M. Sc. Chemistry Examination, 2017

(4th Semester)

ORGANIC CHEMISTRY SPECIAL

PAPER - XIV-O

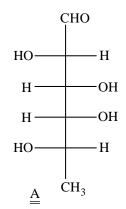
Time: Two hours Full Marks: 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - O - 4141

a) Suggest a scheme for the synthesis of the compound A starting from an easily accessible six carbon containing monosaccharide applying Chiron approach and give the synthetic steps involved in the proposed sequence.



b) Discuss the synthesis of R, R-DIPAMP using *l*-menthol as the chiral auxiliary starting from a racemic phosphorous compound. (No mechanism or rationalization is needed)

c) Delineate the asymmetric synthesis of the following compound <u>B</u> utilizing Sharpless asymmetric epoxidation protocol in one of the steps (only mention the steps with reagents, no mechanism is needed).

d) Predict the structures of $\underline{\underline{C}}$, $\underline{\underline{D}}$, $\underline{\underline{E}}$ and $\underline{\underline{F}}$ in the following sequences and rationalise the stereochemical aspects for the formation of $\underline{\underline{D}}$.

i)

$$\frac{\text{n-BuB(OH)}_{2}}{\text{PhCH}_{3}, \Delta} \stackrel{\text{o-BuB(OH)}_{2}}{\longrightarrow} \underbrace{\text{PhCH}_{3}, \Delta}$$

NHTs

c) Delineate the steps involved in the following conversion.
 Discuss plausible mechanistic and stereochemical interpretations, as necessary.

i)

ii)

(Mixture of diastereoisomers)

UNIT - O - 4142

2. a) Predict the products $\underline{\underline{G}}, \underline{\underline{H}}, \underline{\underline{I}}, \underline{\underline{J}}, \underline{\underline{K}}, \underline{\underline{L}}, \underline{\underline{M}}$ and $\underline{\underline{N}}$ of the following reactions. Suggest appropriate mechanistic and stereochemical interpretations, as necessary, for their formations.

i) O
$$\xrightarrow{PhH} \xrightarrow{Q} \xrightarrow{Al(Oi Pr)_3} \xrightarrow{Br_2/MeOH} \xrightarrow{I}$$
O CO_2Me

$$\xrightarrow{\text{CH}_3\text{CONHBr(leq.)}} \underbrace{J}_{0^0-5^0\text{C}} \xrightarrow{\text{HCO}_2\text{H}-\text{H}_2\text{O}} \underbrace{K} \xrightarrow{14\% \text{ NH}_4\text{F.HF}} \underbrace{Dry \text{ CF}_3\text{SO}_3\text{H}} \underbrace{L} \xrightarrow{0^0\text{C. Ar}} \underbrace{L}$$

iii) MeO OTBDPS
$$N_{3}$$

$$\xrightarrow{PPh_{3}(1\,eq.)} \underline{M} \xrightarrow{NaBH_{4}} \underline{N}_{MeOH-THF}$$

b) Carry out the following transformations. Show all the intermediate products formed. (Mechanism is not required)

i)

[Turn over

ii)

iii)

ii)

$$+ \underbrace{ \begin{array}{c} & & & \\ & & & \\ &$$

- e) Describe the asymmetric synthesis of L-Ornithine using a chiral phase transfer catalyst and account for the stereochemical outcome of this process.
- f) Draw the catalytic cycle and rationalize the stereochemical features of an asymmetric aldol reaction where a chiral ionic liquid acts as an organocatalyst. 3+2
- g) Discuss the role of a suitable double salt towards the outcome of solid state photocycloaddition of cinnamic acid.