Birla Institute of Technology and Science, Pilani

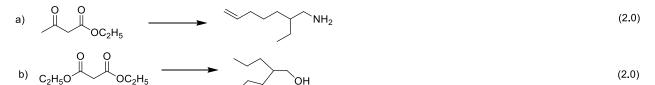
Comprehensive Examination, 1st Semester, 2016-2017

| Course Name: Organic Chemistry-1 | CLOSE BOOK | Date: 12-12-2016 |
|---|---------------|------------------|
| Course No. CHEM F212 | Max. Marks 40 | Time: 3 hours |
| Note for students: Attempt all questions. Attempt all parts of a question together at one place only. | | |

Q. 1 You are in charge of a research group for a large company and you have been assigned the task to synthesize *tert*-butyl methyl ether. You decided to delegate this task to two staff chemists in your company. The first chemists, performs reaction with sodium *tert*-butoxide and methyl iodide and the second chemist with sodium methoxide and *tert*-butyl bromide. In your opinion which one of the two chemists will be successful and why?

2.0

Q. 2 Write all the steps with appropriate reagents for the following transformations. **8.0**

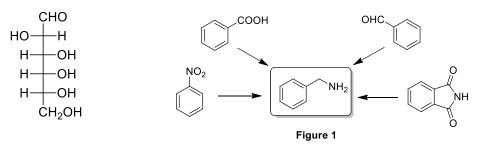


c)
$$Br \longrightarrow OH \longrightarrow CHO$$
 (1.5)

d)
$$(1.0)$$

Q. 3 A mixture of aldoheaxose is obtained by the Killani Fischer synthesis from an aldopentose. The aldoses result in same osazone on reaction with phenylhydrazine as obtained from D-(+)-glucose. Based on this information, write correct stereochemical structure of the aldopentose (in Fischer projection). **1.0**

Q. 4 Draw Howarth projection of the cyclic pyranose form (β -isomer) of the aldohexose given below. 1.0



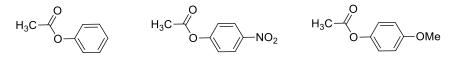
Q. 5 Write all the steps (mentioning appropriate reagents and conditions) for the synthesis of benzylamine from four different substrates as mentioned in Figure 1. Use different method for each reaction. **4.0**

Q. 6 Triethylene glycol is one of the products obtained from the reaction of ethylene oxide and hydroxide (Reaction given below). Propose a mechanism for its formation.1.0

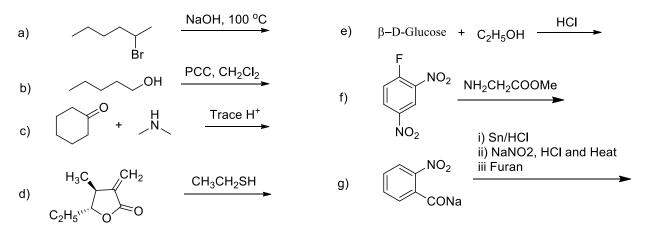
 $\overset{O}{\bigtriangleup} \qquad \overset{Aq. \text{ NaOH}}{\longrightarrow} \qquad HO \overset{O}{\checkmark} O \overset{OH}{\checkmark}$

Q. 7 Write mechanism for acid catalyzed hydrolysis of methyl acetate. List the following esters in order of decreasing reactivity towards hydrolysis. **1.5**

10.5



Q. 8 Give structure of the product(s) of the following reactions.



Q. 9 Which of the following alcohols can be prepared from the reaction of methyl formate with excess of any one Grignard reagent? Write the correct Grignard reagent and show the reaction for the formation of alcohol. 2.0

 $\begin{array}{cccc} OH & OH & OH \\ \swarrow & \swarrow & Ph & Ph \end{array} \begin{array}{c} OH & OH \\ \frown & \frown & OH \end{array}$

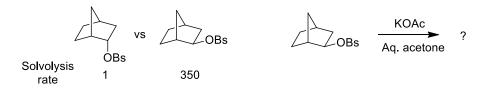
Q. 10 What do you mean by kinetic controlled product? Explain by taking example of enloate formation from 2-methylcyclohexanone and draw energy profile diagram of thermodynamic product vs kinetic product. Write at least two conditions to get a kinetic product. **3.0**

Q. 11 What is kinetic isotope effect? Which of the two steps (Step 1 and Step 2) is rate determining step for the following oxidation reaction based on the observed kinetic isotope effect, explain. 2.0

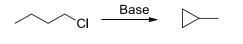
$$(D)H OH step 1 (D)H OCrO_3H step 2 O H_3C CH_3 k_H/k_D = 6.6$$

Q. 12 Provide an appropriate justification for the difference in observed solvolysis rate for the two isomers of norbornyl *p*-bromotosylate (given below). Write the product(s) formed from the solvolysis of exo- norbornyl *p*-bromotosylate.

2.0



Q. 13 Write appropriate mechanism for the following transformation.



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