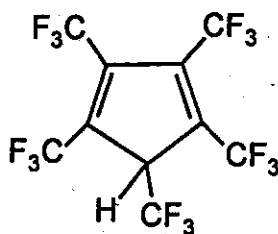
- (a) (i) What is Homo-Aromaticity ? Explain with example.
- (ii) Prepare benzyl radical and write the formation of a resonance stabilized benzyl radical.

- (iii) Discuss the prominent peaks in the mass spectrum of benzene.
- (iv) Explain the stereochemistry of E_2 -elimination.
- (b) (i) Write a short note on Hoffmann Rearrangement.
- (ii) Suggest the mechanism for the following conversions :
- (A) Ester \rightarrow β -keto product
- (B) Carbonyl compound \rightarrow α , β -unsaturated acids
- (iii) The observed value of λ_{\max} of the following compound is 280nm. Explain.

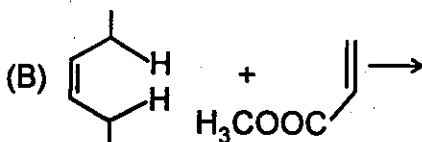
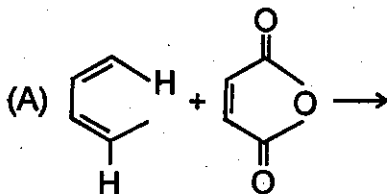


- (iv) How will you prepare pyrrole from succinic acid ?
- (c) (i) Explain Beckmann Rearrangement.

- (ii) What is the chemical shift ? Explain factors affecting chemical shifts.
- (iii) Why this compound is a stronger acid than nitric acid ?



- (iv) Give a brief note on synthetic rubbers.
- (d) (i) Write the product with the stereochemistry of the Diels-Alder reaction ?



- (ii) Calculate the theoretical number of vibrational degrees of freedom in :

- (A) Benzene
- (B) Carbon dioxide
- (C) H_2O

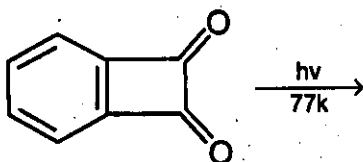
- (iii) Draw an energy profile diagram of the addition of HBr to propylene.
- (iv) Give a brief note on the example of the effect of isotopic substitution on the transition frequencies.

2. Answer the following questions as directed :

(a) Explain the following sentences : 10

(i) (A) Distinguish between bond energy and bond dissociation energy.

(B) Predict the product of the following reaction.



(ii) Predict the product of the following

(C) Why 2, 6-dimethylchlorobenzene does not undergo a nucleophilic aromatic substitution ?

(D) How will ICl add to $\text{Me}_2\text{C} = \text{CH}_2$?

(ii) How you will explain the following sentences ? 10

(A) Why does alcohol react with halide ions only in the presence of a strong acid ?

(B) Why does ethylene react with HCl faster than Vinyl chloride ?

(C) Name one polymer formed by step-growth polymerization. Give the name of its monomers.

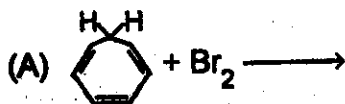
(D) Predict the product of the following reaction.



(b) Answer the following questions as directed :

5×4 = 20

- (i) Discuss the structure and stability of carbanion.
- (ii) Explain the Aromaticity of the following products.

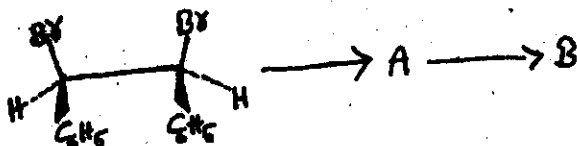


(iii) Benzene undergoes electrophilic substitution more easily than nucleophilic substitution why ?

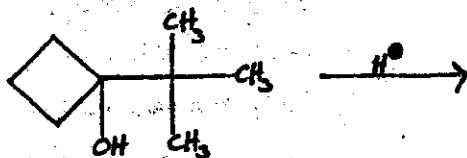
(iv) Discuss Cannizaro reaction.

(c) Predict the following reaction : 5×4 = 20

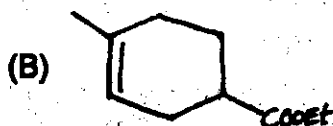
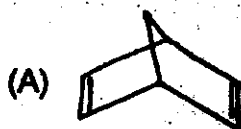
(i) Predict the product from the E₂ elimination of a given compound :



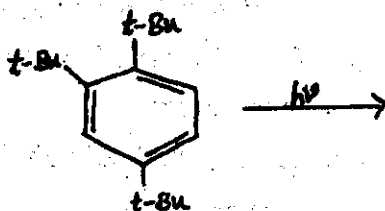
- (ii) Give the product and mechanism for the following reaction :



- (iii) Which diene and dienophile one would employ to synthesize the following compounds ?



- (iv) Predict the product of the following photochemical reaction.



3. (a) Answer the following questions as directed :

5×4 = 20

(i) What is Huckel's rule for Aromaticity ?

Give examples.

(ii) Write the reactions of :

(A) Reimer-Tiemann reaction

(B) Gatterman-Koch reaction

(iii) Discuss Hoffmann Elimination.

(iv) Write the names and structures of the monomers of the following polymers.

(A) buna-S

(B) Dacron

(b) Answer the following questions as directed :

5×4 = 20

(i) Write the reaction of photolysis of 2, 2'-azido biphenyl.

(ii) Explain why pyrrole, furan and thiophene are more reactive than benzene toward electrophilic aromatic substitution.

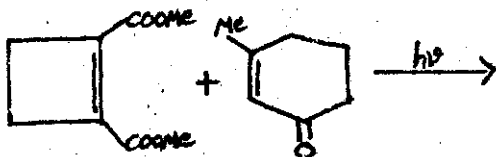
(iii) Give a brief note on the E_{1CB} mechanism.

(iv) Write a short note on Wagner-Meerwein rearrangement.

(c) Answer the following questions as directed :

5×4 = 20

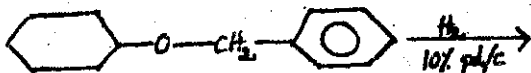
- (i) Predict the product and explain the mechanism of the following reaction.



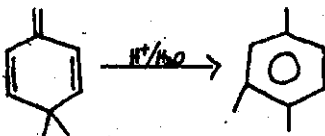
- (ii) Explain the following reaction with the mechanism.

Cyclohexanone \rightarrow Cyclohexane

- (iii) Predict the product of the following reaction.



- (iv) Write a mechanism for the following conversion.

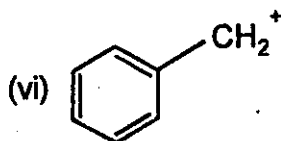
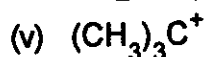
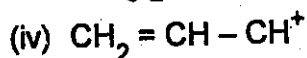
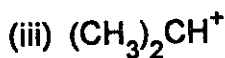
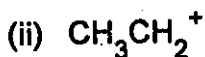
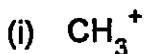


4. Answer any ten questions as directed : 6×10 = 60

- (a) Discuss the direction of dipole moment and Aromaticity of the following compounds.



(b) Arrange the following carbocations in their decreasing order of stability.



(c) Discuss the SN_2 mechanism and give examples.

(d) Give a brief note on Fries rearrangement.

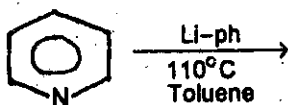
(e) Explain Von-Richter rearrangement.

(f) Give the mechanism of the reaction of ketene with diazomethane to give cyclopropanone.

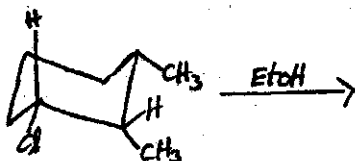
(g) Write the differences between DNA and RNA.

- (h) Draw an energy profile diagram of a three-step exothermic reaction in which the second step is the rate-determining step and the second intermediate is more stable than the first.

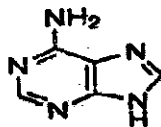
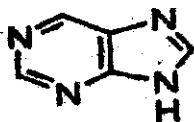
- (i) Predict the product of the following reaction.



- (j) Predict the product of the following reaction.



- (k) What is meant by the secondary structure of proteins ?
- (l) Explain if purine and adenine are aromatic or not.



SECTION – B

5. Answer any three questions of the following :

20×3 = 60

(a) Give a detailed note on competitions between Substitutions and Eliminations.

(b) Explain the following reactions and give two applications :

(i) Reformatsky reaction

(ii) Bischler-Napierlski reaction

(c) Write the synthesis of the following polymers with chemical equations : Polystyrene, Terylene, Teflon, Nylon.

(d) (i) A organic compound (MF : $C_8H_{10}O$) exhibited the following 1H -NMR spectral data :

δ 2.5 (3H, S), 3.8(3H, S), 6.8(2H, d, J8Hz), 7.2(2H, d, J8 Hz) ppm.

predict the structure of the compound.

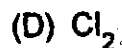
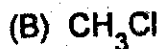
- (ii) In a polymer sample, 30% of molecules have a molecular mass of 20,000, 40% have molecular mass, 30,000, and the rest have 60,000. Calculate the mass average and number average molecular mass.

6. Answer any five questions of the following :

$$12 \times 5 = 60$$

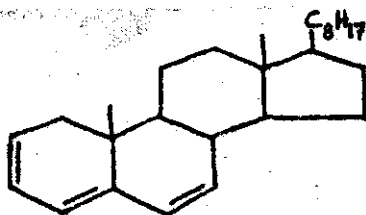
- (a) (i) What is the change in the rotational constant 'B' when hydrogen is replaced by deuterium in the hydrogen molecule ?

- (ii) Give the electronic transitions possible when UV light is observed the following :



(b) (i) Suggest a structure of the compound (m.f. C_9H_{12}) having signals at 7.1, 2.2, 1.5 and 0.9 δ ppm.

(ii) Calculate the λ_{\max} for the triene (I) which contains both a heteroannular and homoannular diene. The calculation should be based on the homoannular diene.



(c) (i) Calculate the vibrational absorption frequency of the carbonyl group, if the force constant for the double bond is 1×10^6 dynes cm^{-1} .

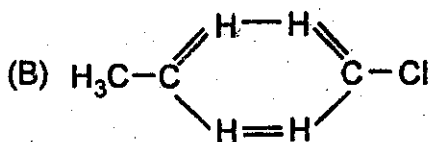
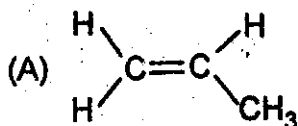
(ii) A compound (molecular formula C_2H_5BrCl) exhibits two doublets ($J = 16Hz$) in its PMR spectrum. Suggest structure.

- (d) (i) Write a short note on the distinction between inter and intramolecular hydrogen bonding.
- (ii) How will you distinguish between cis and trans-stilbenes based on PMR spectroscopy ?
- (e) (i) Give the characteristics of absorption bands in the infrared spectra of benzaldehyde.
- (ii) The UV spectrum of acetone shows two peaks at $\lambda_{\text{max}} = 189 \text{ nm}$ and $\lambda_{\text{max}} = 273 \text{ nm}$. Identify the electronic transition for each peak.
- (f) (i) How do you differentiate the following pairs using IR spectra ?
- (A) Aniline from N-methyl aniline
- (B) Acetaldehyde from ethanol

(C) Acetone from acetylene

(D) Acetonitrile from acetamide

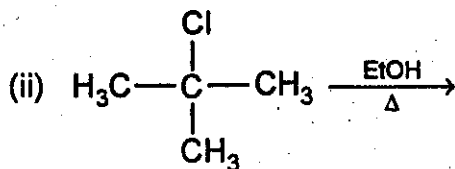
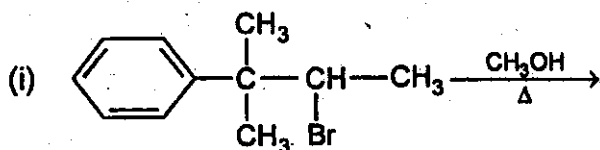
(ii) How many NMR signals would you expect for the following compound ?



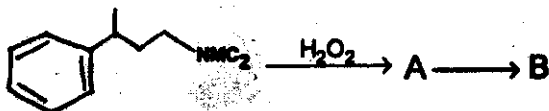
7. Answer any ten questions from the following :

6×10 = 60

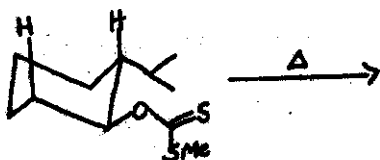
(a) Predict the outcome of the following reactions.



(b) Predict the product of the following reaction.



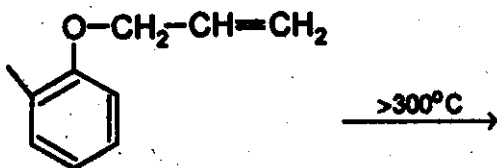
(c) Predict the product of the following given compound.



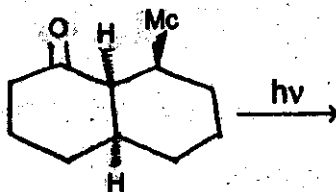
(d) Write the mechanism for the following reaction.



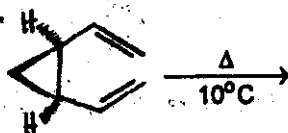
(e) Predict the product of the following reaction.



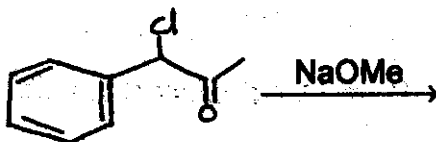
- (f) Write the reaction proceeds and product of the following reaction.



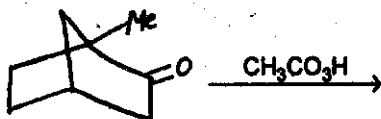
- (g) Predict the product of the following reaction.



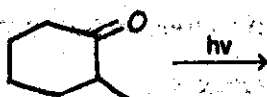
- (h) Suggest a mechanism for the following reaction.



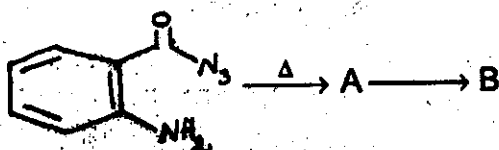
- (i) Predict the major product of the following reaction.



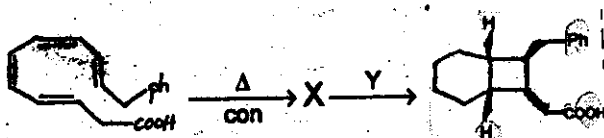
(j) Predict the product of the following reaction.



(k) Predict the intermediate A and the major product B in the following reaction.



(l) Find the following sequences of pericyclic reactions X and Y.



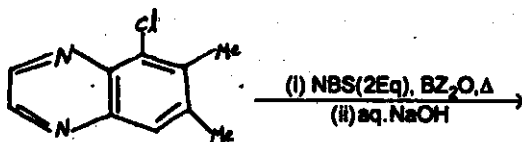
8. Answer any six questions of the following :

10×6 = 60

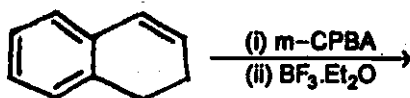
(a) (i) What will the sequence of bases on the strand of DNA that would be complementary to strand having the following sequence of bases :

AATCGTAGGC

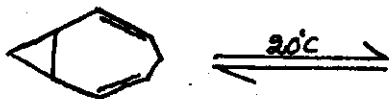
- (ii) Predict the structure of the tricyclic compound formed in the following two-step sequence is :



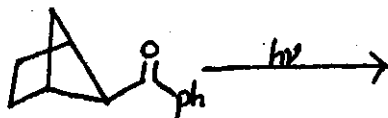
- (b) (i) The major product formed in the following reaction is :



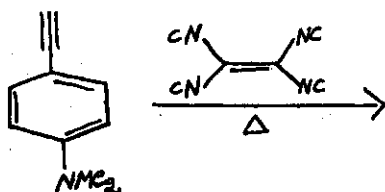
- (ii) Predict the product of the following reaction proceeds through Cope rearrangement.



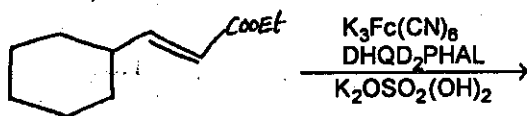
- (c) (i) Predict the product formed in the following photochemical reaction.



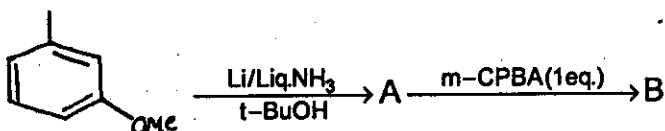
reaction.



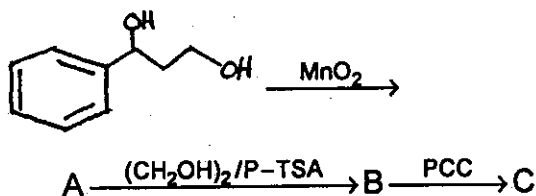
- (d) (i) Predict the product of the following reaction.



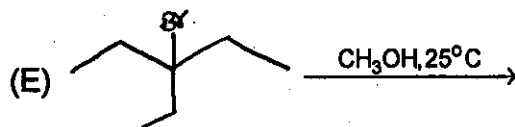
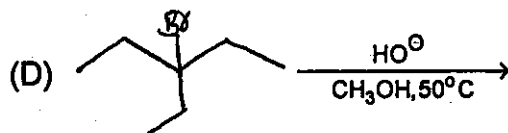
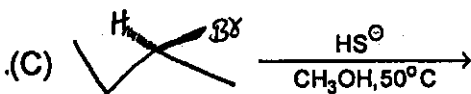
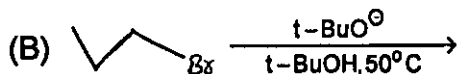
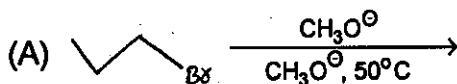
- (ii) Write the major product A and B in the following reaction.



- (e) (i) Predict the product of the following reaction.



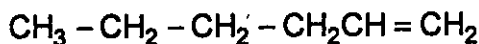
(ii) Give the major product (or products) that you would expect to be formed in each of the following reactions.



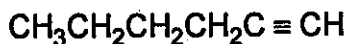
(f) (i) What product would you expect from the following solvolysis?



- (ii) The frequency of O-H stretching vibration in CH_3OH is 3300cm^{-1} . Estimate the frequency of OD stretching vibration in CH_3OD .
- (g) (i) Explain the IR spectra of polyatomic molecules of Diphenyls.
- (ii) How can you distinguish between 1-hexene and 1-hexyne based on infrared spectroscopy?



1-Hexene



1-Hexyne

