addition product initially formed is readily decomposed by dilute mineral addition product initially learners. It is sometimes necessary to activate acids to yield β - hydroxy esters. It is sometimes necessary to activate zinc by adding a few crystals of iodine or mercuric bromide or copper. The β - hydroxy ester can be readily dehydrated to α , β - unsaturated acids by heating with dilute sulphuric acid.

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BrCH-COOC₂H₅ + Zn
$$\xrightarrow{\text{Ether}}$$
 BrZnCHCOOC₂H₅ $\xrightarrow{\text{CH}_3\text{CHO}}$ $\xrightarrow{\text{CH}_3\text{CHO}}$ $\xrightarrow{\text{CH}_3\text{CHO}}$ $\xrightarrow{\text{CH}_3\text{CHO}}$ $\xrightarrow{\text{CH}_3\text{CHO}}$ $\xrightarrow{\text{CH}_3\text{CHO}}$ $\xrightarrow{\text{CH}_2\text{COOC}_2\text{H}_5}$ $\xrightarrow{\text{Acid}}$ $\xrightarrow{\text{H}_3\text{C}}$ $\xrightarrow{\text{CH}_2\text{COOC}_2\text{H}_5}$ $\xrightarrow{\text{CH}_2\text{COOC}_2\text{H}_5}$ $\xrightarrow{\text{Addition product}}$ $\xrightarrow{\text{Ethyl}}$ β -hydroxy butyrate $\xrightarrow{\text{CH}_2\text{COOC}_2\text{H}_5}$ $\xrightarrow{\alpha}$ $\xrightarrow{\beta}$ unsaturated ester $\xrightarrow{\alpha}$ $\xrightarrow{\beta}$ $\xrightarrow{\alpha}$ $\xrightarrow{\beta}$ unsaturated acid $\xrightarrow{\beta}$ $\xrightarrow{$

The mechanism of reformatsky reaction is similar to Grignard reaction. Zinc is used in the place of magnesium. Organic zinc compuonds are less reactive than Grignard reagents and they react only with the carbonyl group of aldehydes or ketones and not with the ester group. The mechanism involves the following steps.

- Formation of the organozine compound I.
- 2) Addition of the organozine compund to carbonyl group to form an
- Acid hydrolysis of the adduct to form β hydroxy ester III.

$$Br-CH_{2}-COOC_{2}H_{5}+Zn \longrightarrow Br Zn CH_{2}COOC_{2}H_{5}$$

$$C = O + CH_{2}-COOC_{2}H_{5} \longrightarrow H_{3}C \longrightarrow CH_{2}COOC_{2}H_{5}$$

$$R_{3}C \longrightarrow H_{3}C \longrightarrow CH_{2}COOC_{2}H_{5}$$

$$H_{3}C \longrightarrow H_{3}C \longrightarrow CH_{2}COOC_{2}H_{5}$$

The β- hydroxy ester III formed on treatment with dilute sulphuric acid eliminates a water molecule to give α , β – unsaturated ester or

 α , β – unsaturated acid IV.

$$(CH_3)_2 - C - CH_2COOC_2H_5 \xrightarrow{H_2SO_4} (CH_3)_2C = CHCOOC_2H_5$$

$$(CH_3)_2 C = CHCOOH$$

$$IV$$
Acid

Significance

This reaction is useful in preparing α , β – unsaturated acids.

* WITTIG REACTION \checkmark

Aldehydes and ketones react with phosphorus ylide to form alkenes.

i)
$$C_6H_5COC_6H_5 + CH_2 = P(C_6H_5)_3 \longrightarrow C_6H_5 - C - C_6H_5 + (C_6H_5)_3P = O$$

Benzophenone ylide CH_2 Triphenyl phosphine alkene oxide

ii)
$$C_6H_5CHO + CH_2 = P(C_6H_5)_3 \longrightarrow C_6H_5CH = CH_2$$

Benzoldehyde ylide styrene

Mechanism

Phosphorus ylides are hybrides of two canonical form.

$$(C_6H_5)_3P = CH_2 \longleftrightarrow (C_6H_5)_3P - CH_2$$
methylene form

ylide form

Ylide form attacks the carbon atom of carbonyl group forming a new C - C bond. As a result of it a dipolar intermediate called betaine is formed. This react further to give an alkene and triphenyl phosphine oxide. The sequence of reactions is shown below.

$$(C_{6}H_{5})_{3}\vec{P} - CH_{2} + R - C - R \longrightarrow R_{2}C \longrightarrow CH_{2} - P(C_{6}H_{5})_{3}$$

$$R_{2}C \longrightarrow CH_{2} - P(C_{6}H_{5})_{3}$$

$$R_{3}C \longrightarrow CR_{2}$$

$$CR_2$$
 CR_2
 CH_2 + $(C_6H_5)_3P = O$
 CH_2 Triphenyl alkene phosphene oxide

REDUCTION USING NaBH,

Sodium borohydride, NaBH, is insoluble in ether. It is used in chanolic solution to reduce carbonyl compounds. It does not reduce carboxyl group. It also does not normally reduce esters [but by using large excess of NaBH, in [methanol], ester may be reduced to primary alcohol.]

$$R-CHO \longrightarrow R CH_2OH$$

E g.,

X

$$R - CO - R' \longrightarrow R CHOHR'$$

Mechanism

The reduction of the carbonyl group by NaBH, occurs in a stepwise manner. It involves hydride ion transfer.

$$NaBH_4 \longrightarrow Na^+ + BH_4^-$$

$$\begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$$

$$R_2CH - O - BH_3 \xrightarrow{R_2CO} (R_2CHO)_2BH_2 \xrightarrow{R_2CO}$$

$$(R_2 \text{ CHO})_3 \text{BH} \xrightarrow{R_2 \text{ CO}} (R_2 \text{ CHO})_4 \text{ B} \xrightarrow{H^+} 4R_2 \text{ CHOH}$$

REDUCTION USING LIAIH,

Lithium aluminium hydride has proved to be a very effective reducing agent. This reduces most functional groups but does not normally reduce the olefinic bond. A special feature of this reagent is its reduction of the carbonyl groups to CH₂. Reduction with LiAIH₄ is usually carried out in ethereal solutions.

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$$R-CHO \longrightarrow R CH_2OH$$
 $R-CO-R' \longrightarrow R CHOH-R'$
 $CH_3-CO-CH_3 \longrightarrow CH_3-CH_2-CH_3$
Acetone Propane

Mechanism

The reduction of the carbonyl group by LiAIH₄ occurs in a stepwise manner. It involves hydride ion transfer.

Experimental work has shown that the rate of reduction is decreased as the size of R increases.

10. WOLF-KISHNER REDUCTION 🗸 🛪

When hydrazones of a carbonyl compound are heated in sealed tube with sodium ethoxide or hydroxide as a catalyst at 180°C nitrogen is eliminated and a hydrocarbon is obtained. The carbonyl group is converted into the methylene group during this reduction

$$C = O \xrightarrow{\text{H}_2\text{NNH}_2} C = N - NH_2 \xrightarrow{\text{NaOH}} CH_2 + N_2$$

Wolf-Kishner reduction is useful in the synthesis of alkylbenzenes containing straight alkyl chains containing many carbon atoms For example n-heptyl benzene is obtained as follows.

Semicarbazones or azines also undergo Wolff-Kishner reduction.

Hydrazone is formed as an intermediate during the reduction

In the case of azine, it must be treated first with alkali in presence of excess of hydrazine hydrate to get hydrazone.

$$R' = N - N = C < R' + H_2N NH_2 \longrightarrow 2 R' = NNH_2$$
echanism

Mechanism

$$R > C = N - NH_2 + B \Longrightarrow R > C = N - NH + BH^+$$
Base

Comparsion of Wolf-Kishner reduction and reduction by sodium borohydride Similarities

1. Both reduce carbonyl groups 2. Both involve stepwise mechanism

Differences

Reaction	Reduction with NaBH	Wolf-Kishner Reduction
Nature	Reduce aldehydes and ketones directly	Aldehydes and ketones are first Converted into

	39	hydrazones which are than reduced
Product	alcohols	Alkanes n-hexyl phenyl
Example	Acetone -> Iso propy!	ketone → n-heptyl benzene
Reagent	alcohol NaBH ₄	NH ₂ -NH ₂ and NaOEt / NaOH

11. MEERWEIN-PONNDORF - VERLEY REDUCTION

Reduction of both aldehydes and ketones to alcohols by heating them with aluminium isopropoxide in iso propanol solution is called MPV reduction. The isopropoxide is oxidised to acetone which is removed from the equilibrium mixture by slow destillation

rom the equilibrium mixture by size
$$3 R C = O + [(CH_3)_2 CHO]_3AI] \rightleftharpoons [(R_2CHO)_3]AI + CH_3COCH_3 \uparrow$$

$$(R_2CHO)_3AI \stackrel{\text{dil. } H_2SO_4}{\longrightarrow} 3 R CHOH$$

CH₃CH = CHCHO
Crotonaldehyde

Al(OC₃H₇)₃
$$\rightarrow$$
 CH₃CH = CHCH₂OH
Crotyl alcohol

Significance

Aluminium iso-propoxide is a specific reagent for the reduction of the carbonyl group. The other functional groups like double bond and nitro group are not affected. Other reagents will reduce these groups also

group are not affected. Other reagents will reduce these groups are

Mechanism

$$R = C = O + CH_3 CHO$$
 $CH_3 CHO$
 $CH_3 CHO$