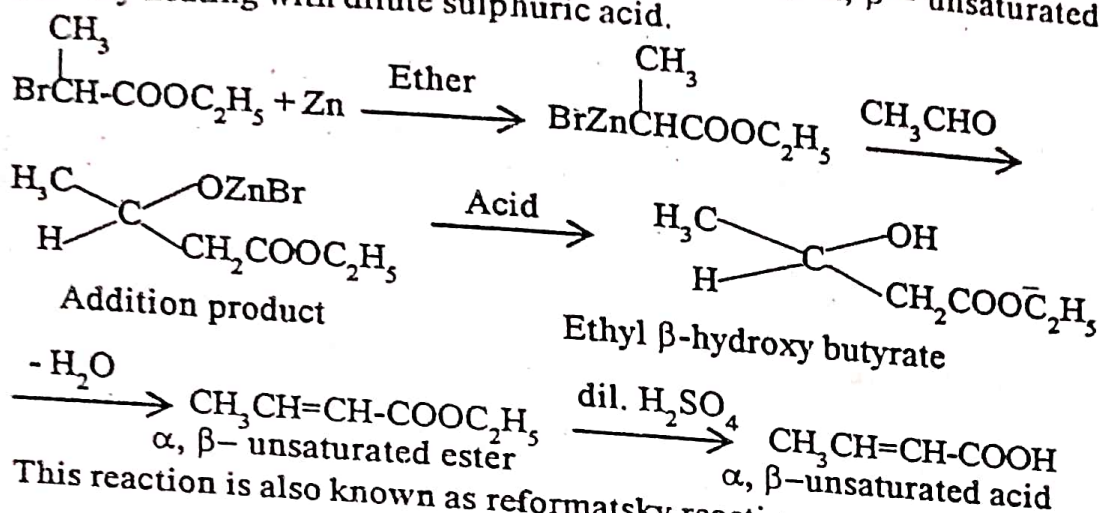


addition product initially formed is readily decomposed by dilute mineral acids to yield β - hydroxy esters. It is sometimes necessary to activate zinc by adding a few crystals of iodine or mercuric bromide or copper. The β - hydroxy ester can be readily dehydrated to α, β - unsaturated acids by heating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

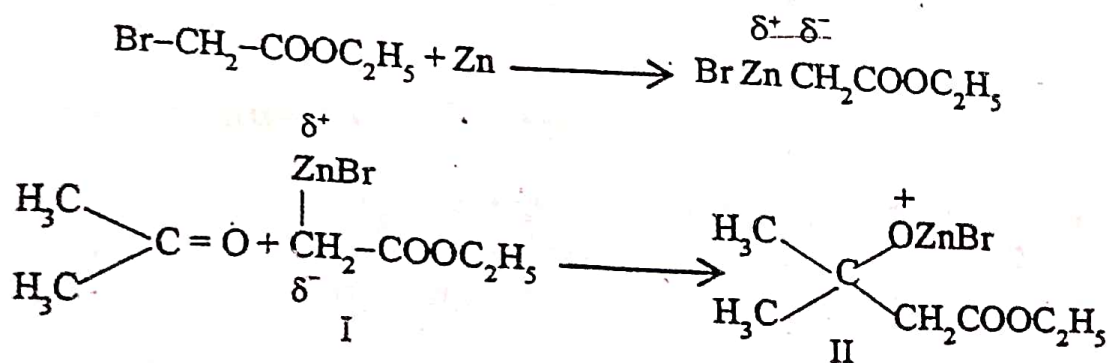


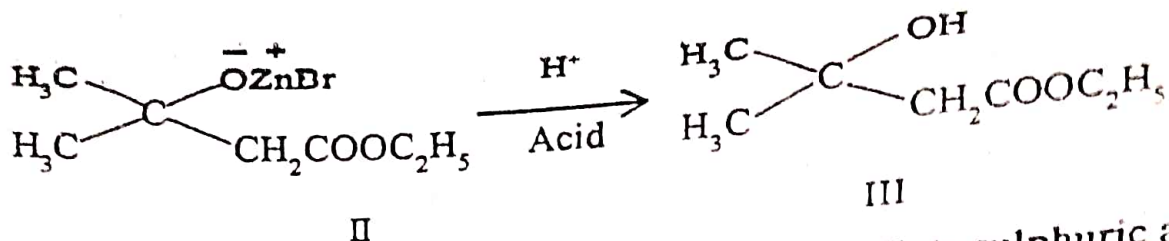
This reaction is also known as reformatsky reaction.

Mechanism

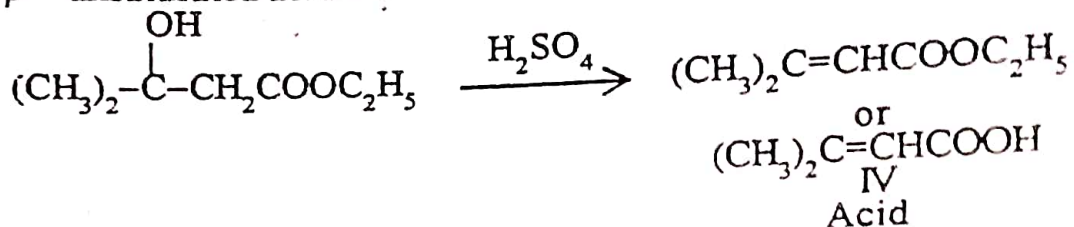
The mechanism of reformatsky reaction is similar to Grignard reaction. Zinc is used in the place of magnesium. Organic zinc compounds are less reactive than Grignard reagents and they react only with the carbonyl group of aldehydes or ketones and not with the ester group. The mechanism involves the following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

- 1) Formation of the organozinc compound I.
- 2) Addition of the organozinc compound to carbonyl group to form an intermediate adduct II.
- 3) Acid hydrolysis of the adduct to form β - hydroxy ester III.





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.

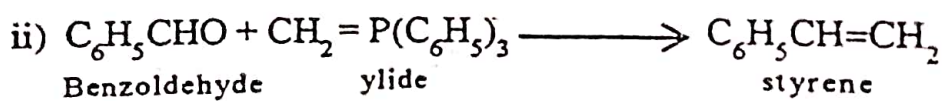
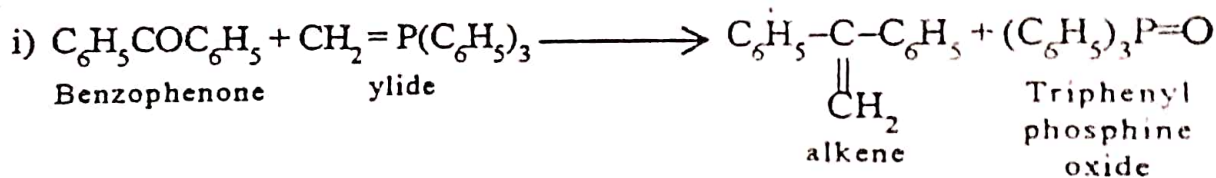


Significance

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

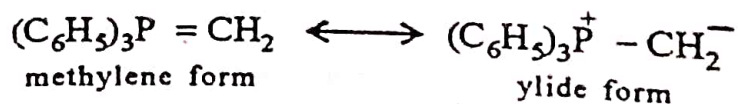
7. WITTIG REACTION ✓ *

Aldehydes and ketones react with phosphorus ylide to form alkenes.

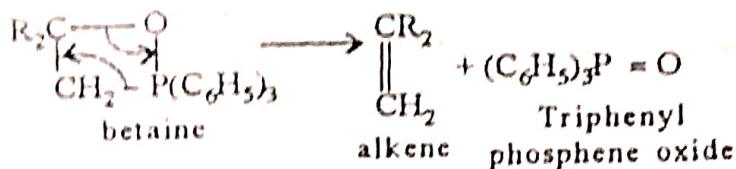
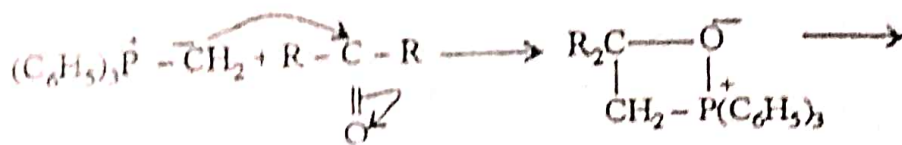


Mechanism

Phosphorus ylides are hybridized in two canonical forms.

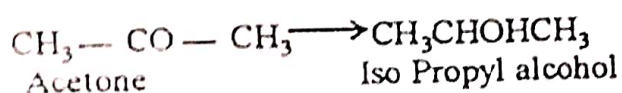
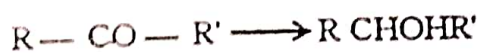
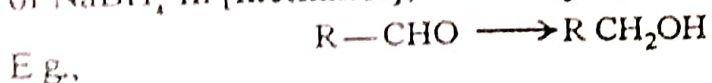


Ylide form attacks the carbon atom of carbonyl group forming a new C-C bond. As a result of it a dipolar intermediate called *betaine* is formed. This reacts further to give an alkene and triphenyl phosphine oxide. The sequence of reactions is shown below.



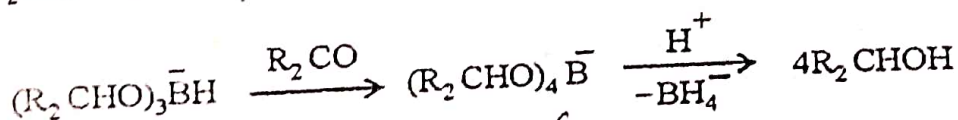
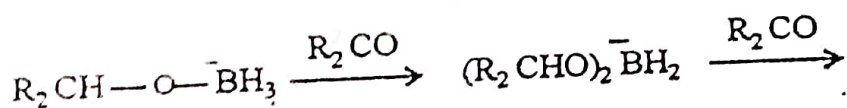
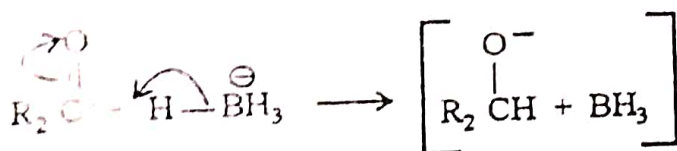
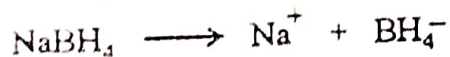
REDUCTION USING NaBH₄

Sodium borohydride, NaBH₄ is insoluble in ether. It is used in ethanolic solution to reduce carbonyl compounds. It does not reduce carboxyl group. It also does not normally reduce esters [but by using large excess of NaBH₄ in [methanol], ester may be reduced to primary alcohol.]



Mechanism

The reduction of the carbonyl group by NaBH₄ occurs in a stepwise manner. It involves hydride ion transfer.



9. REDUCTION USING LiAlH₄

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 LiAlH₄ is usually carried out in ethereal solutions.

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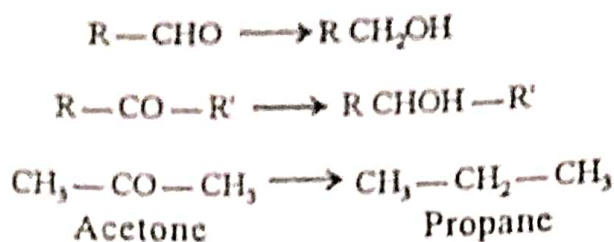
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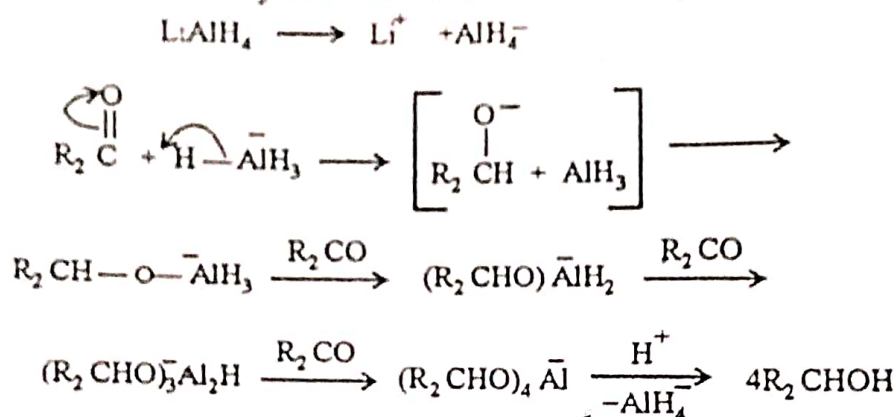
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cont
n-he

Hyd



Mechanism

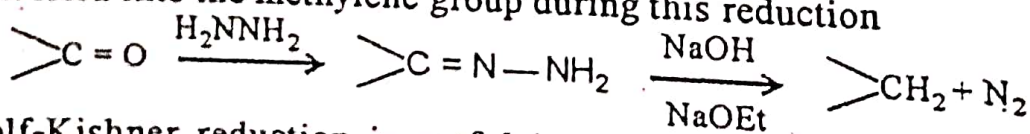
The reduction of the carbonyl group by LiAlH_4 occurs in a stepwise manner. It involves hydride ion transfer.



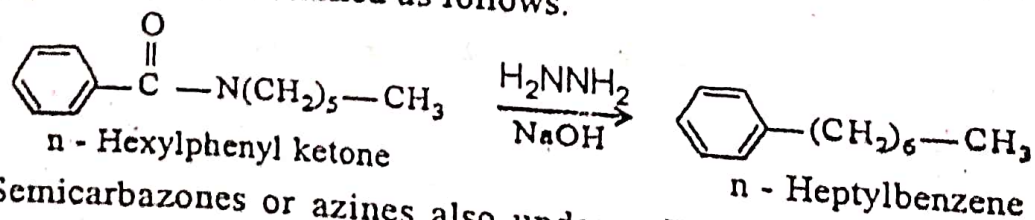
Experimental work has shown that the rate of reduction is decreased as the size of R increases.

10. WOLF-KISHNER REDUCTION ✓ *

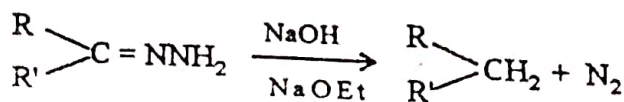
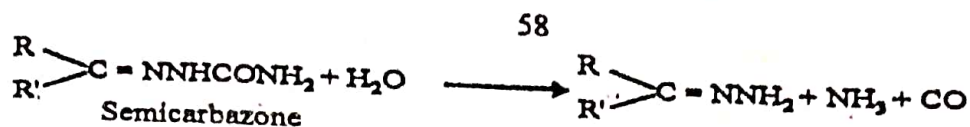
When hydrazones of a carbonyl compound are heated in sealed tube with sodium ethoxide or hydroxide as a catalyst at 180°C nitrogen is eliminated and a hydrocarbon is obtained. The carbonyl group is converted into the methylene group during this reduction



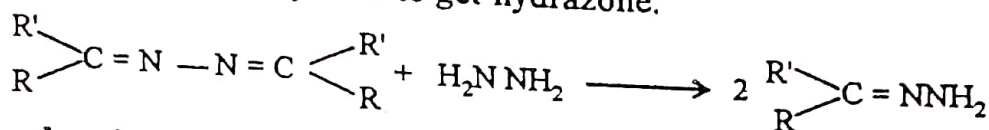
Wolf-Kishner reduction is useful in the synthesis of alkylbenzenes containing straight alkyl chains containing many carbon atoms. For example n-heptyl benzene is obtained as follows.



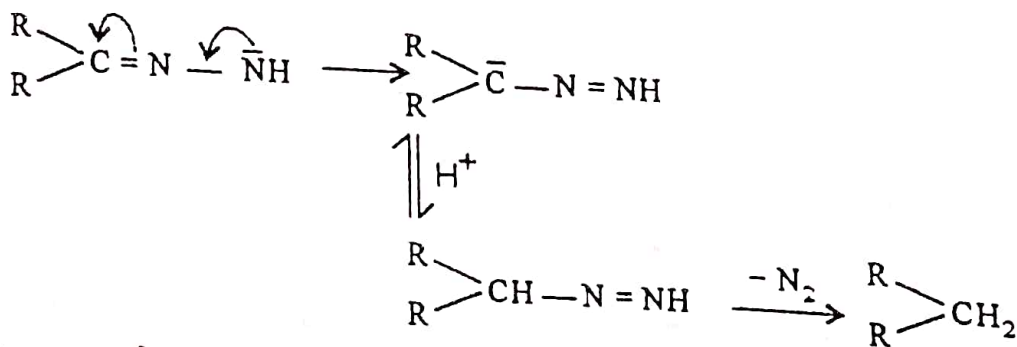
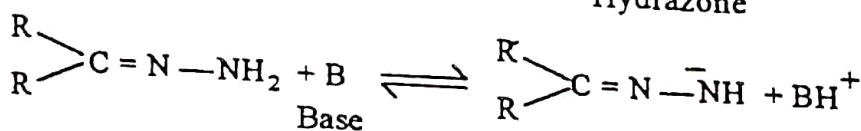
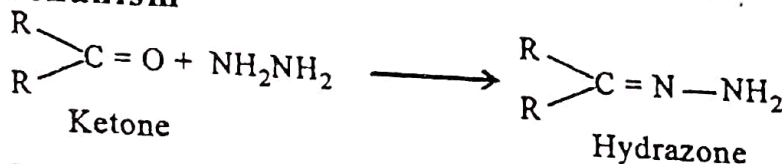
Semicarbazones or azines also undergo Wolff-Kishner reduction. Hydrazone is formed as an intermediate during the reduction



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



Mechanism



Comparison of Wolf-Kishner reduction and reduction by sodium borohydride

Similarities

- Both reduce carbonyl groups
- Both involve stepwise mechanism

Differences

Reaction	Reduction with NaBH_4	Wolf-Kishner Reduction
Nature	Reduce aldehydes and ketones directly	Aldehydes and ketones are first Converted into

Product
Example

alcohols
Acetone →
Iso propyl
alcohol

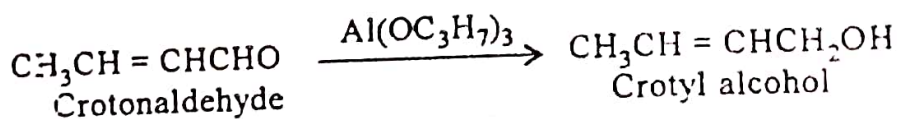
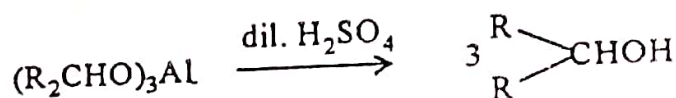
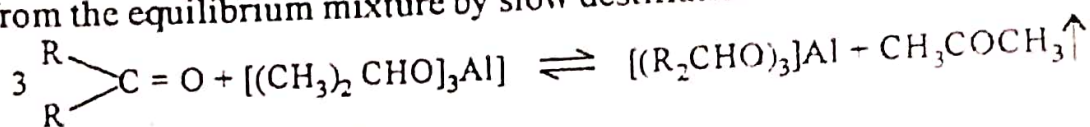
Reagent

NaBH_4

hydrazones which are
than reduced
Alkanes
n-hexyl phenyl
ketone →
n-heptyl benzene
 $\text{NH}_2\text{-NH}_2$ 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 distillation



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

Mechanism

