Birla Institute of Technology & Science, Pilani, Rajasthan 333 031
Second Semester 2021-2022

Comprehensive Examination (Open Book) **ORGANIC CHEMISTRY-IV, CHEM F342**
Time: 180 Minutes **Max. Marks: 80** **Date: 06/05/22**

All questions are compulsory. Answer the sub-parts of a question together.

Q. No. 1. (i). The pKa values determined experimentally for the functional groups present in the tripeptide, **Asp-Gly-Glu** are 3.1, 3.9, 4.2 and 8.0. A sample of this **tripeptide** is titrated from pH = 1.0 to pH = 14.0 with NaOH solution. Draw the predominant structural form(s) and the corresponding charges existing on them, which will be formed in this process of titration. Also, determine the isoelectric point of this tripeptide. [6]

(ii). Design a detailed synthetic strategy for the solution phase synthesis of tripeptide, **Lys-Ala-Tyr**, starting from [**H_2N-CH{$(CH_2)_4NHCbz$}-COOH**] or [**H_2N-Lys(Cbz)-COOH**] *[Do not use any abbreviations in the Scheme]* [6]

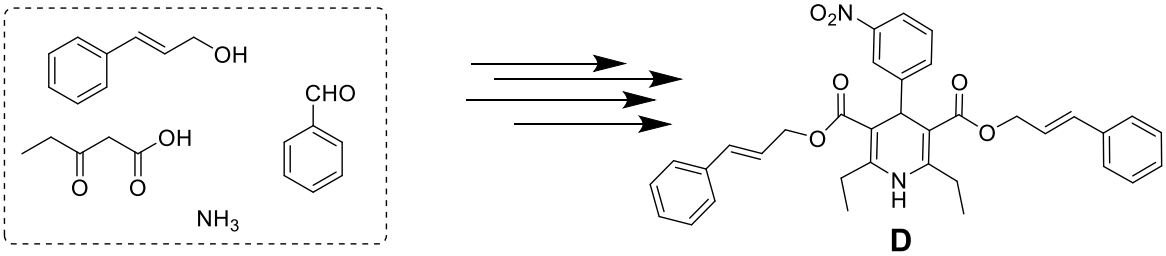
(iii). Design a detailed strategy for converting **Glycine** to **Histidine**? [4]

(iv). (*S*)-Valine is an L-amino acid. Is (*R*)-cysteine, an L or D-amino acid? Explain with the help of Fischer projection of L-cysteine. [2]

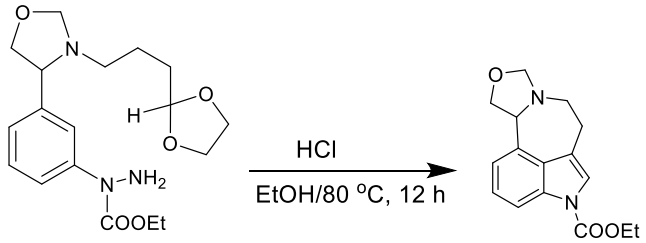
(v). A saponifiable lipid on basic hydrolysis gives a molecule of **sodium palmitate**, **spingosine** and **disodium salt of phosphorylserine**. Chalk down the complete structure of the lipid *(No abbreviations will be accepted).* [2]

Q. No. 2. (i). Treatment of a polypeptide with an enzyme **A** yielded the following peptide fragments: WGA, AGTK, and YLDR, while the treatment of the same peptide with another enzyme **B** yielded the following peptide fragments: GA, LDRW and AGTKY. Further, a chemical reagent **C** typically used in peptide sequencing had no effect when allowed to react with this peptide. Identify the primary structure of this polypeptide, and identify the enzymes **A** and **B**, and the chemical reagent **C**? [5]

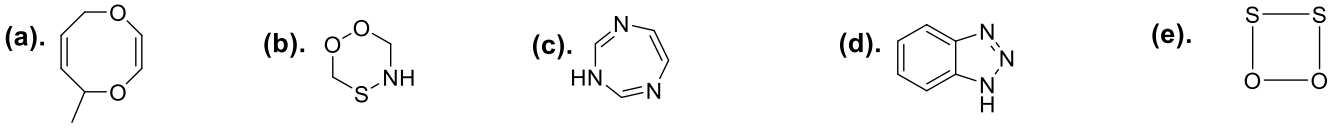
(ii). Design a detailed synthetic scheme for the synthesis of the drug candidate (**D**), utilizing logically the starting material given in the box on left hand side in multiple steps. Show the structures of all intermediates. You may use any other reagents/ solvents. [5]



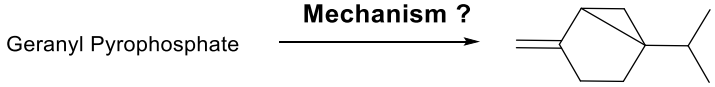
(iii). Propose a detailed mechanism for the following chemical transformation: [5]



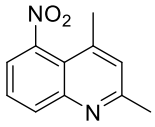
(iv). Write the correct IUPAC names of the following heterocycles: [5]

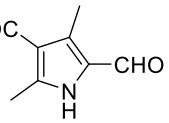


Q. No. 3. **(i).** Propose a detailed mechanism for the biosynthetic conversion of **Geranyl Pyrophosphate** to the following monoterpene? [3]



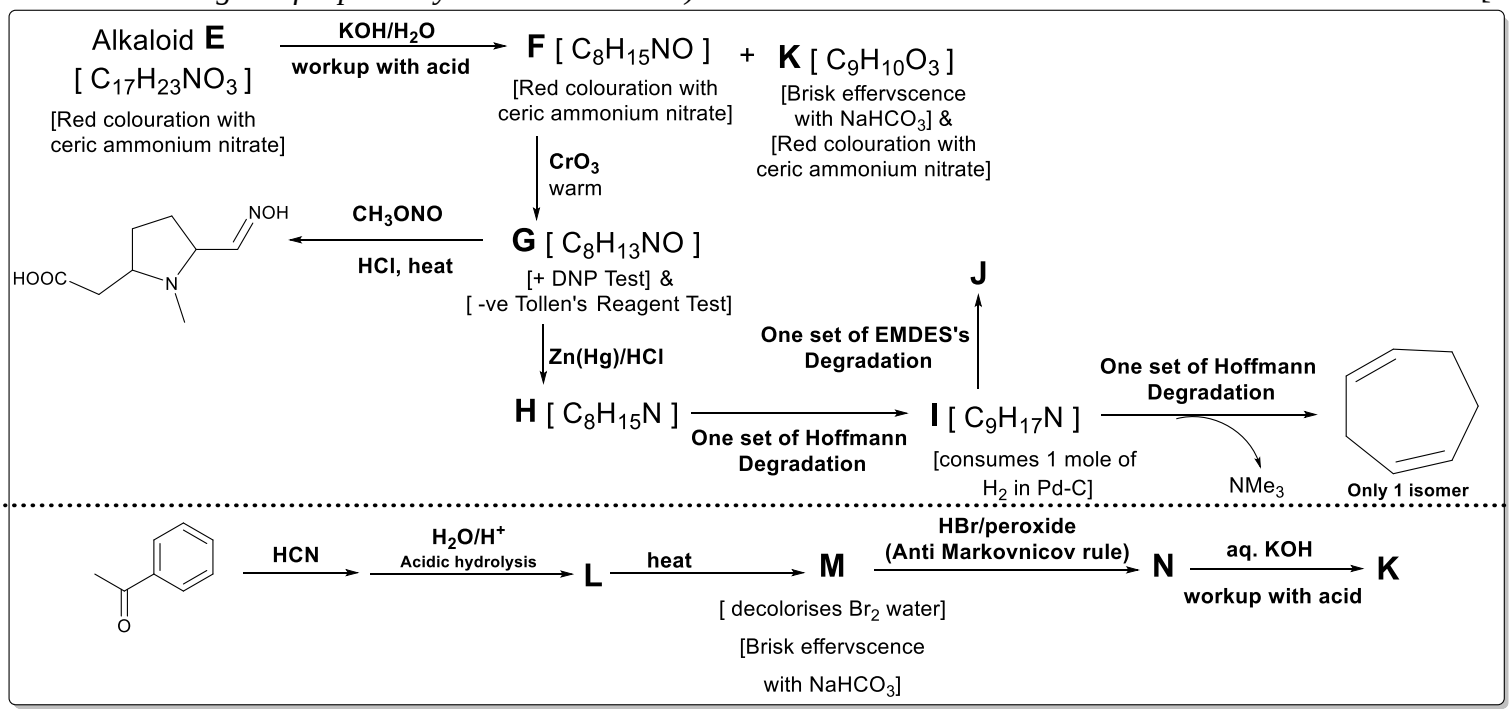
(ii). Carry out the following conversions by using appropriate reagents/solvents/catalysts from the given starting materials. Show all the structures of intermediates formed during these chemical conversions. [5+5]

(a). Aniline ⟶ 

(b). Ethyl acetoacetate (EAA) ⟶ 

(iii). A monoterpene **KAKA** *(molecular formula $C_{10}H_{20}O$)* does not decolorizes Bromine water, but gives a red coloration with Ceric Ammonium Nitrate solution. **KAKA** on heating with dilute sulfuric acid gives **LALA** *(molecular formula $C_{10}H_{18}$)*, which decolorizes Bromine water. Ozonolysis of **LALA** followed by reaction with Zn afforded 3,7-dimethyl-6-oxooctanal. **KAKA** on warming with CrO_3 gives another monoterpene **MAMA,** which gives a yellow precipitate with 2,4-DNP reagent and a negative Tollen's reagent test. **MAMA** on oxidation with acidified $KMnO_4$ gives another compound **NANA** *(molecular formula $C_{10}H_{18}O_3$)*, which on further oxidation with $KMnO_4$ gives *β*-methyl adipic acid. Deduce the structures of **KAKA, LALA, MAMA, NANA.** How many stereoisomers of the compound **KAKA** will exist? [6+1]

Q. No. 4. (i). Deduce the structures of **E-N** from the information given in the following flow chart of chemical reactions. *(No marks will be given for partially correct structures)* [10]



(ii). Based on the information given in the following flow chart of chemical reactions, identify the correct structures of **O-X**? *(No marks will be given for partially correct structures)* [10]