

COVENANT UNIVERSITY
NIGERIA

TUTORIAL KIT
OMEGA SEMESTER

PROGRAMME: CHEMISTRY

COURSE: CHM 221

DISCLAIMER

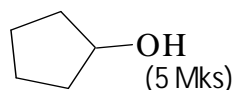
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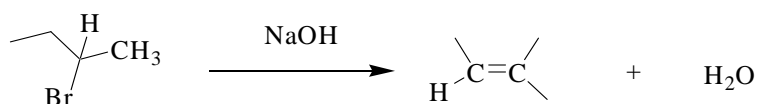
CONTRIBUTORS: Dr Mordi R.C., Dr. Olugbuyiro J.A.O., Dr. Ajani O.O. and Ajanaku C.O.

1. (a) Classify the following species as nucleophiles or electrophiles and give a reason for your classification

(i) NO_2 (ii) NaCN (iii) H_2C (iv) NH_3 (v)



(b) Explain the E1 mechanism using the reaction below:



(6Mks)

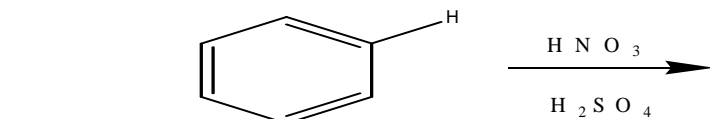
(c) Complete the following reactions:



(2.5Mks)



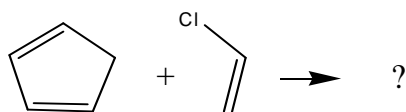
(2 mks)



(2 mks)

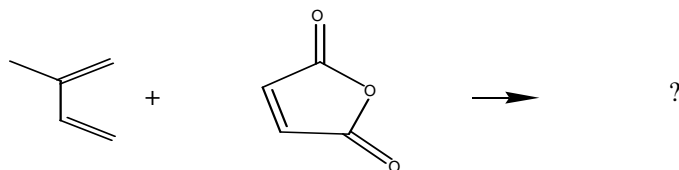
2. Complete the following reactions:

i)



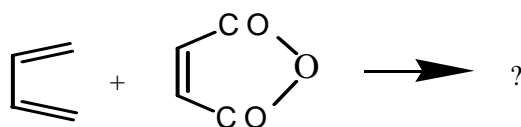
(4 Mks)

(ii)



(4 mks)

(iii)



(4mks)

(iv) Explain the mechanism of electrophilic addition to alkenes using the reaction below:



(5.5 Mks)

3. (a) A sample of 2-bromobutane has an observed specific rotation of +9.2°, if an enantiomerically pure sample of (S)-(+)-2-bromobutane has an observed specific rotation of +23.1°, calculate the amount of each enantiomer in the mixture. (3 Mks)

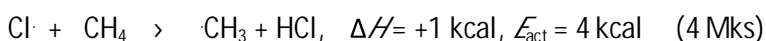
(b) Differentiate between mesomeric effect and inductive effect (1.5Mks)

(c) Give two structural examples of intramolecular hydrogen bonding. (2 Mks)

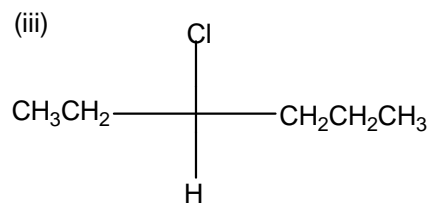
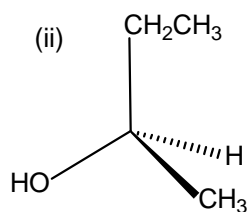
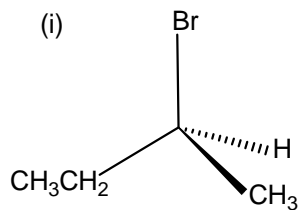
(d) The specific rotation of 50 g of cocaine in 100 ml of dichloromethane is +80°.

Calculate the observed rotation if the path length of the cell is 20 cm. (4 Mks)

(d) Represent the data and the free radical reaction below on an energy profile diagram.



(e) With the aid of the sequence rule, assign an absolute configuration (either R or S notation) to each of the following compounds:



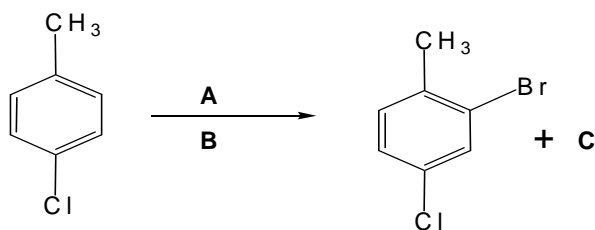
(3Mks)

4 (a) Draw the structure of the following compounds:

- i) Durene ii) m-Bromochlorobenzene iii) Quinoline iv) p-xylene
 v) p-Toluene-sulphonicacid vi) o-nitroacetanilide vii) o-bromo-p-nitrophenol
 viii. Mesitylene ix) 2,4,6-Trinitrotoluene x) Naphthalene (5 Mks)

(b) Show the synthetic pathway of 1,3, 5- trinitrobenzene (TNB)from toluene (8½ Mks)

(c) Complete the scheme below:



(4 Mks)

5 (a) State five (5) chemical symbols that represent deactivating meta directors (2½ Mks)

(b) 1,2,4-tetramethyl-3-bromobenzene can be prepared from 2,4-dimethyltoluene. Show the synthetic pathway of the preparation. (7 Mks)

c. Show (step wisely) the mechanism for electrophilic substitution of the following:

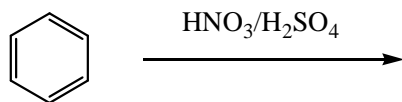
i. Nitration

ii. Acylation

(8Mks)

Q6

- I. Mention three physical properties of Benzene.
- II. What is Resonance ?
- III. Draw the structure of the following compounds:
 - i) Aniline
 - ii) m-Bromochlorobenzene
 - iii) Naphthalene
 - iv) Toluene
 - v) 2,4,6-Trinitrotoluene.
- IV. Mention three types of reactions common to benzene.
- V. List the four criteria for Aromaticity.
- VI. Differentiate between conjugation and Aromaticity.
- VII. What is the major product of the following reaction?



SOLUTION

Q1.

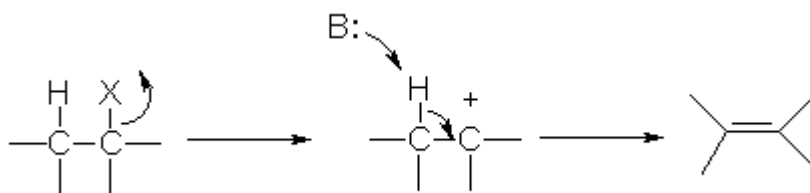
(a)

- i) NO_2 is an electrophile. N is electron -deficient.
- ii) NaCN is a nucleophile CN^- has δ^- end of a polar bond
- iii) H_2C^+ is an electrophile because the C has only six electrons though it possesses an unshared pair of electrons.
- iv) NH_3 is a nucleophile because it has unshared pairs of electrons
- v) ROH is a nucleophile because it has unshared pairs of electrons

(1mk each x 5= 5mks)

(b)

The general form of the E1 mechanism is as follows:

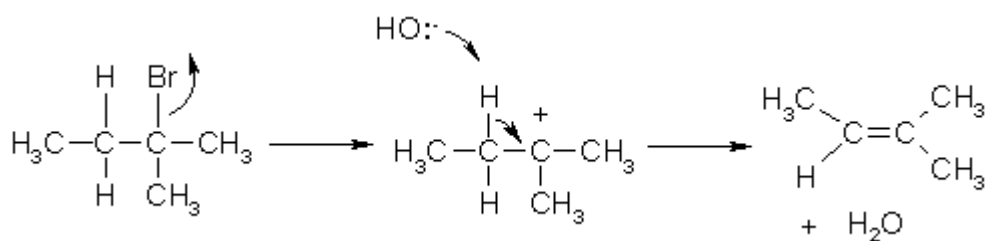


B: = base

X = leaving group (usually halide or tosylate)

In the E1 mechanism, the first step is the loss of the leaving group, which leaves in a very slow step, resulting in the formation of a carbocation. The base then attacks neighboring hydrogen, forcing the electrons from the hydrogen-carbon bond to make the double bond. Since this mechanism involves the formation of a carbocation, rearrangements can occur.

An example of the E1 reaction:



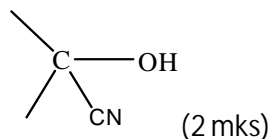
Base Strength: A strong base not required, since it is not involved in the rate-determining step

Leaving groups: A good leaving group is required, such as a halide or a tosylate, since it is involved in the rate-determining step.

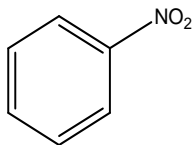
Rearrangements: Since the mechanism goes through a carbocation intermediate, rearrangements can occur.

(c)i) $\text{CH}_3\text{N}^+\text{H}_3 + \text{Br}^-$ (2.5 mks)

ii)



iii)



(2 mks)

Q3.

(a) A sample of 2-bromobutane has an observed specific rotation of $+9.2^\circ$, if an enantiomerically pure sample of (S)-(+)-2-bromobutane has an observed specific rotation of $+23.1^\circ$, calculate the amount of each enantiomer in the mixture.

Solution:

$$\text{Optical purity} = \frac{\text{Observed specific rotation}}{\text{Specific rotation of the pure enantiomer}}$$

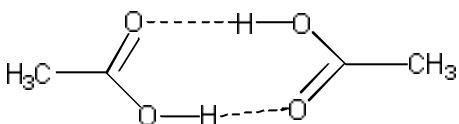
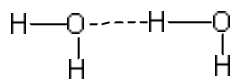
$$\text{Optical purity} = \frac{+9.2^\circ}{23.1^\circ} = 0.40 \text{ or } 40\%$$

Because the observed specific rotation is positive, we know that the solution contains excess (S)-(+)-2-bromobutane. The mixture is 40% optically pure, which means that 40% of the mixture is excess S enantiomer and 60% is a racemic mixture. Half of the racemic mixture plus the amount of excess S enantiomer equals the amount of the S enantiomer present in the mixture

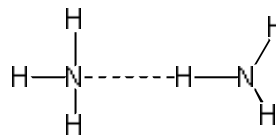
$$\text{i.e. } \frac{1}{2} \times 60 + 40 = 70\%$$

Thus, 70% of the mixture is the S enantiomer and 30% is the R enantiomer. **2Mks**

(b) Structural examples of intramolecular hydrogen bonding

2CH₃COOH

H—F-----H—F

Any two examples for **3Mks**

(c) The specific rotation of 25 g of cocaine in 50 ml of dichloromethane is $+75^\circ$.

Calculate the observed rotation, if the path length of the cell is 20cm.

$$C = 50/100 = 0.5 \text{ g/ml} \quad [\alpha] = +80^\circ \quad l = 20\text{cm} = 2 \text{ dm} \quad = ?$$

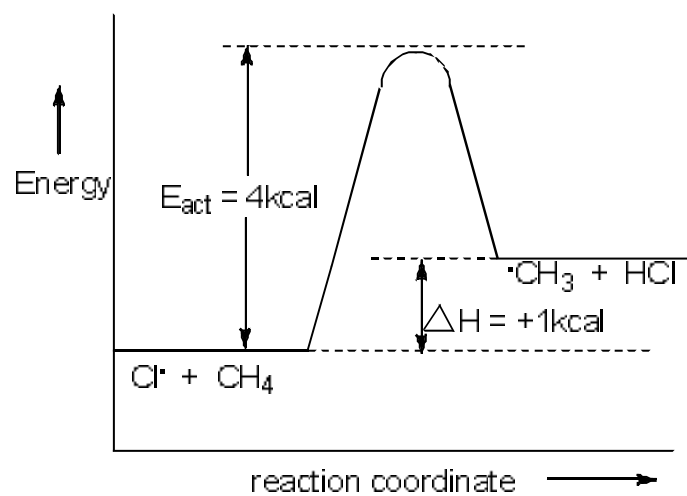
$$\text{Specific Rotation } [\alpha]_D = \frac{\text{observed rotation } \alpha}{\text{concentration} \times \text{path length}}$$

$$\text{Therefore, observed rotation } = [\alpha] \times C \times l = +80^\circ \times 0.5 \times 2$$

$$= +80^\circ$$

4Mrks

(d) Energy Profile Diagram



4Mrks

- (e) (i) S
(ii) R
(iii) R

6Mrks

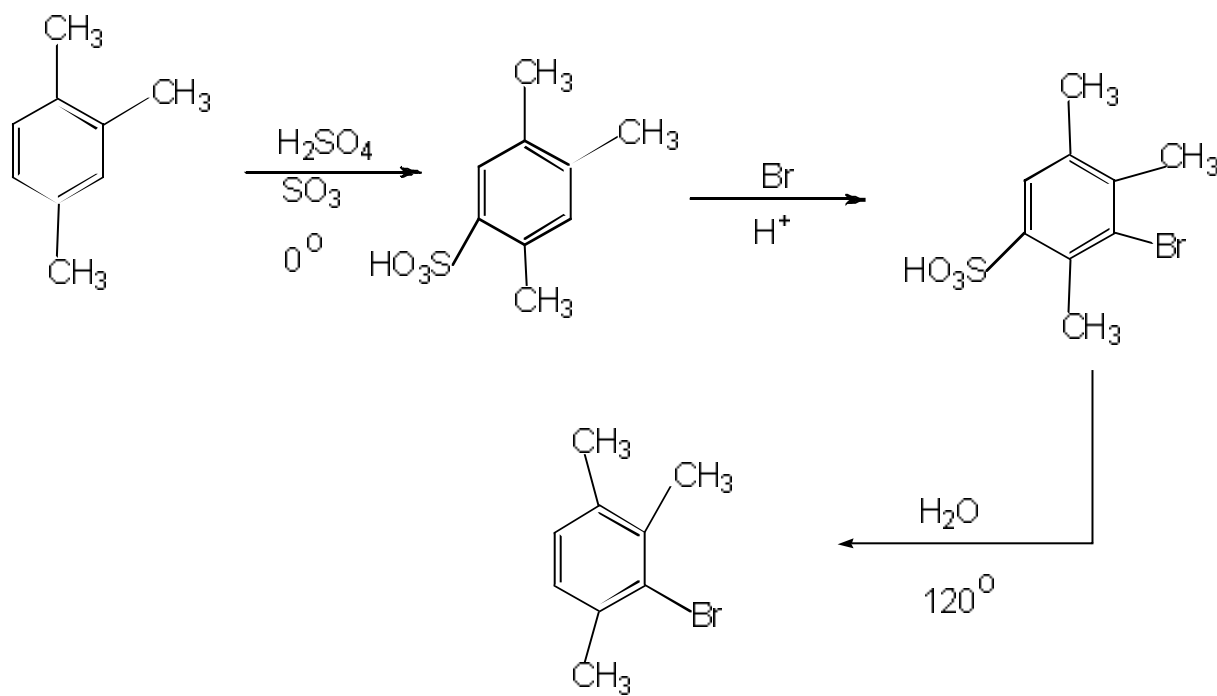
Q5.

(a). Meta Directors *Deactivating* (Any five)

i. $-\text{CN}$ ii. $-\text{COOH}$ iii. $-\text{COOR}$ iv. $-\text{CHO}$ v. $-\text{COR}$ vi. $-\text{NO}_2$ vii. $-\text{NR}_3$

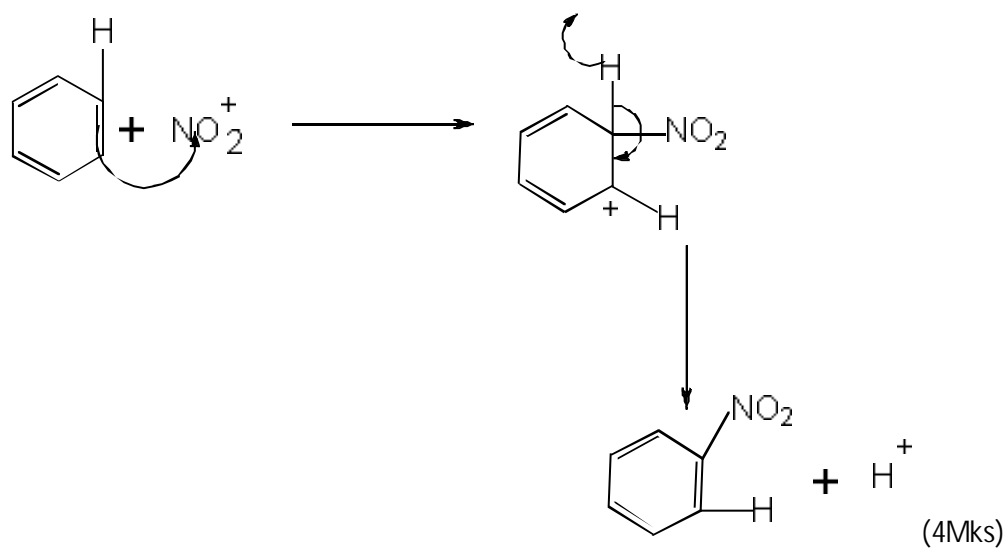
viii. $-\text{NR}_3$ ix. $-\text{SO}_3\text{H}$ x. $-\text{SO}_2\text{OR}$ (2½ Mks)

(b).

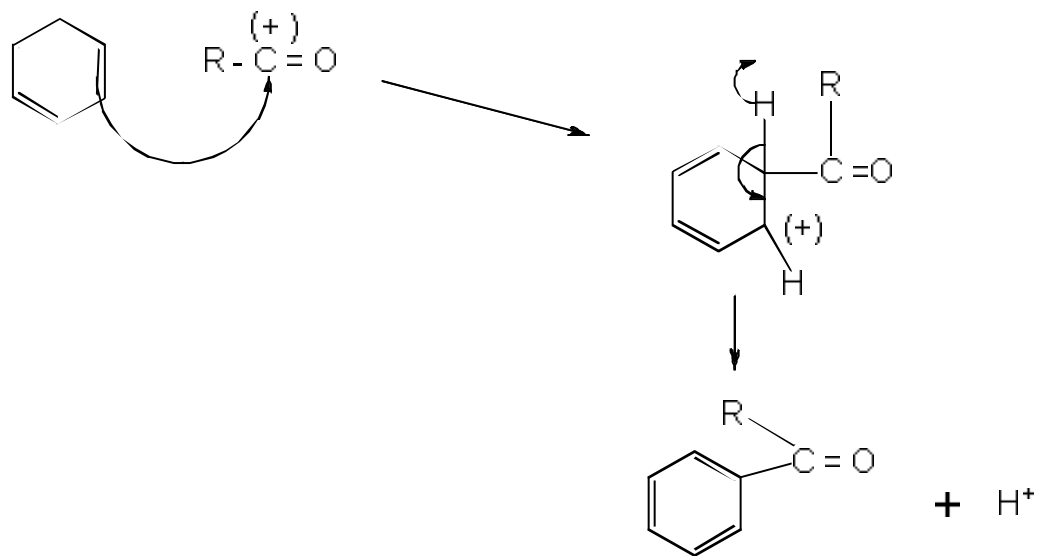
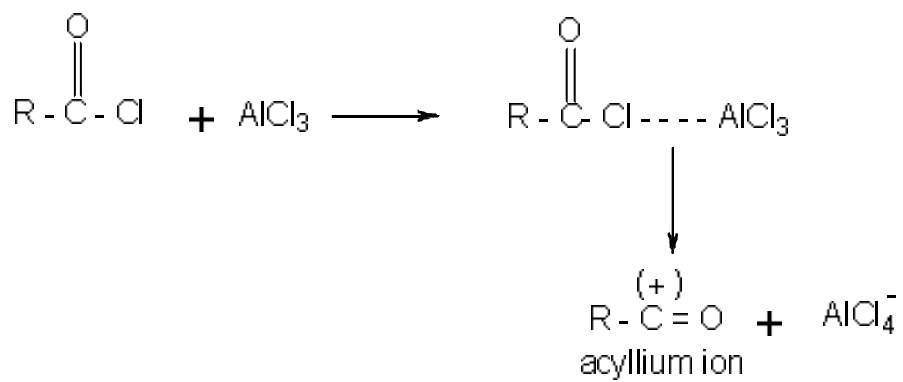


(7Mks)

c. (i) Nitration mechanism



(ii) Acylation



(4Mks)