# Birla Institute of Technology \& Science, Pilani <br> Pilani Campus, Rajasthan - 333031 

II Semester 2016-2017, Comprehensive examination

Course: CHEM F243
Time: 90 min .

Part A: Closed Book Course Title: Organic Chemistry-II
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.
(A)

(B)

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

(B)


Claisen rearrangement
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.
(A)

(B)


| Compound A |
| :--- |
| Pair of hydrogen with same chemical shift: |
| Pair of hydrogen with different chemical shift: |
| Compound B |
| 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).
(A)

(B) Lithium 2-butenolate

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.

(A)
(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.
(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?

(B)
Q. 6 Write correct stereochemical structure of the products $(\mathbf{A}-\mathbf{H})$ in the following reaction.

(v)

a) $\mathrm{t}-\mathrm{BuLi}$
b) $\mathrm{CO}_{2}$
$\xrightarrow{\text { c) } \mathrm{H}^{+}} \quad \mathrm{H}$

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Time: 90 min.

Part B: Open Book

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 $\mathrm{r} / \mathrm{s}$ ) 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).

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

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


(B)

(C)

 and

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?


I


II
(b) Compound $\mathbf{A}$ reacts with $\mathrm{BH}_{3}$ followed by oxidation with $\mathrm{H}_{2} \mathrm{O}_{2}$ to give a mixture of diastereoisomeric alcohol. Write structure of the major diastereisomer and assign $\mathrm{R}, \mathrm{S}$ configuration to all the chiral centers present in the major isomer.

Q. 5 The $o, o^{\prime}$ 'diacetoxymethylbiphenyl (Fig. 2) shows an (AB) $)_{2}$ system for the methylene protons at room temperature, whereas at $127^{\circ} \mathrm{C}$ 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) $\mathbf{H}_{\mathbf{a}}$ and $\mathbf{H}_{\mathbf{d}}$, both at room temperature and at $127^{\circ} \mathrm{C}$.


Fig. 2
Q. 6 Write most appropriate product(s) of the reactions with correct stereochemistry (if any).

Q. 7 (a) Write correct stereochemical structure of an allene $\left[\mathrm{C}_{2} \mathrm{H}_{5}\left(\mathrm{CH}_{3}\right) \mathrm{C}=\mathrm{C}=\mathrm{CH}(\mathrm{Cl})\right]$ obtained by the reaction of $\mathrm{SOCl}_{2}$ with (S)-3-methyl-3-pent-1-ynol and denote the configuration as M or P .
(b) Denote the configuration of the compounds given below as R or S .
i)

ii)


