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CHEMISTRY

ORGANIC CHEMISTRY

Level & Board	CIE (A-LEVEL)
TOPIC:	Halogen Derivatives
PAPER TYPE:	SOLUTION - 1
TOTAL QUESTIONS	11
TOTAL MARKS	105

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Halogen Derivatives - 1

1)

(a) (i) $\text{AlCl}_3 + \text{heat}$

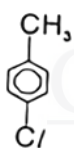
(ii) u.v light.

(b) PCl_5 or SOCl_2 .

(c) (i)

	Place one tick only in this column
A > B > C	
A > C > B	
B > A > C	
B > C > A	
C > B > A	
C > A > B	

(ii) Acyl chloride is most reactive because $\text{R}-\overset{\text{O}^{\delta-}}{\parallel}{\text{C}}^{\delta+}-\overset{\delta-}{\text{Cl}}$ carbonyl carbon atom is very electropositive and easily attacked by nucleophile.



Is least reactive because the benzene ring electrons are delocalised

Over the ring causing the $\text{C}-\text{Cl}$ bond to become stronger.

2)

(a) (i) stage I reagent(s): Cl_2 gas

conditions(s): U.V. light

stage II reagent(s): KCN

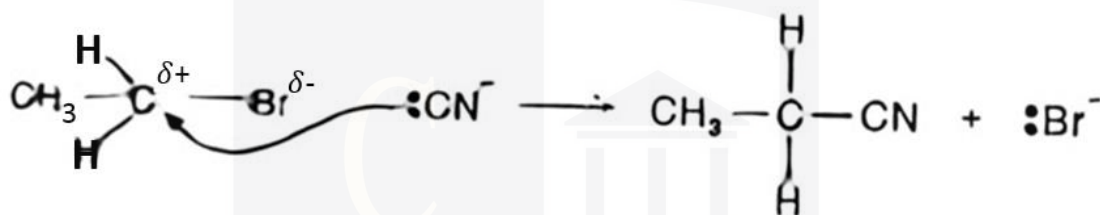
conditions(s): heat in ethanol.

(ii) Reagent(s): Br_2

condition(s): U.V. light

3)

(b) Nucleophilic substitution



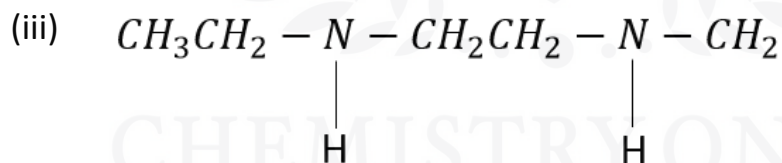
. CN^- acts as a nucleophile and attacks the electron deficient carbon atom C.

$\text{C} - \text{CN}$ bond is formed, while $\text{C} - \text{Br}$ bond cleaves heterolytically.

(c) (i) $\text{J} = (\text{CH}_3)_2\text{C} = \text{CH}_2$

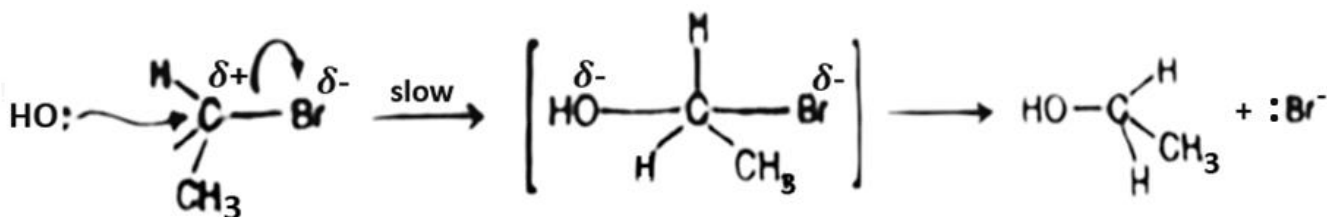
(ii) $\text{K} = (\text{CH}_3)_2\text{CHCN}$

$\text{L} = (\text{CH}_3)_2\text{CHCO}_2\text{CH}_2\text{CH}_3$



4)

(a)



The $\text{C} - \text{Br}$ bond is polar due to the electronegative Br. The negatively charged nucleophile, OH^- , attacks the electron deficient C to C - Br. The $\text{C} - \text{O}$ bond is formed while the $\text{C} - \text{Br}$ bond is cleaved at the same time, going through a

pentavalent transition state which is unstable and breaks to form the products.

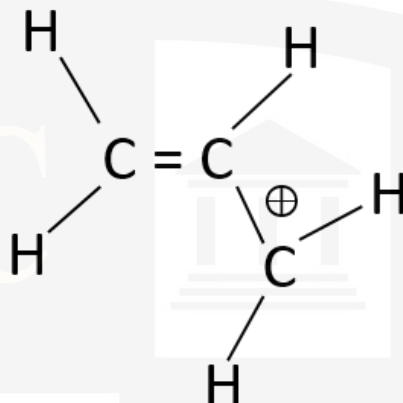
(b) (i) order with respect to $\text{CH}_2 = \text{CHCH}_2\text{Br}$ 1

order with respect to NaOH 0

(ii) $\text{CH}_2 = \text{CHCH}_2\text{Br} + \text{NaOH} \rightarrow \text{CH}_2 = \text{CHCH}_2 + \text{NaBr}$

(c) (i) NO. This reaction has a first order kinetics. In 3(a), the reaction has a second order kinetics.

(ii)



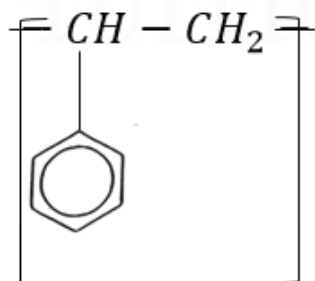
(b) The p-orbital of Br can interact with the π -orbital in the $\text{C} = \text{C}$ bond. This strengthens the $\text{C} - \text{Br}$ where it has partial double bond character.

5)

(a) (i) U.V light.

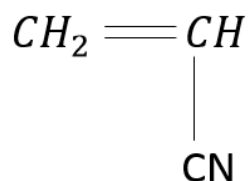
(ii) Alcoholic KOH and heat.

(iii)

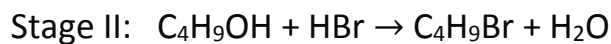
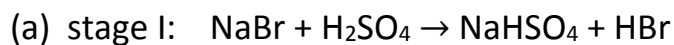


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(iv)



6)



(b) Moles of NaBr = $\frac{35}{103} = 0.34$

\Rightarrow moles of HBr = 0.34

moles of $\text{C}_4\text{H}_9\text{OH} = \frac{20}{74} = 0.27$

0.27 moles of $\text{C}_4\text{H}_9\text{OH}$ will react with 0.27 moles of NaBr, \therefore NaBr is in excess

(c) moles of $\text{C}_4\text{H}_9\text{OH} = \frac{15.4}{74} = 0.208$

Moles of $\text{C}_4\text{H}_9\text{Br}$ expected = 0.208

Actual yield of $\text{C}_4\text{H}_9\text{Br} = \frac{22.5}{137} = 0.164$ moles

percentage yield = $\frac{0.164}{0.208} = 78.8\%$

(d) inorganic by-product : Bromine.

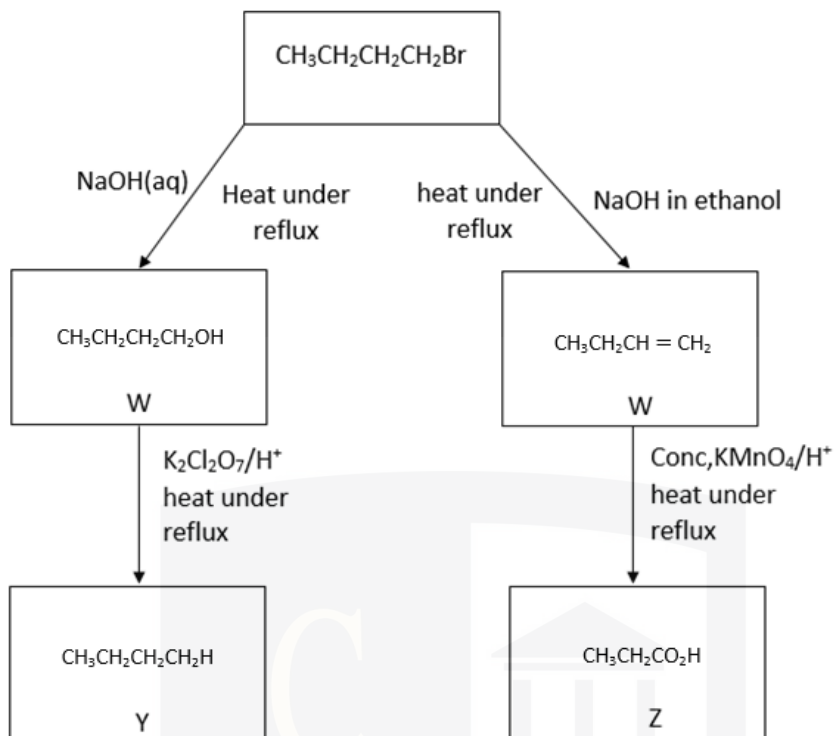
Role of conc. H_2SO_4 : Acts as an oxidizing agent.

Organic by-product : but-1-ene.

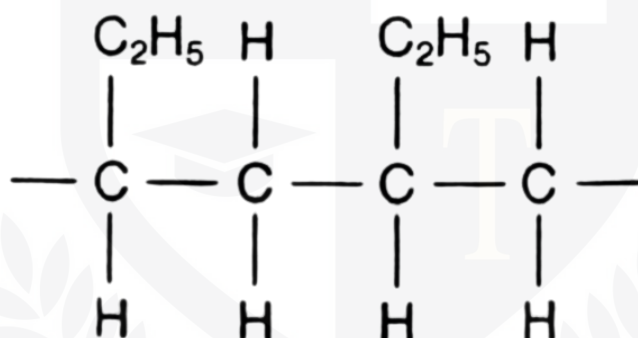
Role of conc. H_2SO_4 : Acts as a dehydrating agent.

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7)



(c) (i) X



8)

(a) reaction 1 reagent: NaOH or KOH

Solvent: H_2O Reaction 2 reagent: NH_3 /ammonia

Solvent: Alcohol or ethanol

Reaction 3 reagent: NaOH or KOH

Solvent: Ethanol

(b) The rate of reaction with iodobutane will be faster than with bromobutane because C – I bond is weaker than C – Br bond.

B.E for C– Br bond is 280 KJ/mol

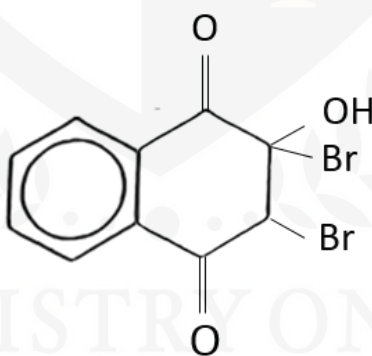
Hence C – I bond is easier to break. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ reacts faster than



- (c) 1. Nontoxic or inertness.
 2. Easy to vaporise or volatile compound.
- (d) (i) It is a type of bond breaking in which each atom takes its electron and forms free radical in the presence of u.v. light.
- (ii) $\text{CCl}_2\text{F}_2 \rightarrow \cdot\text{CClF}_2 + \cdot\text{Cl}$
- (e) These compounds are highly flammable and can easily catch fire.

9)

- (e) (i) Ketone, Alcohol, Alkene
- (ii) Add 2,4-Dinitrophenylhydrazine (DNPH) to both compound A and lawsone and heat. Lawsone will give an orange/red precipitate whereas no reaction will be observed with compound A.
- (iii) NaBH_4
- (iv)

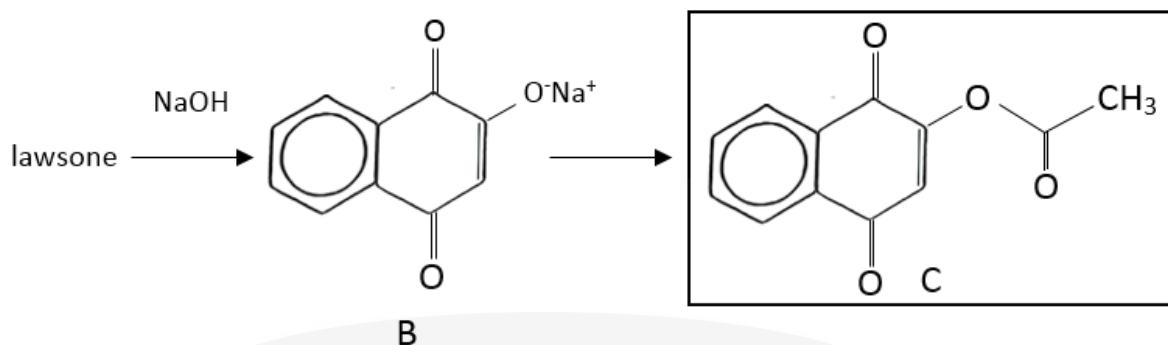


- (b) (i) $E_{\text{cell}} = 1.33 - 0.36 = (+) 97 \text{ V}$
- (ii) $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 3\text{C}_{10}\text{H}_8\text{O}_3 \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 3\text{C}_{10}\text{H}_6\text{O}_3$
- (iii) Moles of $\text{K}_2\text{Cr}_2\text{O}_7 = \frac{7.50}{1000} \times 0.05 = 3.75 \times 10^{-4} \text{ mol}$
- $\text{K}_2\text{Cr}_2\text{O}_7 : \text{A} :: 1 : 3$
- \therefore moles of A = $3.75 \times 10^{-4} \times 3 = 1.125 \times 10^{-3} \text{ mol}$
- Concentration of A = [A]

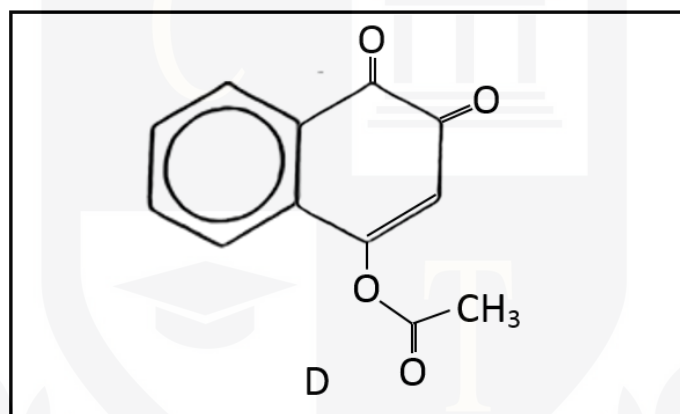
$$= \frac{1.125 \times 10^{-3}}{20} \times 1000$$

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 $= 5.625 \times 10^{-2} \approx 5.63 \times 10^{-2} \text{ mol/dm}^3$

(c) (i)



(ii)



diagram

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10)

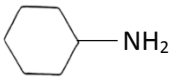
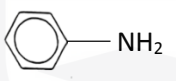
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(a) Acidities: $\text{CHCl}_2\text{CO}_2\text{H} > \text{CH}_2\text{ClCO}_2\text{H} > \text{CH}_3\text{CO}_2\text{H}$.

$\text{CHCl}_2\text{CO}_2\text{H}$ and $\text{CH}_2\text{ClCO}_2\text{H}$ have chlorine atoms which are more electron withdrawing than H. The anions formed by $\text{CHCl}_2\text{CO}_2\text{H}$ and $\text{CH}_2\text{ClCO}_2\text{H}$ are more stabilized than that formed from $\text{CH}_3\text{CO}_2\text{H}$, since the negative charge of the anions of $\text{CHCl}_2\text{CO}_2\text{H}$ and $\text{CH}_2\text{ClCO}_2\text{H}$ is more greatly dispersed by the electron

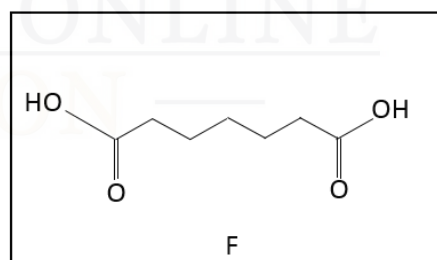
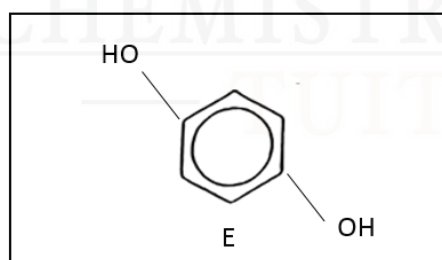
withdrawing chlorine atoms. Since $\text{CHCl}_2\text{CO}_2\text{H}$ has two chlorine atoms as compared to $\text{CH}_2\text{ClCO}_2\text{H}$, the charge on $\text{CHCl}_2\text{CO}_2^-$ is more greatly dispersed than on $\text{CH}_2\text{ClCOO}^-$. Hence, $\text{CHCl}_2\text{CO}_2\text{H}$ dissociates to a greater extent than $\text{CH}_2\text{ClCO}_2\text{H}$ which in turn dissociates more than $\text{CH}_3\text{CO}_2\text{H}$.

(b)

First compound	Second compound	Test (reagents and conditions)	Observation with first compound	Observation with second compound
		$\text{Br}_2(\text{aa})$	None	White ppt formed
$\text{CH}_3\text{CH}_2\text{COCl}$	$\text{CH}_3\text{COCH}_2\text{Cl}$	2, 4-DNPH	None	Orange ppt formed
$\text{CH}_3\text{CH}_2\text{CHO}$	CH_3COCH_3	Tollen's Reagent + warm	Silver/Black ppt	none

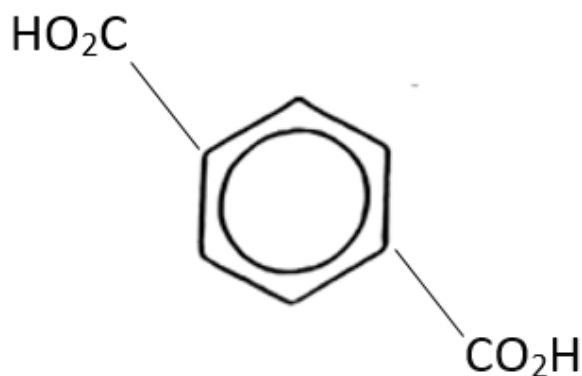
(c) (i) Condensation

(ii)



(iii) Convert **F** into a diacyl chloride and add it to a solution of aqueous sodium hydroxide and **E**.

(iv) Monomer to be changed: **F**

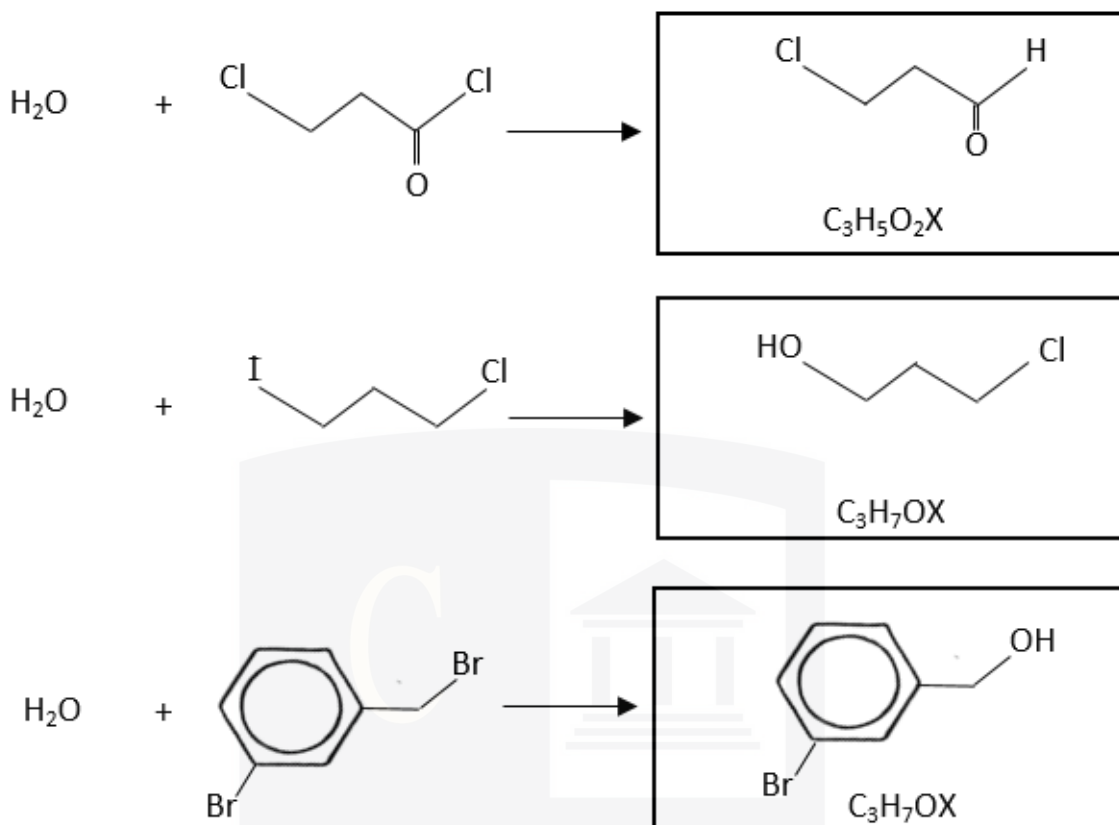


11)

- (a) The enthalpy change when 1 mole of bonds is broken in a molecule with the reactants and products in the gas phase under standard conditions of 298K and 1 atm.
- (b) (i) The bond energy decreases from F to I. This is because the C – X bond becomes longer, and hence weaker, from F to I.
- (ii) From F to I, as the bond energy of C – X decreases, the reactivity of the halogenoalkanes increases.
- (c) The C – Cl bond, with bond energy 340KJ/mol, is weaker than the C – H bond, with bond energy 410 KJ/mol, and the C – F bond. Hence it is easily broken down into chlorine radicals, that causes the breakdown of O_3 in the ozone to produce O_2 .

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(d)



(e) (i) Ultraviolet light.

(ii) Free radical substitution.

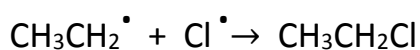
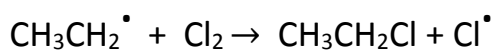
(iii) Bond energy of C – H bond = 410 kJ mol^{-1} Bond energy of H – Cl bond = 431 kJ mol^{-1}

$$\begin{aligned} \therefore \Delta H &= (410 \times 6) - (410 \times 5 + 431) \\ &= 2460 - 2481 = -21 \text{ kJ mol}^{-1} \end{aligned}$$

(iv) Bond energy of C – H = 410 kJ mol^{-1} Bond energy of C – I = 299 kJ mol^{-1}

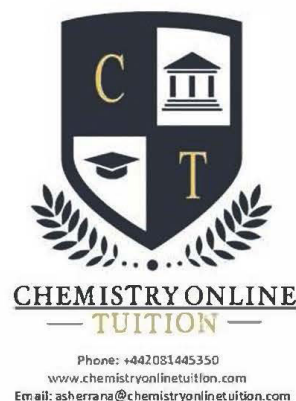
$$\begin{aligned} \therefore \Delta H &= (410 \times 6) - (410 \times 5 + 299) \\ &= 2460 - 2349 = +111 \text{ kJ mol}^{-1} \end{aligned}$$

(v) The reaction of iodine and ethane is endothermic and requires energy.

(vi) $\text{Cl}_2 \rightarrow 2\text{Cl}^\bullet$ 



DR. ASHAR RANA



- Founder & CEO of Chemistry Online Tuition Ltd.
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