B.Sc. (Honours) Examination, 2017

Semester-II

Chemistry (Honours)

Course: BCHC-22

(Organic Chemistry)

Time: Three Hours **Full Marks: 30**

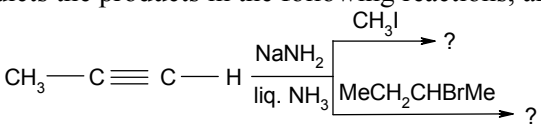
Questions are of value as indicated in the margin.

Answer ***any three*** questions.

1. a) *n*-Butyl chloride reacts with 0.01 M NaCN in ethanol to give primarily *n*-butyl cyanide, whereas under the same conditions *tert*-butyl chloride to give primarily Me_3COEt. Account for the fact. 2

   b) Discuss the course of reaction when octadecylbromide is separately treated with CH_3ONa/CH_3OH and with *t*-BuONa/*t*-BuOH. 1.5+1.5

   c) Predicts the products in the following reactions, and offer your justifications in each case:

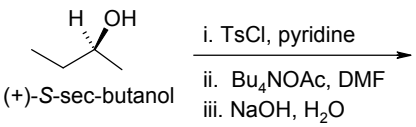


   1.5+1.5

   d) Optically active 2-bromobutane undergoes racemization on treatment with a solution of KBr. In contrast, optically active 2-butanol does not racemize on treatment with a solution of KOH. Offer possible explainations for both the observations highlighting mechanistic approach. 2

2. a) Because the S_N1 reaction goes through a flat carbocation, we might expect an optically active starting material to give a completely racemized product. In most cases, however, S_N1 reactions actually give more of the inversion product. In general, as the stability of the carbocation increases, the excess inversion product decreases. Extremely stable carbocations give completely racemic products. Explain these observations. 4

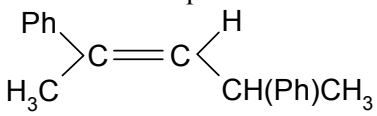
   b) Predict the major product (with proper stereochemistry) highlighting the mechanistic aspect in each step of the following conversion: 3



   c) Tertiary butyl alcohol undergoes dimerisation in presence of concentrated sulfuric acid. Justify this experimental observation with plausible mechanism. 3

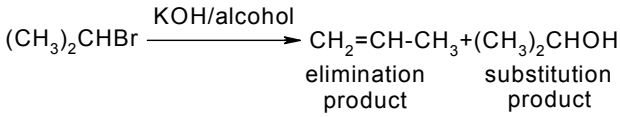
3. a) When ethyl bromide reacts with potassium cyanide in methanol, the major product is CH_3CH_2CN. Some CH_3CH_2NC is formed as well, however. Provide a mechanistic explanation of the course of the reaction. 2

   b) What stereochemistry is required in your alkyl halide so that only the following stereoisomer of the product is formed? 2



P.T.O.

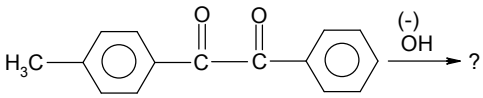
c) Look at the following reaction:



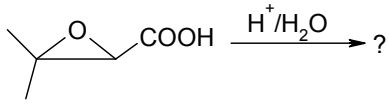
Now, when the deuterated analogue (i.e. $CD_3CHBrCD_3$) reacts under the same conditions, the rate of formation of the substitution product is unchanged but the rate of formation of the elimination product is slowed by a factor of 7. How do you explain the situation? 2

d) An S_N2 reaction, when carried out in gaseous phase, shows two potential minima which do not exist for the reaction in solution. Justify. 2

e) Predict the product highlighting the mechanistic aspect in the following transformation: 2



4. a) Predict the product with plausible mechanism for the following reaction: 2

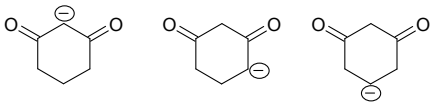


b) Provide mechanistic explainations for each of the following occurrences: 1.5+1.5

i) Dehydrohalogenation of (1*S*,2*R*)-1-bromo-1,2-diphenyl propane produces only *E*-1,2-diphenyl propene.

ii) Addition of 1-2 drops of an organic base can change the course of an S_Ni reaction.

c) Arrange the following carbanions as per their increasing stability order. Give also proper justification. 1+1



d) Predict the product in each of the following reactions:

What is the name of the common intermediate involved in these two reactions? Give another example of such similar reaction. 0.5+0.5+1

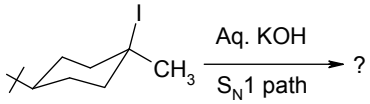
e) What type of solvent is used for radical reaction and why? 1

5. a) Among the following two carbenes, which one is more stable and why? 1+1

$:CH_2$ and $:CCl_2$

b) $Ph_3COH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4}$ yellow colour $\xrightarrow{+H_2O}$ colour disappeared. Explain the observation. 2

c) Considering carbocation as a planar trigonal structure, predict both the structure of the carbocation intermediate involved and the product(s) formed in the following conversion: 1+1



d) Both of the following 1,2-diols produce same product on treatment with conc. H_2SO_4. Offer explanation of this observation showing mechanistic aspects of the conversions and commenting on the carbocationic stability factor, if involved in these particular cases. 4

$Ph_2C(OH)C(OH)Me_2$ and $Ph(CH_3)C(OH)C(OH)Ph(CH_3)$