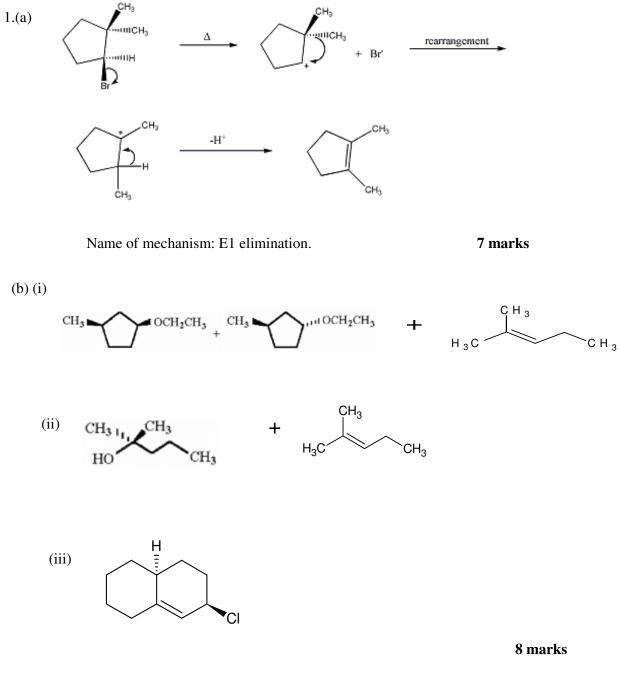
#### KOT121 Sem II 09/10

# **SECTION B:**

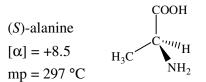


(c) The intermediate carbocation resulting from 3-bromobut-1-ene is resonance stabilized .

$$CH_3CH-CH=CH_2 \iff CH_3CH=CHCH_2$$
 3 marks

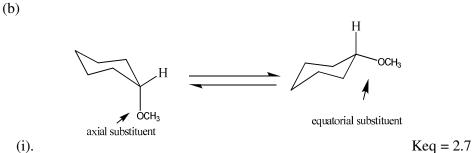
 $(d) (CH_3)_3COH < (CH_3)_3CO^{-} < CH_3CH_2O^{-} < CH_3CH_2S^{-}$  2 marks

1



- (i). The melting point is **same** as the *S* isomer.
- (ii). The melting pint of a racemic mixture is often different from the melting point of the enantiomers.
- (iii). The specific rotation of (R)-analanine is equal to <u>-8.5</u>, same as (S) but opposite sign.
- (iv). The optical rotation of a recemic mixture is equal to **Zero**. A racemic mixture is optically inactive.
- (v). (1) Solution of pure (S)-alanine  $\Rightarrow$  **optically active** (2) Equal mixture of (*R*) and (*S*)-alanine  $\Rightarrow$  **optically inactive** (3) 75% (S) and 25% (R)-alanine  $\Rightarrow$  optically active.

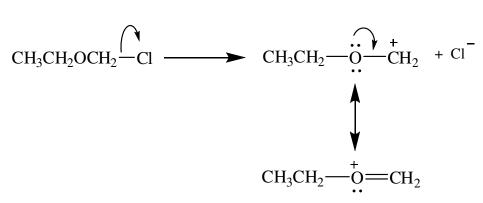
8 marks



- (i).
- The Keq is > 1 and therefore the product (the conformation of the right) is favored at (ii). equilibrium.
- The  $\Delta G^{\circ}$  for this process must be negative since the product is favored. (iii).

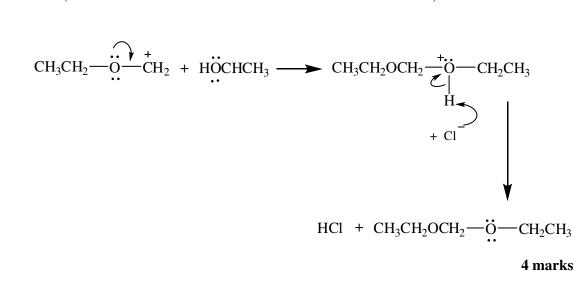
4 marks

(c)  $CH_3CH_2OCH_2Cl$  affords a resonance-stabilized carbocation, making an  $S_N1$  reaction possible even though the alkyl halide is 1°.

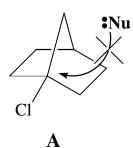


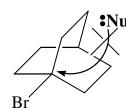
Two resonance structures can be drawn for the carbocation, stabilizing it

The carbocation can then continue the reaction: ( *can use either resonance structures to illustrate the reaction*)



(d) **A** and **B** can't react by  $S_N^2$  mechanism because <u>the backside attack of the nucleophile</u> is **blocked**:



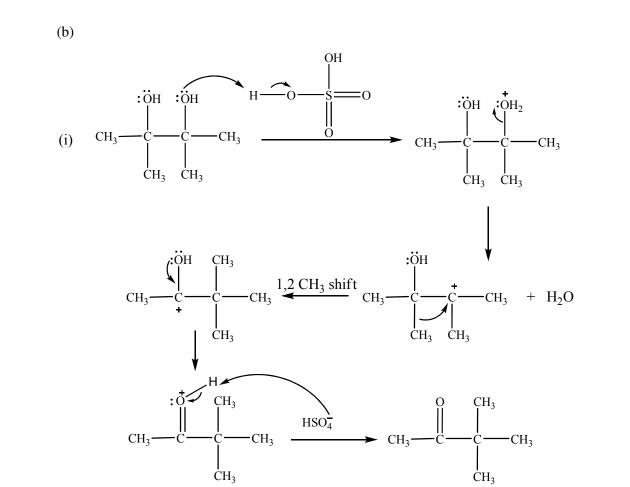


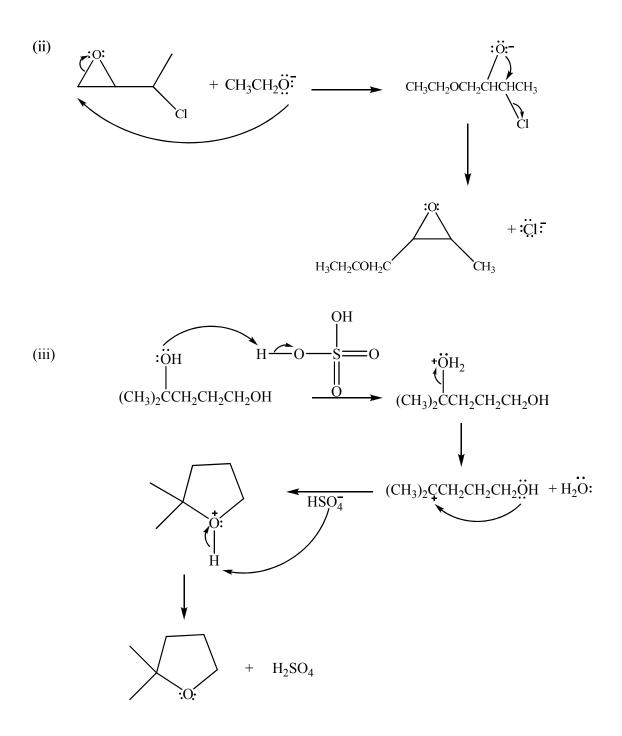


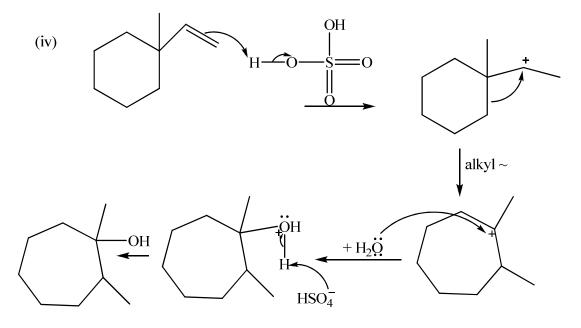
4 marks

3 (a) 1-pentanol (1° alcohol)
2-pentanol (2° alcohol)
3-pentanol (2° alcohol)
2-methyl-1-butanol (1° alcohol)
2-methyl-2-butanol (3° alcohol)
3-methyl-2-butanol (2° alcohol)
3-methyl-1-butanol (1° alcohol)
2,2-dimethyl-1-propanol (1° alcohol)
Also all cyclic alcohols having 5 carbon atoms.

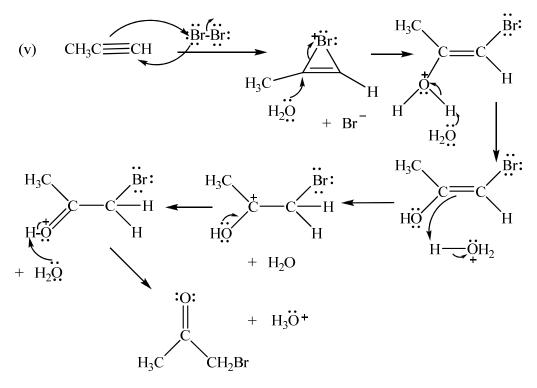
5 marks







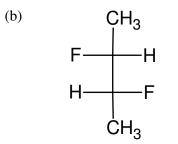
+  $H_2SO_4$ 



15 marks

4 (a) (i) 6-ethyl-2,6,7-trimethyl-5-propylnonane

(ii) 1-bromo-4-ethyl-2-methyl-3-isopropylhexane 4 marks



4 marks

# (c)

(i). **False**. The reaction is endothermic

(ii). **True**. This assumes that  $\Delta G^{\circ}$  is approximately equal to  $\Delta H^{\circ}$ .

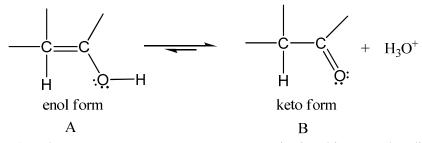
(iii). False. Keq < 1

(iv). True.

(v). **False**. The starting material is favored at equilibrium.

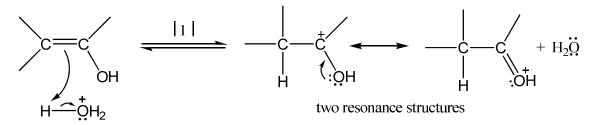
6 marks

### (d) (i) Keto-enol tautomers



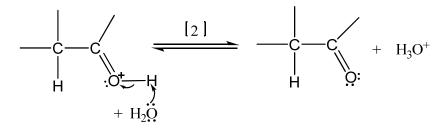
A and B are tautomers. Tautomers are constitutional isomers that differ in the location of a double bond and a hydrogen atom. An enol tautomer has an O-H bonded to a C=C. Whereas a keto tautomer has a C=O and an additional C-H bond. Equilibrium favors the keto form largely because a C=O is much stronger than a C=C. The process of converting one tautomer to the other is catalysed by both acid and base. An example would be the following steps showing the conversion of an enol form to the keto form using an acid.

Step [1] Protonation of the enol double bond



**Protonation** of the enol C=C with acid  $(H_3O^+)$  adds H<sup>+</sup> to form a **resonance stabilized carbocation**.

Step [2] Deprotonation of the OH group



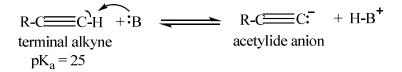
**Loss of a proton** forms the carbonyl group. Because the acid used in step [1] is reformed in step [2] tautomerization is **acid catalysed**.

(ii) Williamson ether synthesis

A Williamson ether synthesis is the synthesis of an ether via the  $S_N^2$  mechanism. The substrat is usually a primary alkyl halide (since it is less sterically hindered) and the reagent is a strong base i.e. the alkoxide anion. An example reaction is the synthesis of methyl ethyl ether. Either bromomethane or bromoethane can be used to react with  $CH_3CH_2O$  or  $CH_3O^-$  respectively. The preffered reaction would be bromomethane with the ethoxide ion as this is less sterically hindered. Bromoethane has a methyl group attached to the reaction centre whereas bromomethane does have any bulky groups attached to it.

#### (iii) Acidity of terminal alkynes

The C-H bond in the terminal alkyne is *sp* hybridized and all *sp* hybridized C-H bonds are more acidic than the  $sp^2$  and  $sp^3$  C-H bonds because of the higher *s* character. Therefore terminal alkynes are readily deprotonated with a strong base in a Bronsted-Lowry acid-base reaction. The resulting anion is called an acetylide anion.



Since an acid-base equilibrium favors the weaker acid or base, only base having conjugate acids with  $pK_a$  values higher than 25 are strong enough to form a significant concentration of acetylide anion.