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Expt. No. DH Part-I, Paper II, Group B Page No. 29

Chem. Prop. of Aldehyde DR. S. K. Jha

Chemical properties of Aldehyde & Ketone: Lect. 7

Aldehyde and Ketone both contain Carbonyl group hence they show same Chemical properties. Aldehyde and ketone shows mainly following type of chemical reactions:

A. Nucleophilic addition reactions
B. Nucleophilic addition reactions followed by elimination
C. Reduction reactions
D. Oxidation reactions
E. Reaction due to α-Hydrogens
F. Electrophilic substitution reaction.
G. Halo-form reaction.
H. Polymerisation reaction.

[A] Nucleophilic addition reaction: →

In aldehyde or ketone there is a Carbonyl group i.e $>C=O$, due to high electronegativity of Oxygen the shared pair of electron is attracted towards it, so it get δ- (delta negative) charge and in the meantime C get δ+ (delta positive) charge, so it becomes polar.

During this reaction substrate is $\begin{matrix} H \\ R \end{matrix}>C=O$ or $\begin{matrix} R \\ R \end{matrix}>C=O$; and the reagent is nucleophile (An electron rich species), in Carbonyl group ($>\overset{\delta+}{C}=\overset{\delta-}{O}$) the present Carbon get δ+ charge & Oxygen get δ- charge, so the nucleophile attacks on electrophilic centre ($\overset{\delta+}{C}$).

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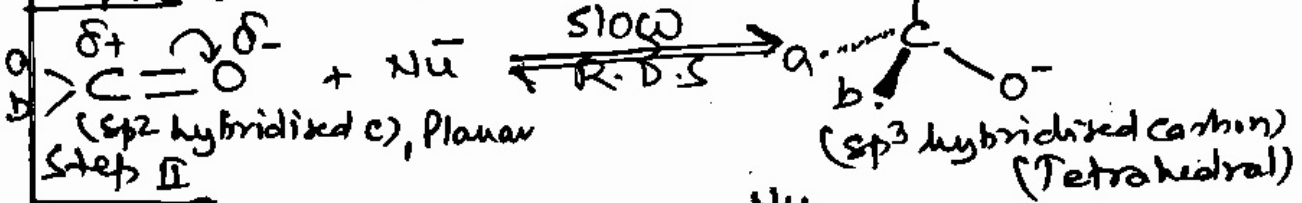
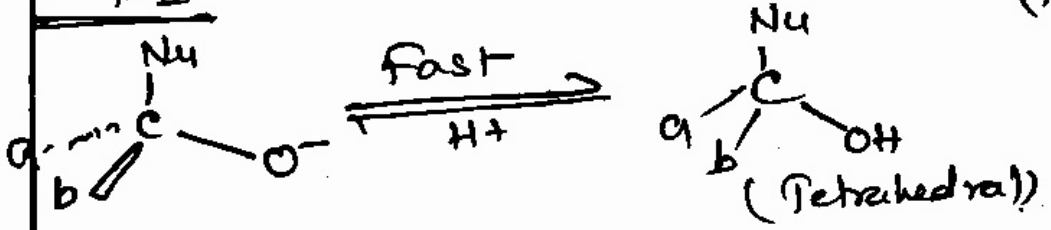
Carbonyl group (>C=O) has sp^2 hybridised Carbon but after nucleophilic attack (which is a slow reaction, because a neutral stable molecule converts into unstable ionic species) first it form such an intermediate i.e alkoxide intermediate which has sp^3 hybridised carbon (i.e tetrahedral), further this intermediate capture a proton (i.e H^+) from the medium of the reaction and finally converts into an electrically neutral molecule (this step of the reaction is comparatively fast because unstable ionic species converts into stable electrically neutral molecule).

Step I (Nucleoplic attack on Aldehyde) Nu



Step II



Note: If a & b are R & H, then it is aldehyde but if a & b are R & R then it is ketone.

- Aliphatic aldehydes are more reactive than aliphatic ketones — this is because of i) steric hindrance or steric effect ii) electronic effect or +I effect.

Date .....

Expt. No. .....

Page No. 25

In case of aldehyde there is only one alkyl group (R) so it's steric hindrance is comparatively less but in ketone there are two bulky alkyl groups are present so steric hindrance is comparatively more and as steric hindrance increases reactivity of nucleophilic addition reaction decreases. In other hand ketone contain two alkyl groups attached to carbocation so +I effect is more which make more stable to 'C+' & decrease the reactivity but the same is not in aldehyde because they have only one alkyl group so aliphatic aldehydes are more reactive than aliphatic ketones.

- Comparison in reactivity of aliphatic aldehyde and aromatic aldehyde :- → Aliphatic aldehydes are more reactive than aromatic aldehydes this is because carbon present in carbonyl group of aromatic aldehyde is less electrophilic or the polarity of carbonyl group of aromatic aldehydes are reduced or lesser due to it's resonance structure, but the electrophilic nature of carbonyl group in more in aliphatic aldehydes because it do not show such resonance, hence aliphatic aldehydes are more reactive than aromatic aldehydes.

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Some examples of nucleophilic addition reaction:-

1) Reaction with Hydrogen Cynide (HCN):- It form aldehyde Cynohydrin.

$$>C^{\delta+}=O^{\delta-} + CN^- \underset{R.D.S}{\overset{Slow}{\rightleftharpoons}} >C<^{O^-}_{CN} \xrightarrow{H^+} >C<^{OH}_{CN}$$

(Aldehyde Cynohydrin)

2) With Sodium bisulphite ($NaHSO_3$) → It forms bisulphite addition product.

$$>C=O + NaHSO_3 \rightleftharpoons >C<^{SO_3H}_{ONa} \xrightleftharpoons{H^+} >C<^{SO_3Na}_{OH}$$

(Bisulphite addition Product)

3) With Grignard reagent (Alkyl Magnesium halide) $RMgX$:→ First it gives addition product further on hydrolysis with dil HCl it gives alcohol (which may be 1° or 2° or 3°).

$$>C=O + R-Mg-X \longrightarrow >C<^{R}_{OMgX} \xrightarrow{H_3O^+} >C<^{R}_{OH} \text{ (Alcohol)} + Mg<^{OH}_{X} \text{ (Basic Magnesium-halide)}$$

Note

a) If $>C=O$ is $HCHO$ (Methanal) it gives 1° Alcohol.

b) If $>C=O$ is CH_3CHO (Ethanal) ~~or~~ any other aldehyde it gives 2° Alcohol.

c) If $>C=O$ is ketone it gives 3° Alcohol.

4) With alcohol:→ When aldehyde react with ~~primary~~ ~~Alcohol~~ or monohydric alcohol first it gives alkoxy alcohol as intermediate known as hemiacetal which on further reaction with monohydric alcohol to gives final product i.e Acetal (gem-dialkoxy compound), but ketone react with dihydroxy alcohol (glycol) under same condition it gives finally ethylene glycol ketal.