

1

69738

(3 Hours)

Total Marks: 80

- N.B.: 1. All questions are compulsory  
2. Answer all sub questions together  
3. Figures to right indicate full marks

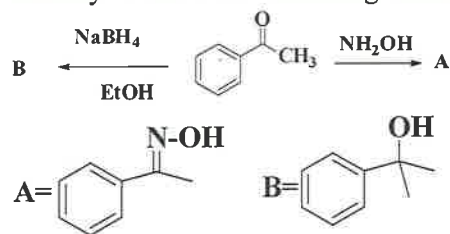
Q1 a. Match the following in terms of type of reaction involved. (04)

| Sr. No | Name of the reaction         | Sr. No. | Types of reaction   |
|--------|------------------------------|---------|---|
| 1.     | Oxymercuration-Demercuration | a.      | Nucleophilic substitution at C=O with loss of carbonyl oxygen |
| 2.     | Imine formation              | b.      | Electrophilic aromatic substitution reaction                  |
| 3.     | Friedel Craft acylation      | c.      | Electrophilic addition to alkene                              |
| 4.     | Cannizzaro reaction          | d.      | Nucleophilic addition to C=O                                  |

1- c, 2-a, 3-b, 4-d

Q1b. Answer the following questions (Any Eight) (16)

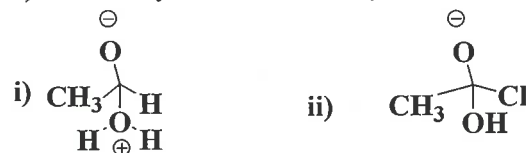
- 1 Identify A and B for following reaction.



- 2 Write structure of tetrahedral intermediates formed for following reactions.

i) Acetaldehyde with water

ii) Acetyl chloride with hydroxyl ion

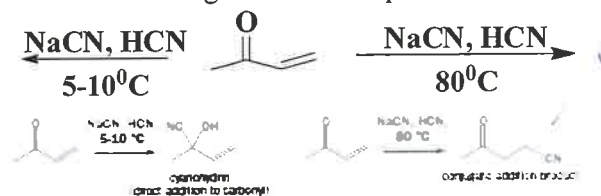


- 3 Identify whether following compounds are enolizable or non-enolizable when treated in presence of base.

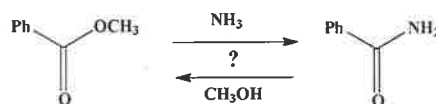


- 4 Justify using suitable examples: acid or base catalyst increase rate of equilibrium of hemiacetals but does not shift position of equilibrium. **Clayden 223/224**

- 5 Predict the product for following molecule at specified reaction conditions

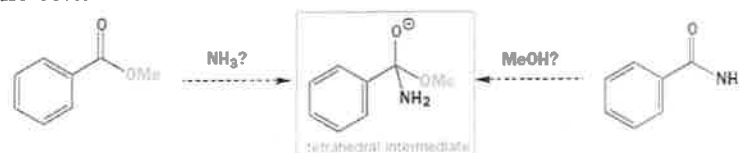


6. In the reaction given below, predict which of the following reaction is feasible?



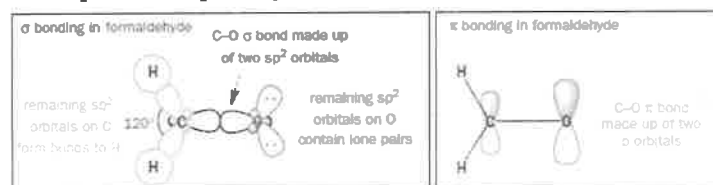
②

The conversion of ester to amide is faster whereas amides cannot be converted to esters. In both the cases, the tetrahedral intermediate would be the same. The leaving group ability of  $\text{RO}^-$  is better than  $\text{NH}_2^-$ . Hence,  $\text{RO}^-$  of the ester can easily leave and the amide can be formed, whereas it is difficult for  $\text{NH}_2^-$  of the amide to leave to form the ester.

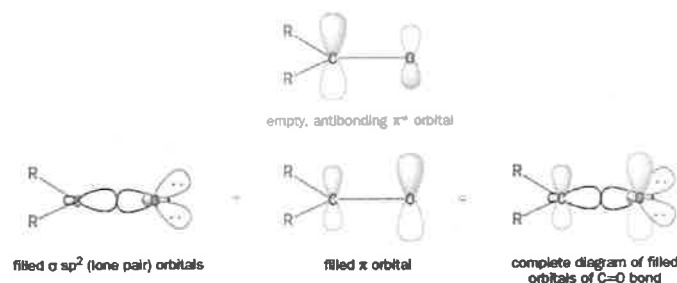


| Possible leaving groups | $\text{p}K_{\text{aH}}$ |
|-------------------------|-------------------------|
| $\text{Ph}^-$           | 45                      |
| $\text{NH}_2^-$         | 35                      |
| $\text{MeO}^-$          | 16                      |

7. Draw a picture depicting the HOMO and LUMO of formaldehyde.



Notice that we have drawn the  $\pi$  bond skewed towards oxygen. This is because oxygen is more electronegative than carbon, polarizing the orbital as shown. Conversely, the unfilled  $\pi^*$  antibonding orbital is skewed in the opposite direction, with a larger coefficient at the carbon atom. Put all of this together and we get the complete picture of the orbitals of a carbonyl group.



8. Aldehydes are more reactive than ketones in nucleophilic addition reaction; account for the same.

**Less steric hinderance to aldehyde so better nucleophilic attack.**

**Carbonyl carbon is more electron deficient in aldehyde as compared to ketones.**

9. Using phenol, suggest a suitable scheme for synthesis of 5-nitrosalicylaldehyde.

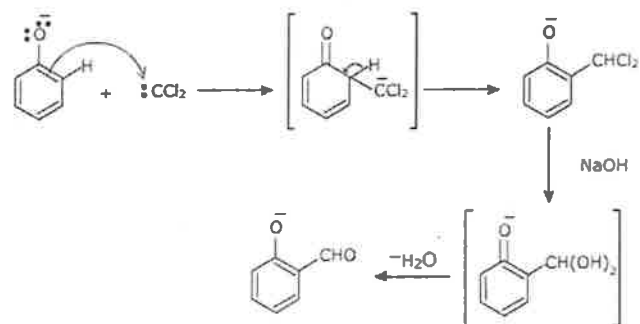
**i) reimer tiemann reaction using chloroform and NaOH followed by ii) nitration using Conc  $\text{HNO}_3$**

Q2 a. Give the mechanism for the following reactions (Any three): (06)

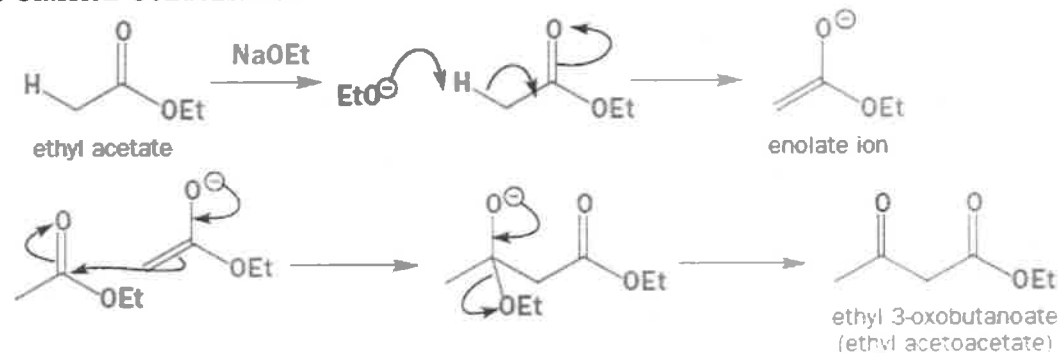
- i) Kolbe reaction                      ii) Claisen condensation  
 iii) Mannich reaction                iv) Cannizzaro reaction

1. Kolbe's reaction



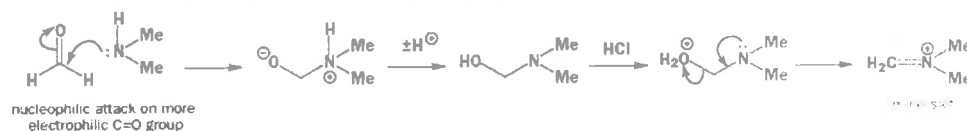


## 2. Claisen Condensation

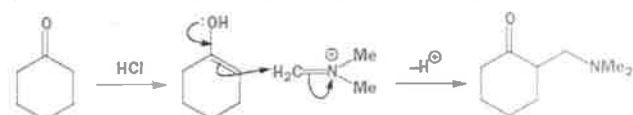


## 3. Mannich Reaction

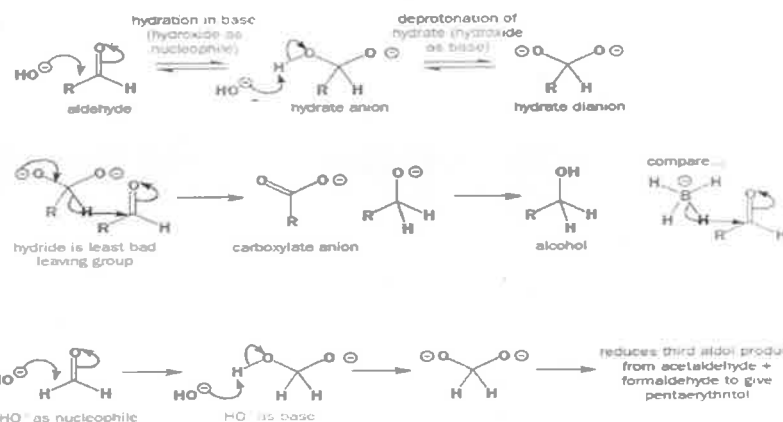
The mechanism involves the preliminary formation of an imine salt from the amine and formaldehyde. The amine is nucleophilic and attacks the more electrophilic of the two carbonyl compounds available. That is, of course, formaldehyde. No acid is needed for this addition step, but acid-catalysed dehydration of the addition product gives the imine salt. In the normal Mannich reaction, this is just an intermediate but it is quite stable and the corresponding iodide is sold as 'Eschenmoser's salt' for use in Mannich reactions.



The electrophilic salt can now add to the enol (we are in acid solution) of the ketone to give the product of the reaction, an amine sometimes called a Mannich base.



## 4. Cross Cannizzaro



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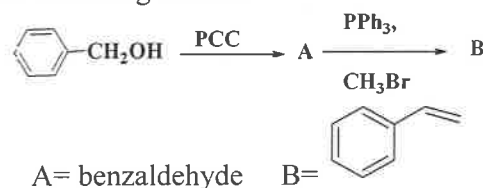
b Answer the following questions

(06)

1. Identify product obtained when bromobenzene is treated with:  
i) Conc.  $\text{H}_2\text{SO}_4$       ii)  $\text{NaOH}$  at high temperature and pressure  
i) o and p-bromo benzene sulhonic acid    ii) phenol

2. o-Bromoanisole and m-bromoanisole yield m-anisidine by reaction with  $\text{NaNH}_2$  and Liq.  $\text{NH}_3$ . Justify **M&B 501 7<sup>th</sup>ed**

3. Identify A and B from the following reaction



Q3 a. Compare the reactivity of amides and acid chlorides

(04)

Discuss answer based on (ANY ONE OF THE FOLLOWING CONCEPTS)

1. Nucleophilicity

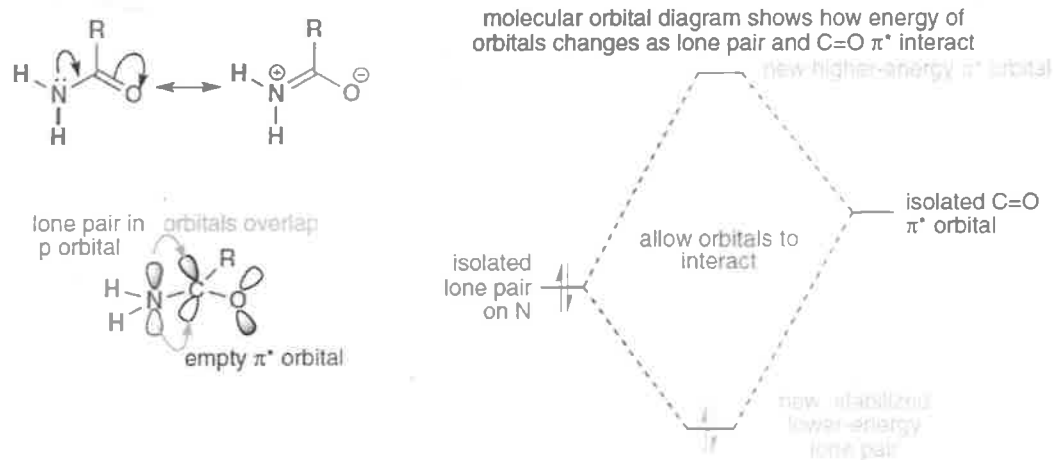
2. pKa leaving gp ability

3. Molecular orbitals

Amides are the least reactive towards nucleophiles because they exhibit the greatest degree of delocalization. In an amide, the lone pair on the nitrogen atom can be stabilized by overlap with the  $\pi^*$  orbital of the carbonyl group—this overlap is best when the lone pair occupies a p orbital (in an amine, it would occupy an  $\text{sp}^3$  orbital). The molecular orbital diagram shows how this interaction both lowers the energy of the bonding orbital (the delocalized nitrogen lone pair), making it neither basic nor nucleophilic, and raises the energy of the  $\pi^*$  orbital, making it less ready to react with nucleophiles. The degree of delocalization depends on the electron-donating power of the substituent and increases along the series of compounds below from almost no delocalization from Cl to complete delocalization in the carboxylate anion, where the negative charge is equally shared between the two oxygen atoms.

The greater the degree of delocalization, the weaker the  $\text{C}=\text{O}$  bond becomes. Amides react as electrophiles only with powerful nucleophiles such as  $\text{HO}^-$ . Acid chlorides, on the other hand, react with even quite weak nucleophiles: neutral  $\text{ROH}$ , for example. They are more reactive because the electron-withdrawing effect of the chlorine atom increases the electrophilicity of the carbonyl carbon atom.

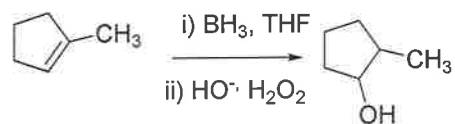
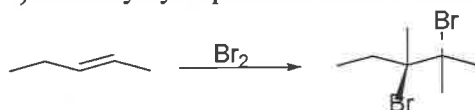
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| Infrared stretching frequency of the C=O group $\nu / \text{cm}^{-1}$ | very weak delocalization | weak delocalization | some delocalization | strong delocalization  | complete delocalization |
|---|--------------------------|---------------------|---------------------|------------------------|-------------------------|
| 1790–1815   | 1800–1850<br>1740–1790   | 1735–1750           | 1690                | 1610–1650<br>1300–1420 |                         |
| C=O strongest   |                          |                     |                     |                        | weakest                 |

b. Suggest suitable reagents to obtain the following products and comment on stereochemistry of addition (04)

- 2,3-Dibromobutane from 2-butene
- 2-methylcyclopentanol from 1-methylcyclopentene



c. Attempt the following conversions (Any four): (04)

- Acetaldehyde to 2-butenal 1) NaOH, 2) Reflux
- Benzene to p-nitrotoluene 1)  $\text{CH}_3\text{Cl}$ ,  $\text{AlCl}_3$  2) Conc.  $\text{HNO}_2$
- 2-methyl-2-butene to 2-methyl-2-butanol **Makanikov addition of water**
- Phenol to 2-hydroxy benzaldehyde **Chloroform NaOH**
- Acetophenone to phenylacetate **any peracid**

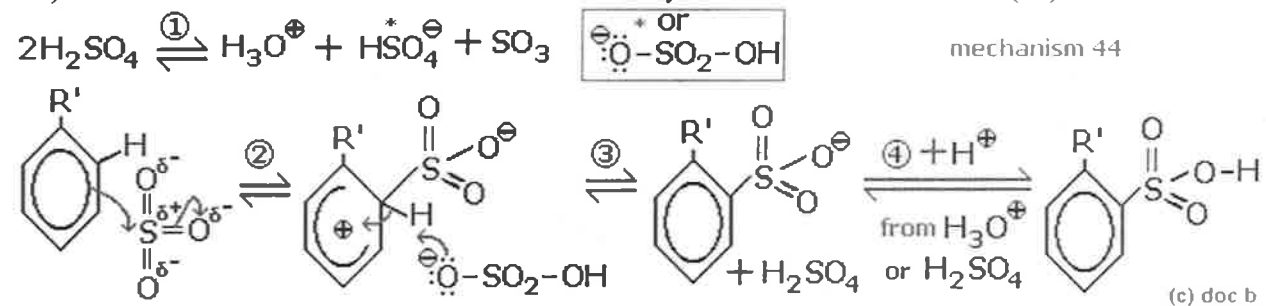
Q4 a. Using organomagnesium and organolithium compounds, suggest suitable schemes for synthesis of 2-Phenyl-2-butanol and n-Pentanol (04)

Clayden 133

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b. i) Give the mechanism for sulfonation of benzaldehyde

(02)

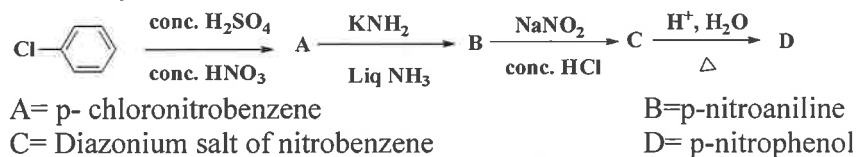


Students should consider resonance of benzaldehyde and consider meta product.

ii) Indicate the position of nitration of 2-chloroaniline and designate whether the starting aromatic compound is activated or deactivated relative to benzene (02)

Nitration will take place at *para* position to NH<sub>2</sub> group. Starting compound is activated relative to benzene.

c. Identify A, B, C and D (04)



Q 5 a. Acid catalyzed hydrolysis of ester is reversible while base catalyzed is irreversible. Justify with mechanism. Clayden 209,210

(04)

OR

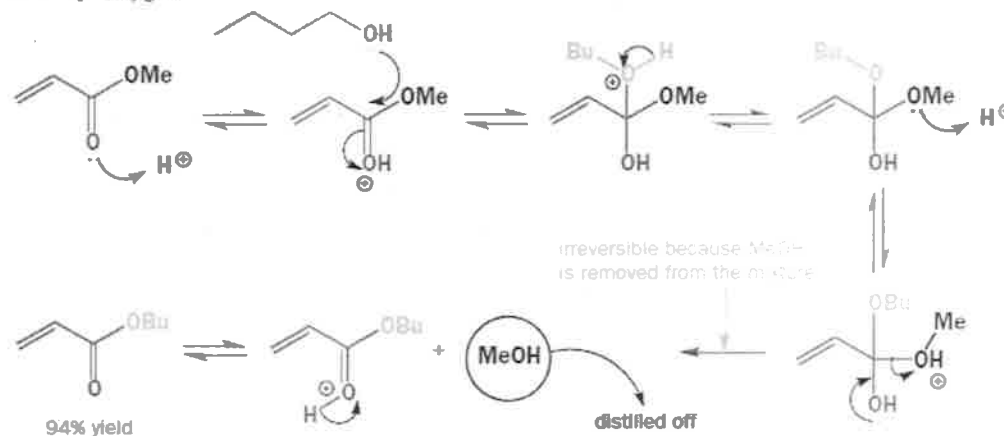
a. Answer the questions pertaining to following reaction: Clayden 209,210



- i) Predict the product of reaction.
- ii) Write the type of reaction involved.
- iii) Write in detail mechanism for the same.

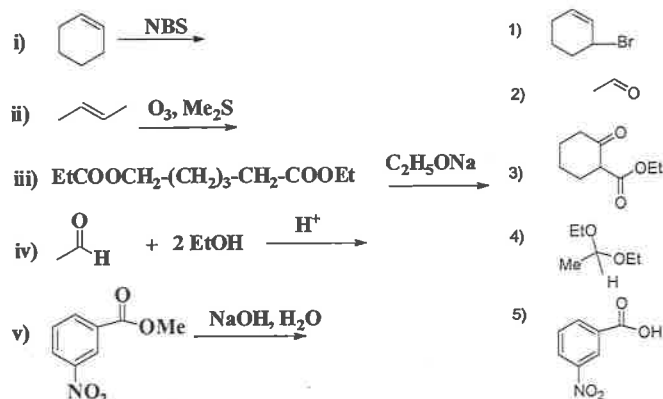
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The mechanism for this transesterification simply consists of adding one alcohol (here BuOH) and eliminating the other (here MeOH), both processes being acid-catalysed. Notice how easy it is now to confirm that the reaction is *catalytic* in  $H^+$ . Notice also that protonation always occurs on the *carbonyl* oxygen atom.



b. Compound A ( $C_7H_5O_4N$ ) reacts with  $POCl_3$  to give compound B ( $C_7H_4O_3NCl$ ). Compound B is reduced with  $Sn/HCl$  to compound C ( $C_7H_6ONCl$ ). Compound C on treatment with ammonia gives D ( $C_7H_8ON_2$ ). Identify A, B, C and D. (04)  
**A = p-nitrobenzoic acid, B = p-nitrobenzoyl chloride, C = p-aminobenzoyl chloride, D = p-amino benzamide**

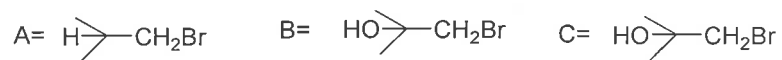
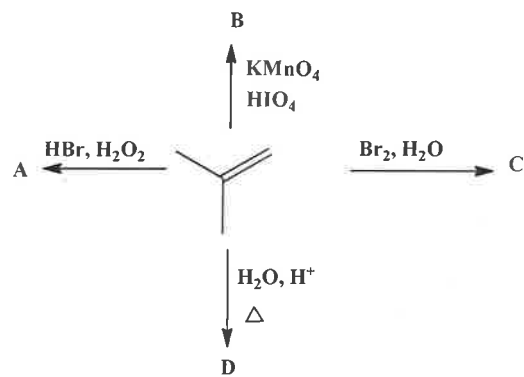
c. Give the products of the following reactions (Any four): (04)



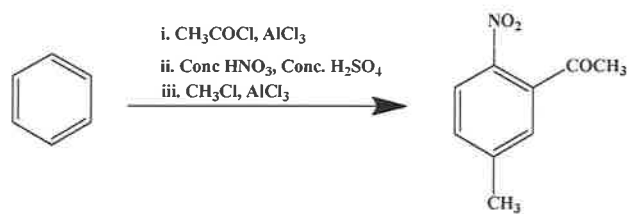
Q.6. a. Propose mechanisms for synthesis of *syn* and *anti* diol from 2-hexene using suitable reagents. (04)

b. Identify A, B, C and D (04)

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c. Predict whether the said order of reaction conditions would yield the desired product. Suggest suitable modifications, if necessary: (04)



1) F.C. alkylation 2) nitration 3) F.C acylation

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