

FINAL B. SC. EXAMINATION, 2017

(1st Semester)

CHEMISTRY (HONOURS)**PAPER - XII****ORGANIC CHEMISTRY**

Time : Two hours

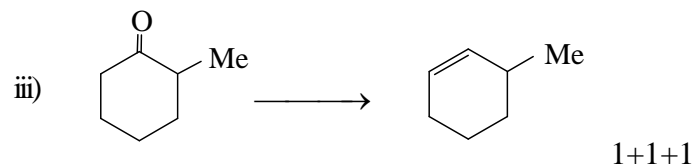
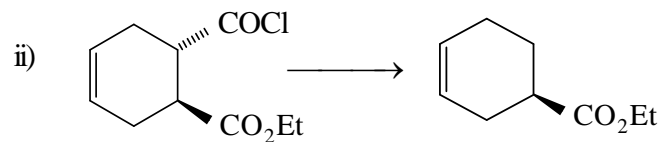
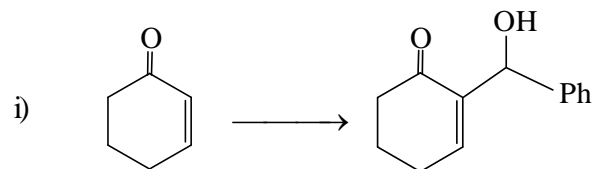
Full Marks : 50

Use a separate answerscript for each group.

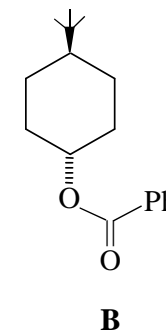
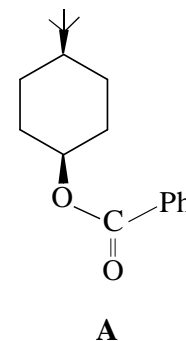
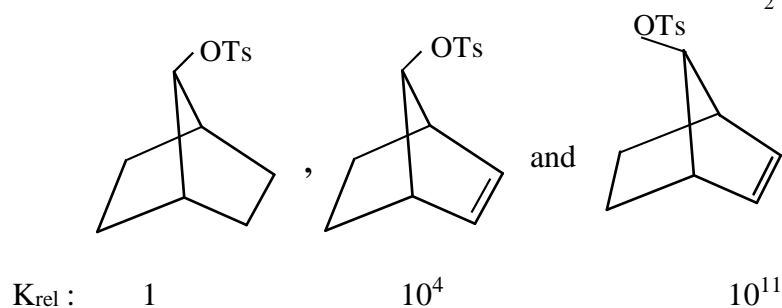
GROUP - A

1. a) Comment on the relative stability, chirality and optical activity of *cis*-1,2-dimethylcyclohexane and *trans*-1,2-dimethylcyclohexane. 2½ + 1 + 1½
- b) Between *cis*- and *trans*-1,2-dibromocyclohexane, which one will have higher dipole moment and why? 1½
- c) Which one of the following compounds **A** and **B** will undergo faster saponification and why? 2

c) Mention the reagents for the following transformations :



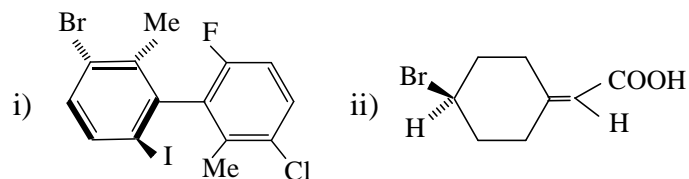
d) How will you explain the relative rate of acetolysis of the following bicyclic compounds using $\text{CH}_3\text{CO}_2\text{K}$ in acetone? 2½



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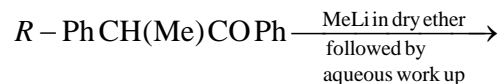
[2]

- d) Assign *R/S* to the following molecules indicating relative priority of the ligands. $1\frac{1}{2} + 1\frac{1}{2}$



- e) Assign topic descriptors to the diastereotopic hydrogens in *S*-2-butanol with a suitable diagram. $1\frac{1}{2}$
- f) Suggest an experiment to prove that using Wilkinson's catalyst, the hydrogenation of an olefinic bond occurs with *syn*-facial selectivity. 2
- g) Attempt **any one** of the following questions : 2

- i) Predict the major product of the following reaction using Felkin-Anh model.

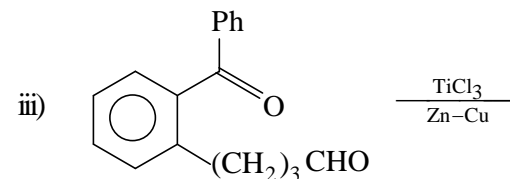
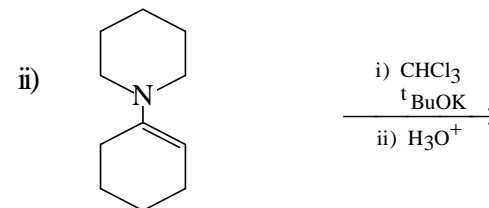
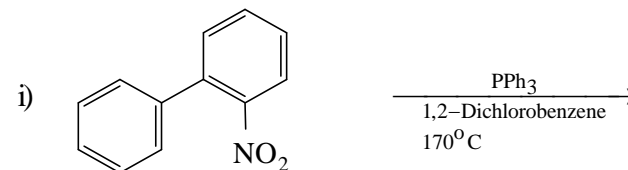


- ii) Logically choose the correct enantiomer of 1-phenylethanol which can be used as a chiral auxiliary for the enantioselective synthesis of *S*-atrolactic acid (*S*-2-hydroxy-2-phenylpropanoic acid) through an appropriate pyruvate ester.

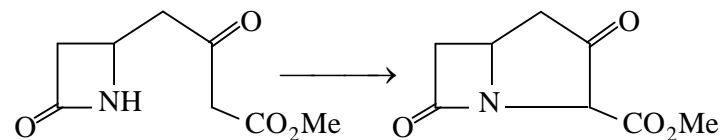
[5]

GROUP - B

3. a) Predict the product(s) of the following reactions and explain with plausible mechanism. $2\frac{1}{2} \times 3$



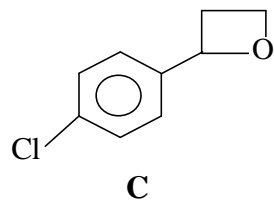
- b) How can you carry out the following transformation? Explain with mechanism. $1\frac{1}{2} + 1\frac{1}{2}$



[Turn over

[4]

- ii) What is meant by chemical shift in NMR ? Why is it preferably expressed as ppm instead of Hz ? 2
- iii) Mention how many types of proton peaks are obtained in the ^1H -NMR of isopropylbenzene ? Discuss on the corresponding spin multiplicity and relative position of peaks in the ^1H -NMR spectrum ?
- iv) Thermal decomposition at 560°C of compound **C** generates compounds **D** and **E**. $2\frac{1}{2}$

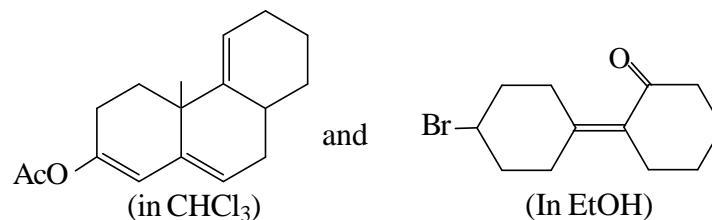
**E** ($\text{C}_8\text{H}_7\text{Cl}$)[**D** reduces Tollens' reagent.]Spectral properties of **D** and **E** are as follows :**D** : IR : $\bar{\nu}$ at $\sim 1700\text{ cm}^{-1}$ ^1H -NMR (60 MHz, CCl_4 solvent) : δ 7.58 (4H) and 9.95 (1H) ppm.**E** : IR : no $\bar{\nu}_{\text{C}=\text{O}}$ ^1H -NMR (CCl_4) : δ 5.10 (1H), 5.51 (1H), 6.50 (1H) and 7.10 (4H) ppm.

With the help of spectroscopic properties deduce the structures of **D** and **E** and show how these are formed from **C**.

[3]

GROUP - B

2. a) i) N-H bond vibrates at a frequency 3400 cm^{-1} . Calculate the force constant of the bond. $1\frac{1}{2}$
- ii) How are the following compounds distinguished by IR ? Answer *any two* : $1\frac{1}{2} \times 2$
- I. β -Aminobenzoic acid and 2-amino phenylacetic acid.
 - II. Diethyl ether and ethyl vinyl ether
 - III. Phenyl acetate and methyl benzoate
- b) i) What is meant by hypsochromic shift in UV-vis spectroscopy ? 1
- ii) Discuss with diagram on the effect of polar solvent on $n \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions. 2
- iii) With the help of Woodward-rule deduce the λ_{max} of the following compounds : 2



- c) i) Why does N-H appear as a broad peak in the corresponding ^1H -NMR Spectrum ? $1\frac{1}{2}$

[Turn over