Birla Institute of Technology & Science, Pilani Pilani Campus, Rajasthan - 333 031

II Semester 2016-2017, Comprehensive examination

Course: CHEM F243 Course Title: Organic Chemistry-II Part A: Closed Book

Time: 90 min. Max. Marks: 40 Instruction to students: Answer all questions and answer all parts of a question together

Q. 1 Write appropriate reagents, conditions for the following transformations.

4.0

(B)
$$HO \longrightarrow HO \longrightarrow Ph$$

Q. 2 Write structure of the major product with appropriate stereochemistry for the following reactions. **6.0**

Q. 3 Identify all the pair of hydrogens (from labeled ones) in the following compounds that will show peaks at same and at different chemical shift in NMR. Provide your answer in tabular form as mentioned. **5.0**

(A)
$$H_a$$
 H_a H_b H_c H_b H_c H_c H_d H_c H_d H_c H_d H_c H_d H_c H_d H_d H_d H_d H_d H_d

Pair of hydrogen with same chemical shift:
Pair of hydrogen with different chemical shift:
Compound B

Compound A

Pair of hydrogen with same chemical shift: Pair of hydrogen with different chemical shift:

Q. 4 Based on the product observed in the following reaction, write correct stereochemical structure of the substrates (wherever applicable). 5.0

Q. 5 (a) Looking from top of the given compound (A), state whether we are looking at the Re or the Si face for each of the carbonyl and alkene groups. 2.0

$$H \xrightarrow{O} \xrightarrow{D} \xrightarrow{O} \xrightarrow{CH_3} \xrightarrow{Ph}$$

- (b) Reaction of an optically active 3-methylbutan-2-ol with racemic 2-phenylbutyric anhydride followed by hydrolysis gives (R)-(-)-2-phenylbutyric acid as residual acid. Based on this observation write the correct stereochemical structure of the alcohol and assign (R/S) configuration for the chiral center in the alcohol.

 3.0
- (c) How many stereoisomers are observed for the compound (B) given below? What is the measure of twist angle and what are the factors that affect this twist angle?

 3.0

$$(H_3C)_2HCO_2C$$
 (B)

12.0

Q. 6 Write correct stereochemical structure of the products (**A-H**) in the following reaction.

*****END*****

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II Semester 2016-2017, Comprehensive Examination

Course: CHEM F243 Part B: Open Book Course Title: Organic Chemistry-II

Time: 90 min. Max. Marks: 40

Instruction to students: Answer all questions and answer all parts of a question together.

Q. 1 Convert the following compound into Fischer formulas and assign appropriate notation (R/S, E/Z or r/s) for all the stereogenic centers. Is C-4 chirotopic or achirotopic? Comment on the chirality of the compound and mention symmetry elements present (if any).

6.0

Q. 2 (a) Paternò-Büchi reaction of benzaldehyde and *trans*-butene results in mixture of two stereoisomeric products (non-stereospecific) whereas that of acetaldehyde gives predominantly one isomer (>95% stereospecific). Explain the results obtained and write stereochemical structure of the products.

3.0

(b) Draw most stable chair conformation for the polycyclic compounds (Fig. 1) mention R/S designation for the carbon 4a, 4b, 8a and 10a labelled in the given structure.

5.0

Q. 3 Write mechanism of the following reactions to explain formation of the given product(s). **6.0**

Q. 4 (a) Which of the two 4-*tert*-butylcyclohexanols (**I** & **II**) is expected to give corresponding ester when reacted with acetic anhydride at faster rate and why?

3.0

(b) Compound A reacts with BH₃ followed by oxidation with H₂O₂ to give a mixture of diastereoisomeric alcohol. Write structure of the major diastereisomer and assign R,S configuration to all the chiral centers present in the major isomer.

3.0

$$H_3C_{I_2}$$
 OC H_2 Ph

Q. 5 The o, o '-diacetoxymethylbiphenyl (Fig. 2) shows an (AB)₂ system for the methylene protons at room temperature, whereas at 127 °C the pattern collapses to a single peak. Based on this information, mention the relationship (homotopic, enantitopic or diastereotopic) between protons i) $\mathbf{H_a}$ and $\mathbf{H_b}$ ii) $\mathbf{H_a}$ and $\mathbf{H_c}$ and iii) $\mathbf{H_a}$ and $\mathbf{H_d}$, both at room temperature and at 127 °C.

Q. 6 Write most appropriate product(s) of the reactions with correct stereochemistry (if any).

6.0

- (C) (2R,3S)-2,3-Dibromobutane PhSNa
- Q. 7 (a) Write correct stereochemical structure of an allene [C₂H₅(CH₃)C=C=CH(Cl)] obtained by the reaction of SOCl₂ with (S)-3-methyl-3-pent-1-ynol and denote the configuration as M or P. **3.0**
- (b) Denote the configuration of the compounds given below as R or S. 2.0

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