

REASONING QUESTIONS FROM ORGANIC CHEMISTRY (CH. 1 & 2)

1.) Why do haloalkenes under go nucleophilic substitution whereas haloarenes under go electrophilic substitution .

Ans. Due to more electro negative nature of halide atom in haloalkanes carbon atom becomes slightly positive and is easily attacked by nucleophilic reagents.

While in haloarenes due to resonance, carbon atom becomes slightly negative and attacked by electrophilic reagents.

2.) When an alkyl halide is treated with ethanolic solution of KCN, the major product is alkyl cyanide where as if alkyl halide is treated with AgCN, the major product is alkyl isocyanide.

Ans. KCN is ionic they can attach through C or N but C-C bond is strong than C-N bond. So alkyl cyanide is the major product but AgCN is covalent so more electronegative N can attach to C and forms isocyanides.

3.) How do 1° 2° 3° alcohols differ in terms of dehydrogenation?

Ans. 1°alcohol $\xrightarrow{\hspace{2cm}}$ aldehyde

2°alcohol $\xrightarrow{\text{Cu, 300}^\circ\text{C}}$ ketone

3°alcohol $\xrightarrow{\text{Cu, 300}^\circ\text{C}}$ alkene

4.) Why are the reaction of alcohol /phenol with acid chloride in the presence of pyridine ?

Ans. Because esterification reaction is reversible and presence of base (pyridine) neutralises HCl produced during reaction thus promoting forward reaction .

5.) Explain why o-nitrophenol is more acidic than o-methoxy phenol ?

Ans. $-\text{NO}_2$ group is electron withdrawing group, e^- density on O decreases and loss of H^+ is easy whereas $-\text{OCH}_3$ group is electron releasing group , which increases e^- density on O , which makes difficult to the loss of H^+ , hence are less acidic .

6.) Aryl halides cannot be prepared by the action of sodium halide in the presence H_2SO_4 .Why?

Ans. Due to resonance the carbon- oxygen bond in phenols has partial double bond and it is stronger than carbon oxygen single bond.

7.) Why Grignard reagent should be prepared under anhydrous conditions?

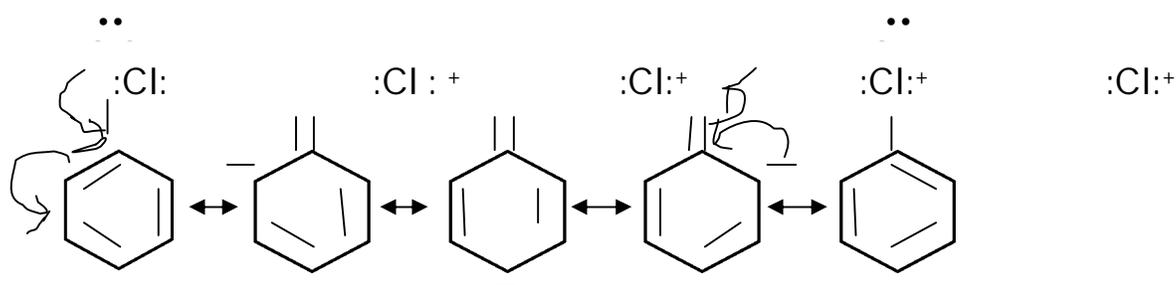
Ans. Grignard reagent reacts with H_2O to form alkanes, therefore they are prepared under anhydrous conditions.

8.) Why is Sulphuric acid not used during the reaction of alcohols with KI?

Ans. It is because HI formed will get oxidized to I_2 by concentrated Sulphuric acid which is an oxidizing agent.

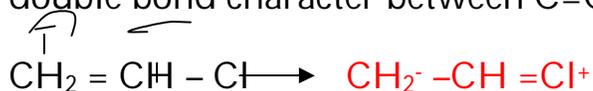
9.) Although chlorine is an electron-withdrawing group, yet it is ortho and para directing in electrophilic aromatic substitution reactions. Why?

Ans. Chlorobenzene is a resonance hybrid, there is a $-ve$ charge at ortho and para positions, electrophilic substitution reaction will take place at ortho and para positions due to the $+R$ effect. The $+R$ effect is dominating over the $-I$ effect.



10.) Explain why vinyl chloride is unreactive in nucleophilic substitution reaction?

Ans. Vinyl chloride is unreactive in nucleophilic substitution reaction because of the double bond character between the $C=Cl$ bond, which is difficult to break.



11) Explain why o-nitrophenol is more acidic than o-methoxy phenol?

Ans. Due to the $-R$ and $-I$ effect of the $-NO_2$ group, the electron density on the $O-H$ bond decreases, and the loss of H^+ is easy. In contrast, in o-methoxy phenol, due to the $+R$ effect, the $-OCH_3$ group increases the electron density on the $O-H$ group, and hence the loss of H^+ is difficult. (Both $-ve$ charges repel each other)

12) Of benzene and phenol, which is more easily nitrated and why?

Ans. Nitration is an electrophilic substitution. The $-OH$ group in phenol increases the electron density at the ortho and para positions as follows. Since phenol has a higher electron density due to its electron-releasing nature,

of -OH group, compared to benzene, therefore nitration is easy in phenol than benzene.

13) How will you account for the following? Ethers possess a net dipole moment even if they are symmetrical in structure?

A. Because of greater electronegativity of O-atom than carbon C-O bonds are polar.

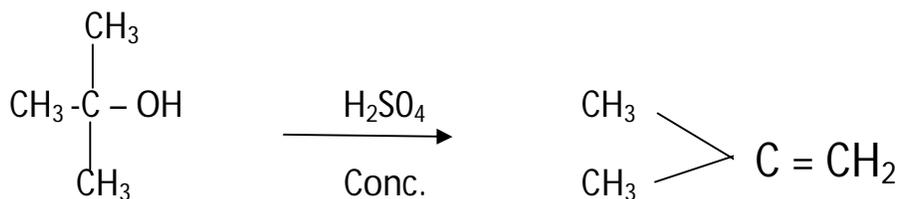
C-O bonds are inclined to each other at an angle of 110° (or more), two dipoles do not cancel out each other.

14) Why are reactions of alcohol/phenol and with acid chloride in the presence of pyridine?

Ans. Because esterification reaction is reversible and presence of base (pyridine) neutralises HCl produced during reaction thus promoting forward reaction.

15) Why Preparation of ethers by acid dehydration of secondary or 3° alcohols is not a suitable method?

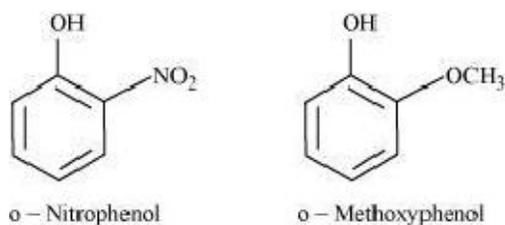
Ans:- The formation of ethers by dehydration of alcohol is a bimolecular reaction (S_N2) group is hindered. as a result elimination dominates substitution as 3° carbocation is more stable. Hence in place of ethers, alkenes are formed.



16) Phenols do not give protonation reactions readily. Why?

Ans:- The lone pair on oxygen of O-H in phenol is being shared with benzene ring through resonance. Thus, lone pair is not fully present on oxygen and hence phenols do not undergo protonation reactions.

17) Explain why is ortho nitrophenol more acidic than ortho methoxyphenol?



ANS. The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O-H bond. As a result, it is easier to lose a proton. Also, the o-nitrophenoxide ion formed after the loss of proton is stabilized by resonance. Hence, ortho-nitrophenol is stronger acid. On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density in the O-H

bond and hence, the proton cannot be given out easily. Therefore ortho-nitrophenol is more acidic than ortho-methoxyphenol.

Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

ANS. The formation of ethers by dehydration of alcohol is a bimolecular reaction ($\text{S}_{\text{N}}2$)

involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution.

(i) Why is the Dipole moment of methanol higher than that of phenol? (ii) . Explain why phenols do not undergo substitution of the -OH group like alcohols.

ANS. (i) Due to electron withdrawing effect of phenyl group, the C—O bond in phenol is less polar, whereas in case of methanol the methyl group has electron releasing effect and hence C—O bond in it is more polar.

(ii) C—O bond in phenols has partial double bond character due to resonance and hence is difficult to cleave.

Nitration of phenol gives ortho- and para- products only.

ANS (1) -OH group increases the electron density more at ortho and para positions through its electron releasing resonance effect.

Account for the following:

i) Phenols has a smaller dipole moment than methanol

ii) Phenols do not give protonation reactions readily.

ANS. (a). In phenol the electron withdrawing inductive effect of -OH group is opposed by electron releasing the resonance effect of -OH.

(b). The lone pair on oxygen of -OH in phenol is being shared with benzene ring through resonance. Thus, lone pair is not fully present on oxygen and hence phenols do not undergo protonation reactions.