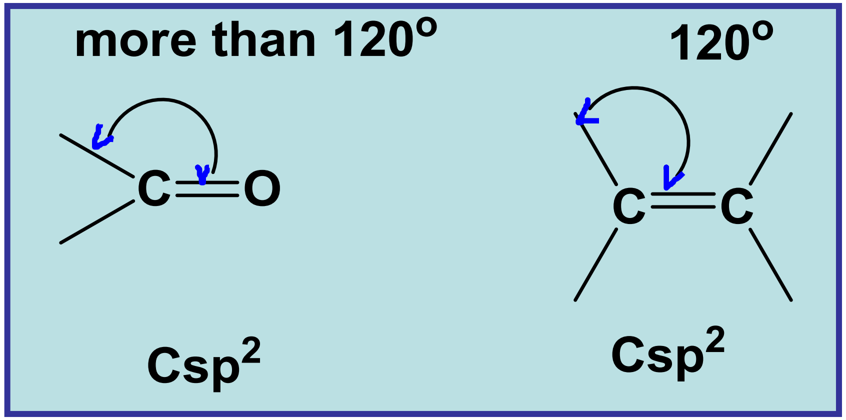
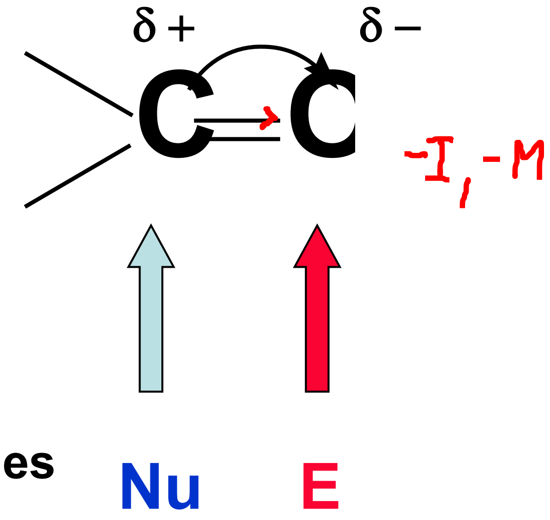
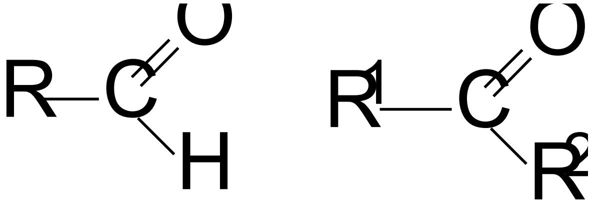
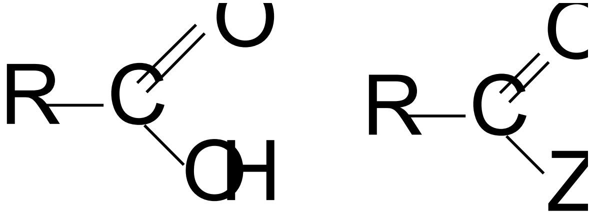
Carbonyl derivatives





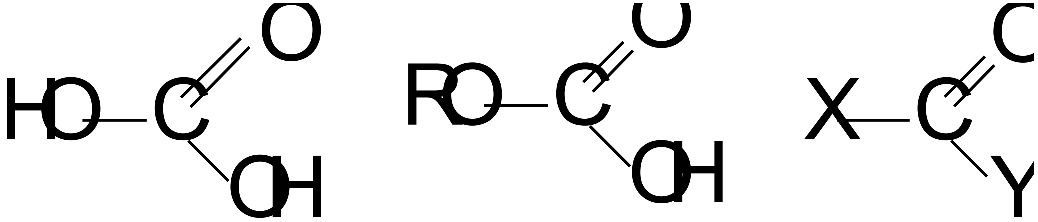


1.aldehydes, ketones



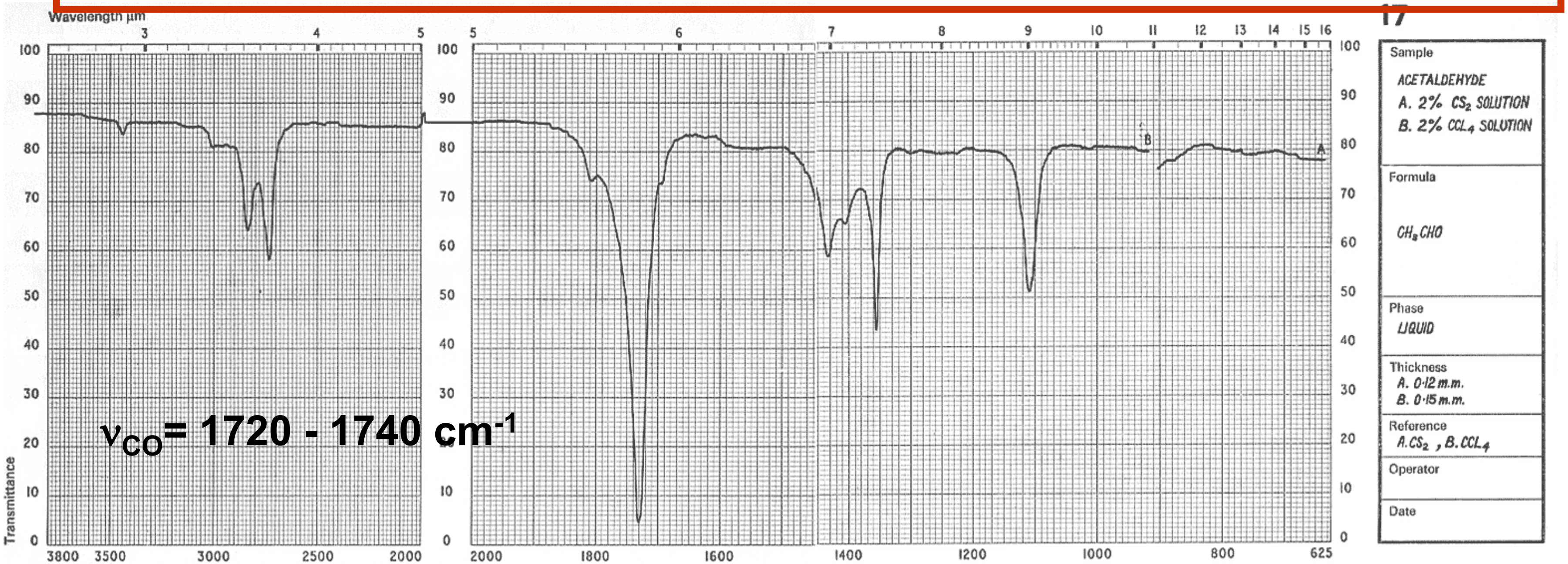
2. karboxylic acids and functional derivatives

3. derivatives of carbonic acid



Carbonyl derivatives

17



ν_{CO}= 1720 - 1740 cm^{-1}

Sample
ACETALDEHYDE
A. 2% CS_2 SOLUTION
B. 2% CCL_4 SOLUTION

Formula
CH_3CHO

Phase
LIQUID

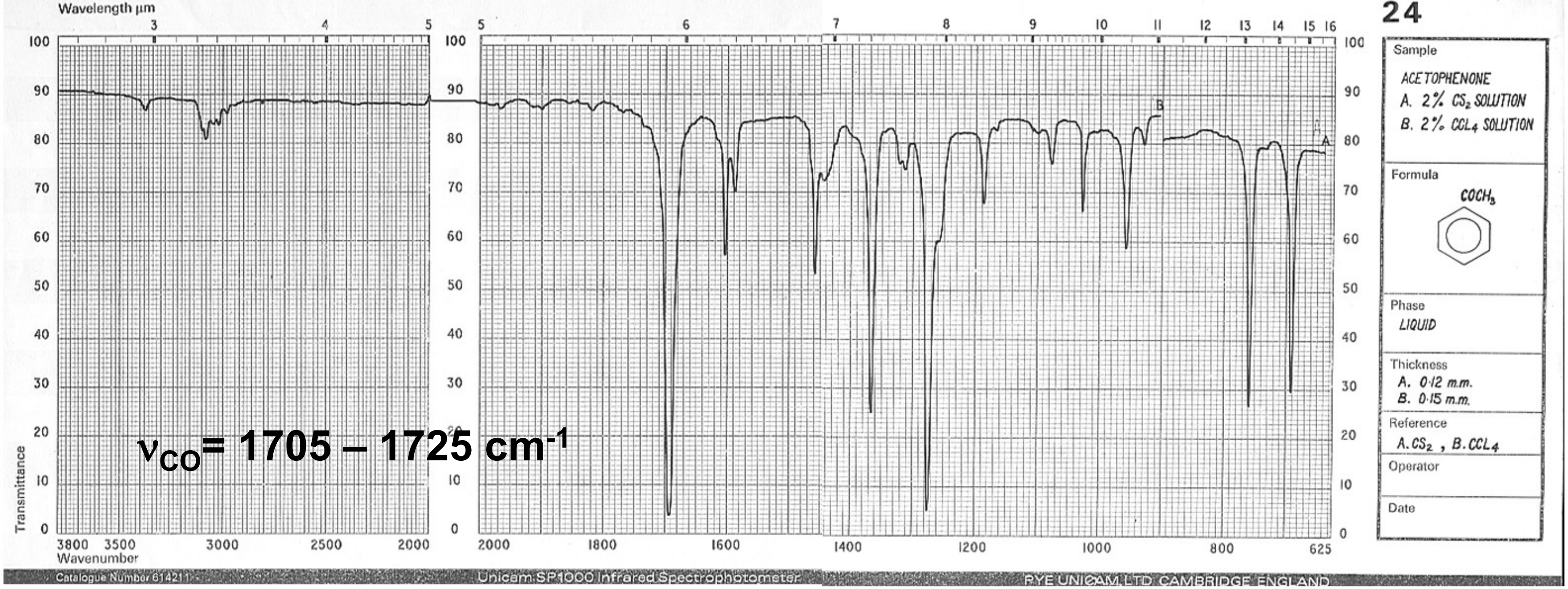
Thickness
A. 0·12 m.m.
B. 0·15 m.m.

Reference
A. CS_2 , B. CCL_4

Operator

Date

24



ν_{CO}= 1705 – 1725 cm^{-1}

Sample
ACETOPHENONE
A. 2% CS_2 SOLUTION
B. 2% CCL_4 SOLUTION

Formula

Phase
LIQUID

Thickness
A. 0·12 m.m.
B. 0·15 m.m.

Reference
A. CS_2 , B. CCL_4

Operator

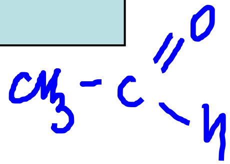
Date

Carbonyl derivatives

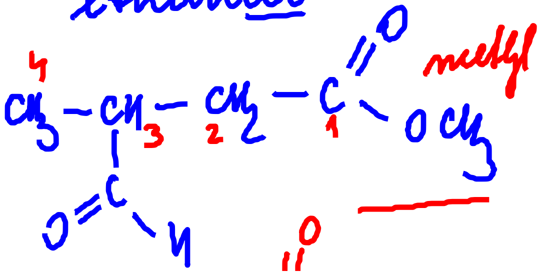
ALDEHYDES

-al

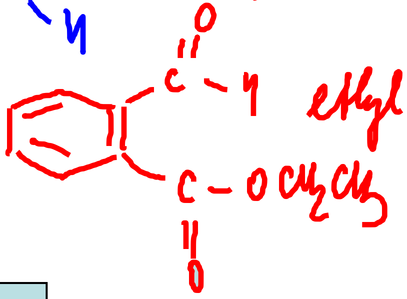
formyl



ethanal



methyl-3-formylbutanoát

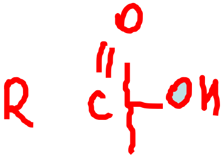


ethyl-2-formylbenzoát

KETONES

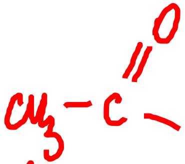
-on

-oxo-



acyl

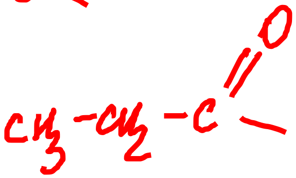
acetyl



ethanoyl

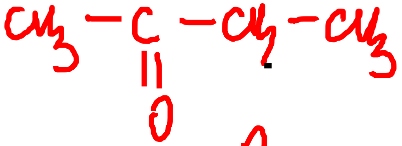
alkyl^{1}alkyl^{2}keton

propionyl



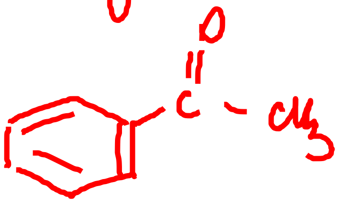
NÁZVOSLOVÍ

Carbonyl derivatives

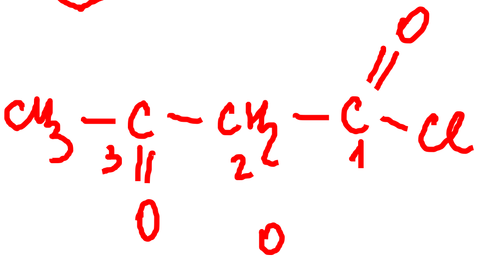


$CH_3-\underset{\overset{\|}{O}}{C}-CH_2-CH_3$

ethylmethylketon
butan-2-on

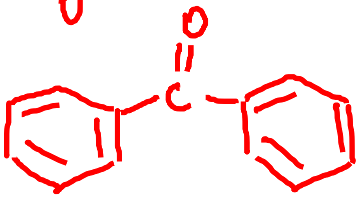


acetofenon

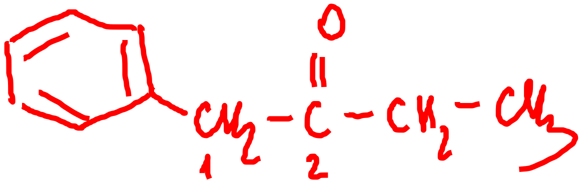


$\underset{}{CH_3}-\underset{\overset{3\ \|}{O}}{C}-\underset{2}{CH_2}-\underset{1}{\overset{O\ /\!/}{C}}-Cl$

3-oxobutanoylchlorid

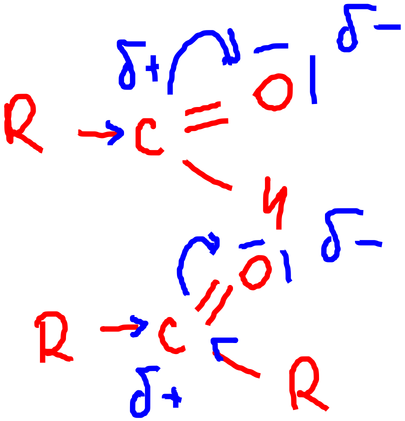


benzofenon



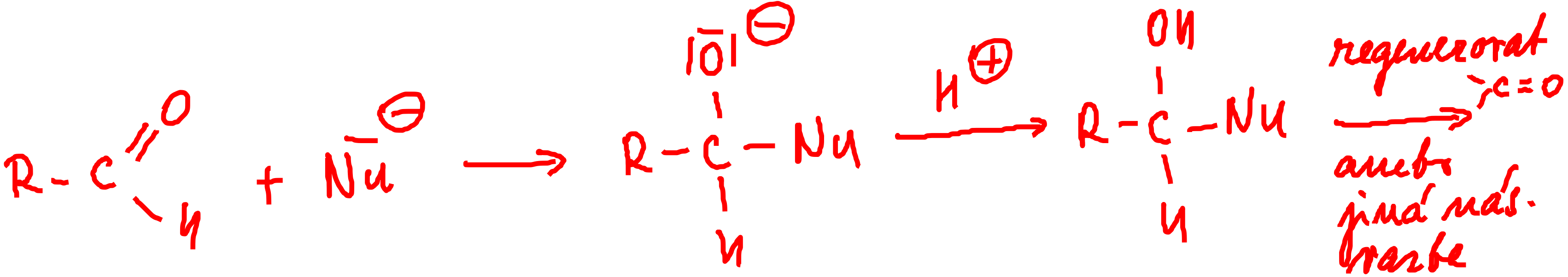
1-fenylbutan-2-on

Carbonyl derivatives



aldehydy jsou reaktivnější pro vstup nukleofilu

elektronová mezera je u aldehydů větší

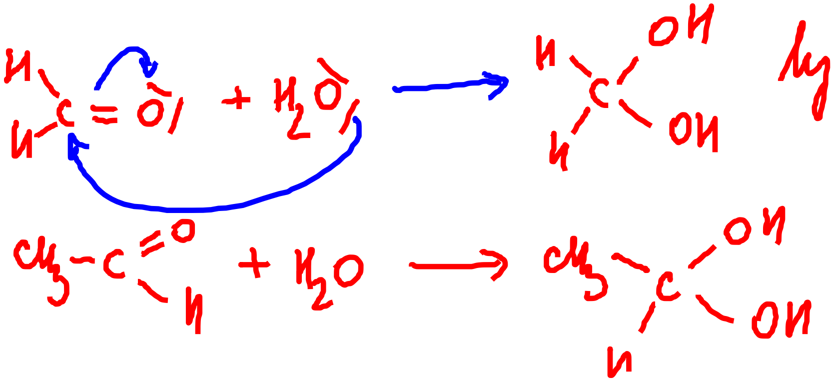


regenerovat

anebo jiná nás. vazbe

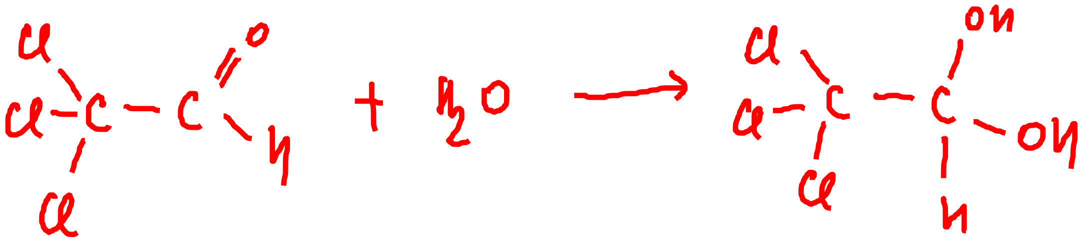
$>C=Z-$

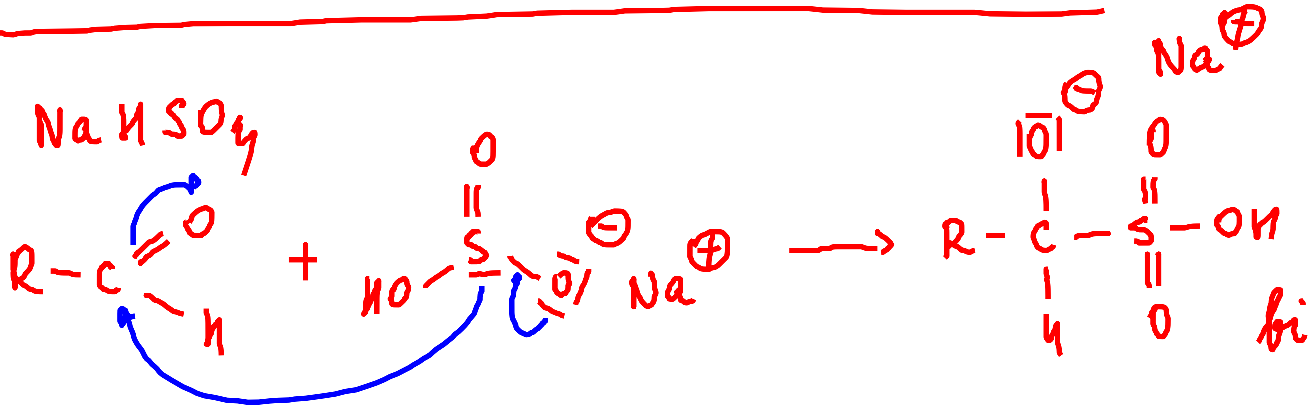
$R-CH=CH-R$



hydrát formaldehydu 99%

hydrát acetaldehydu 58%

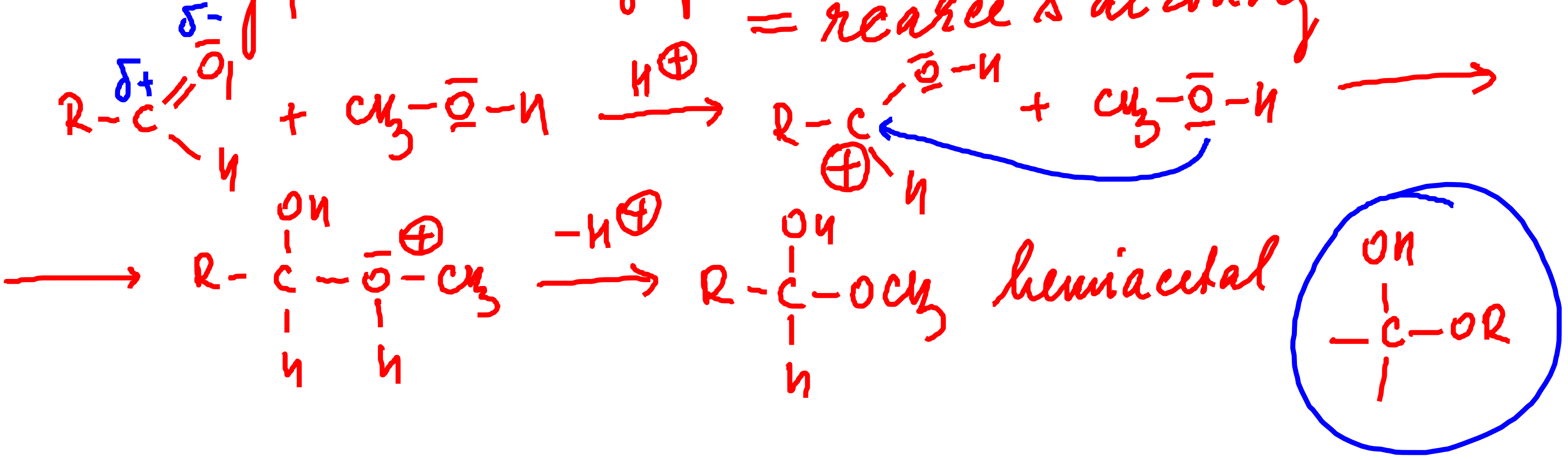




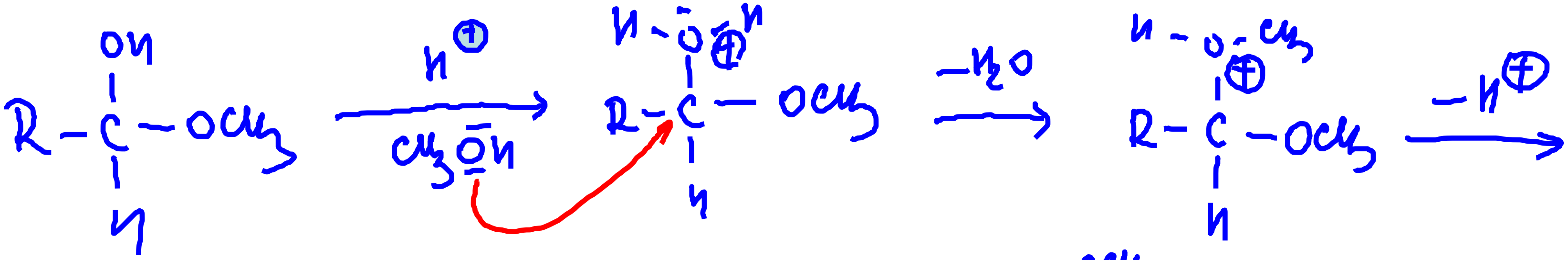
bisulfitická sloučenina

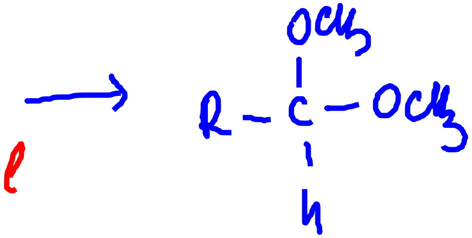
---

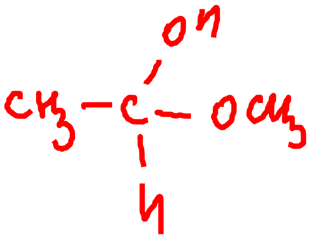
acetaly, hemiacetaly (poloacetaly) = reakce s alkoholy



hemiacetal



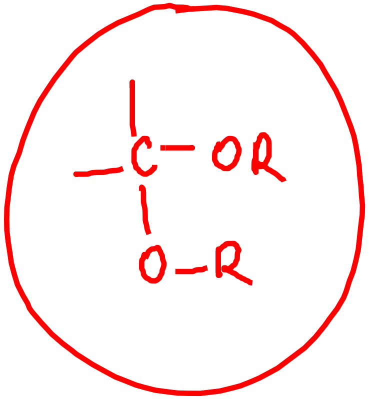


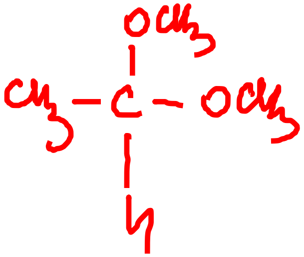


methylhemiacetal acetaldehydu

1-methoxyethanol

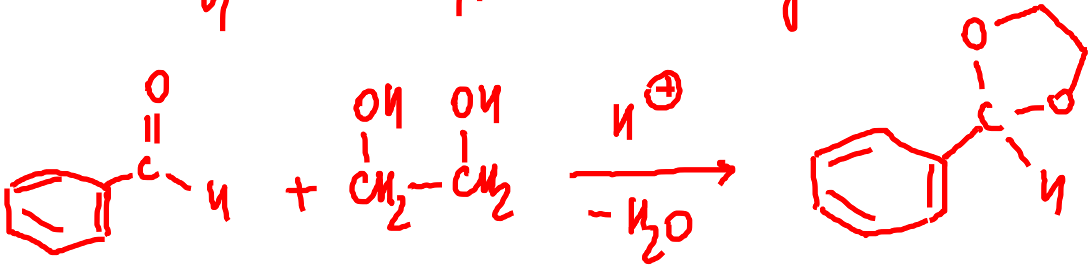
acetal





dimethylacet acetaldehydu

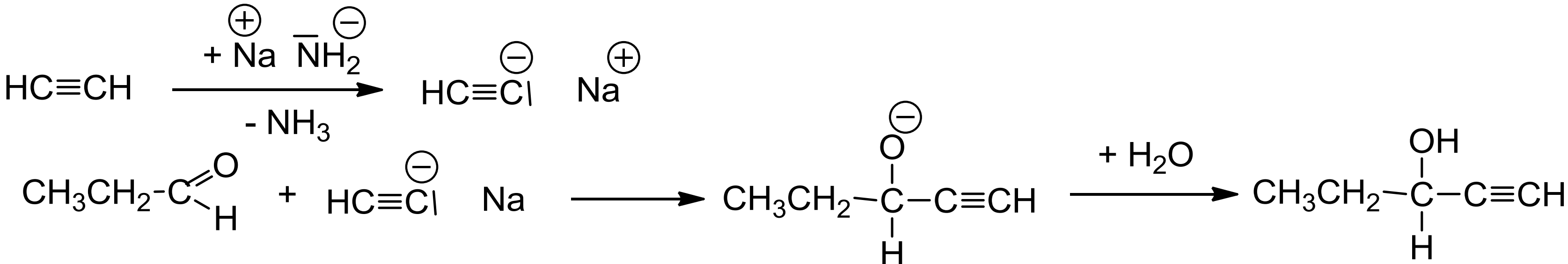
1,1-dimethoxyethan



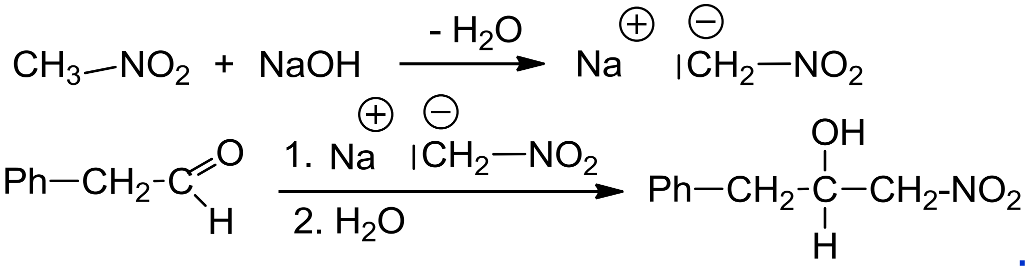
obdobně budou reagovat thioly a sulfan

Carbonyl derivatives - addition

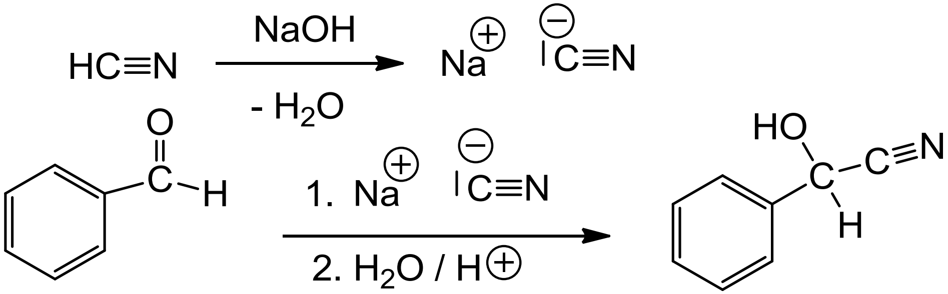
Nucleophilic additions proceed with strong nucleophiles without problems, nucleophile is before the reaction mostly generated from its conjugated acid



ethynylation (ethynyl introduction)



nitromethyl introduction

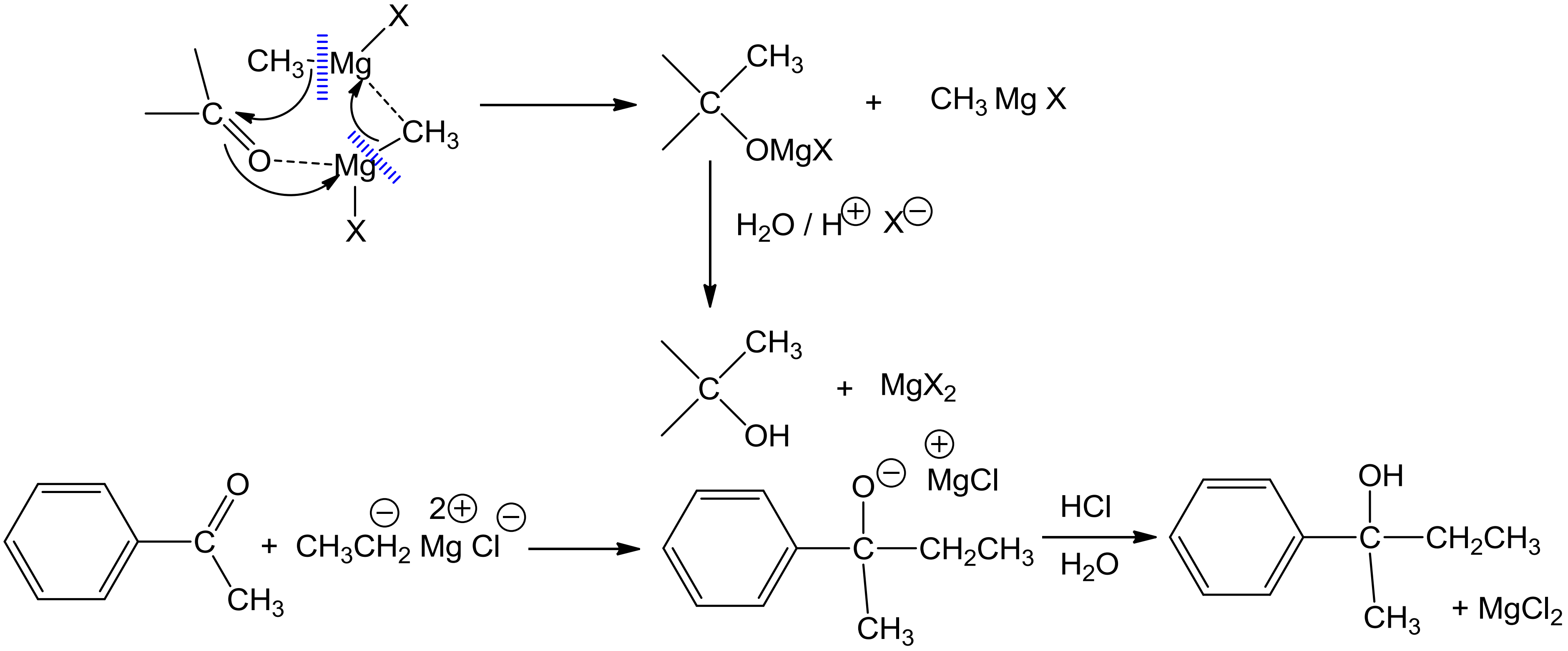


preparation of cyanohydrines

Carbonyl derivatives - addition

Addition of Grignard reagents

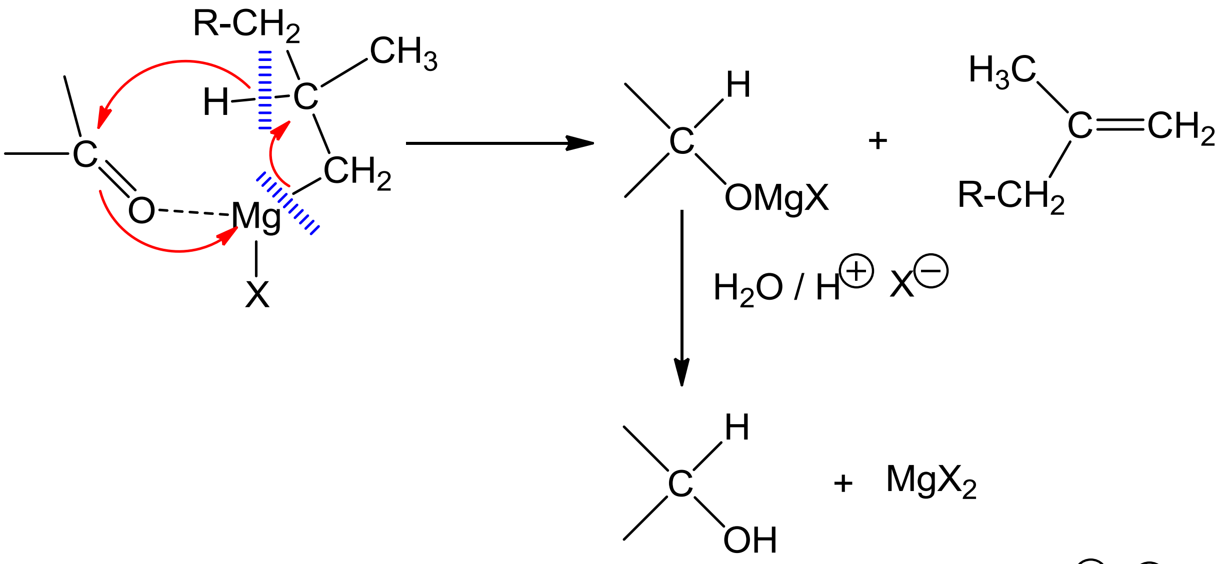
for the reaction 2 mols of reagents are necessary to 1 mol of aldehyde or ketonene

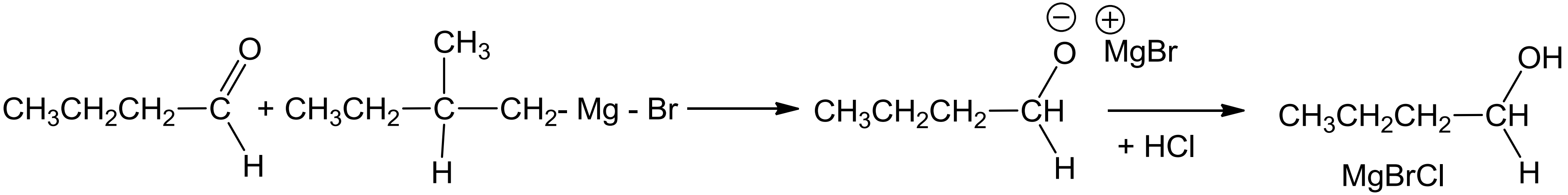


After acidification of the reaction mixture in reaction with aldehydes are produced second. alcohols
with ketones tert. alcohols
with formaldehyde prim. alcohol

Carbonyl derivatives - addition

Bulky alkyles in Grignard reagent may surprise by different reactivity: in a case they have β-hydrogen, then aldehyde or ketone is reduced to corresponding alcohol



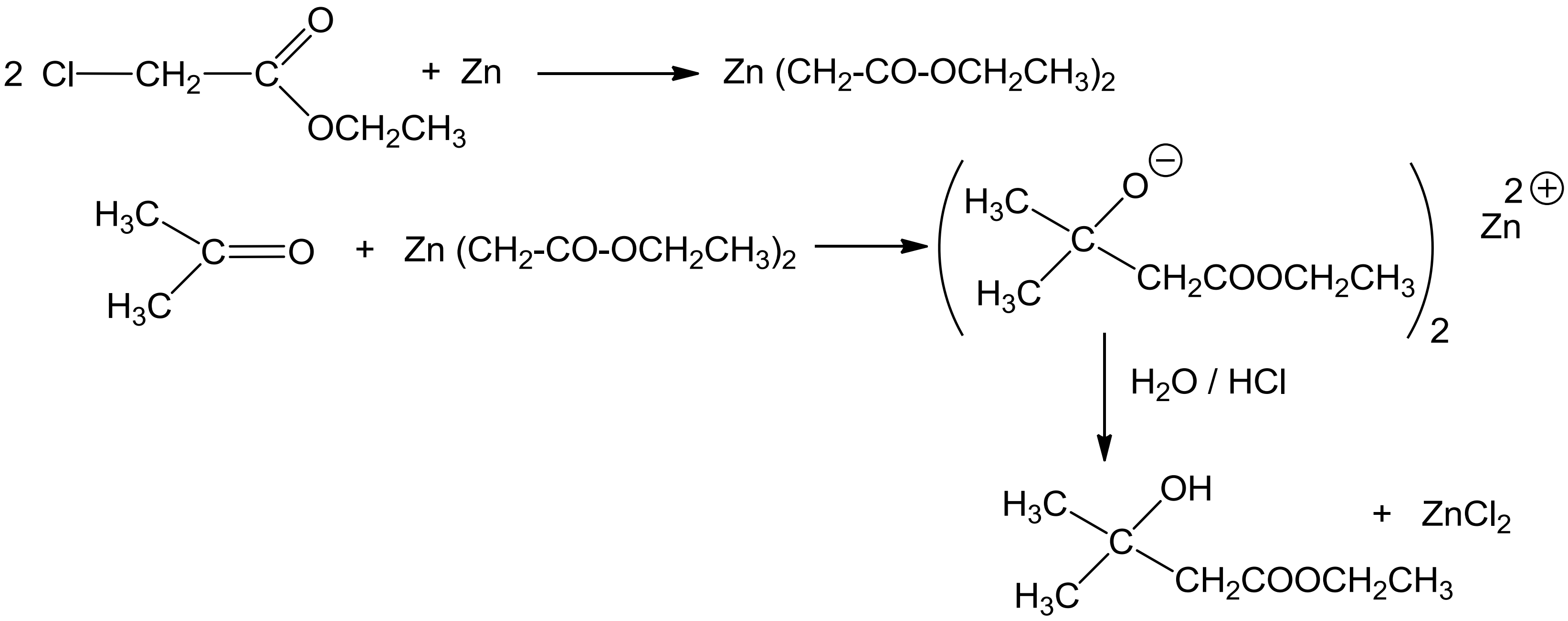


$$CH_3CH_2CH_2{-}\overset{O}{\underset{H}{C}} + CH_3CH_2{-}\overset{CH_3}{\underset{H}{C}}{-}CH_2{-}Mg{-}Br \longrightarrow CH_3CH_2CH_2{-}\overset{\ominus\; \oplus}{\overset{O\quad MgBr}{\underset{H}{CH}}} \xrightarrow[+\,HCl]{} CH_3CH_2CH_2{-}\overset{OH}{\underset{H}{CH}} \quad MgBrCl$$

In case they have in β–position no hydrogen atom, then Grignard reagent reacts as a strong base and is transferring carbonyl compound to enolate

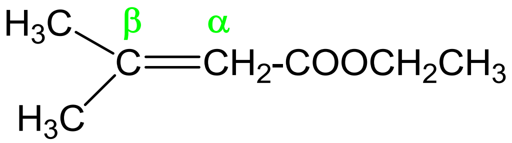
Carbonyl derivatives - addition

REFORMATSKY REACTION



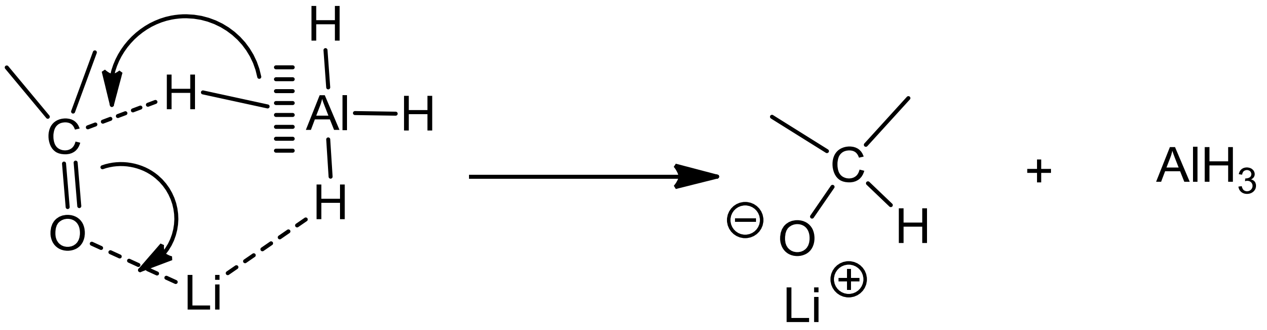
In this reaction less reactive organometallic compound reacts with the keto group only without any attack of the present ester forming β-hydroxyester.

Product in an acidic medium can loose water and affords α,β-nonsaturated ester.



Carbonyl derivatives - reduction

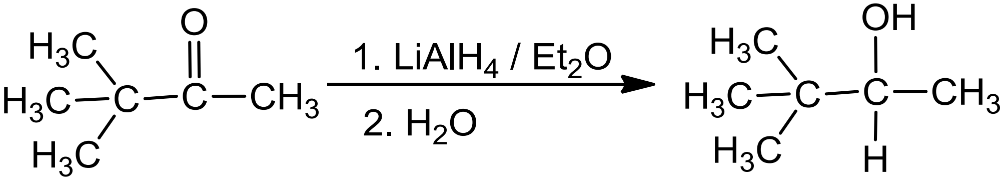
REDUCTION

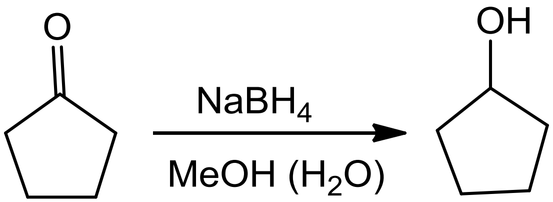


reduction with aluminium hydride proceeds via the same cyclic intermediate, we saw in reaction with Grignard reagents

$NaBH_4$– is reducing only carbonyl (without touching esters functions, NO_2, CN), reactions can be carry out also in a polar solvents like water and alcohols.

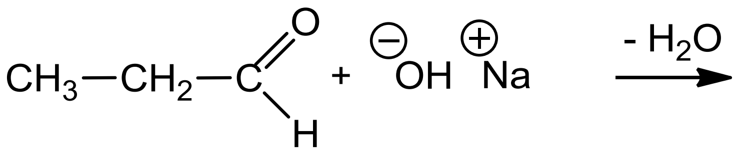
$LiAlH_4$– is reducing also other functions, but reacts violently with water; reactions are carried out in ether.

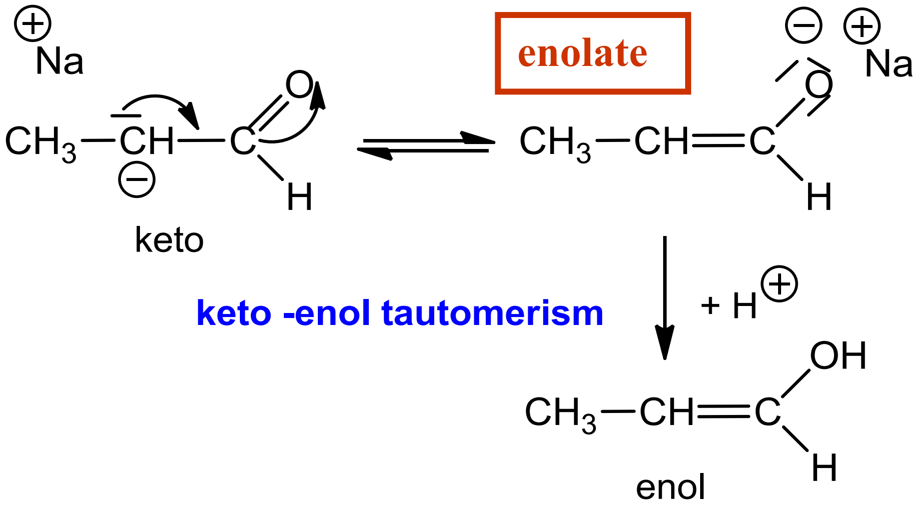




Aldolisation and aldol condensation– catalysed by a base

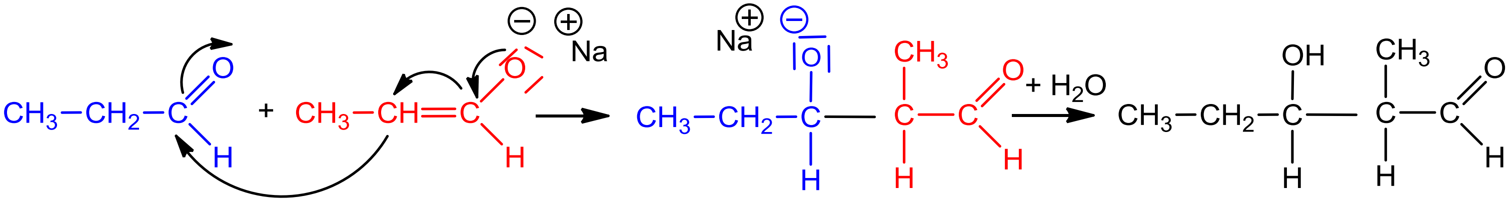
–I a –M efect of oxygen in carbonyl is activating α–hydrogen atoms , which are acidic





keto -enol tautomerism

By the action of base is generated enolate, which reacts with the second molecule (non enolised)



During **aldolisation** the hydrocarbon chain is prolonged

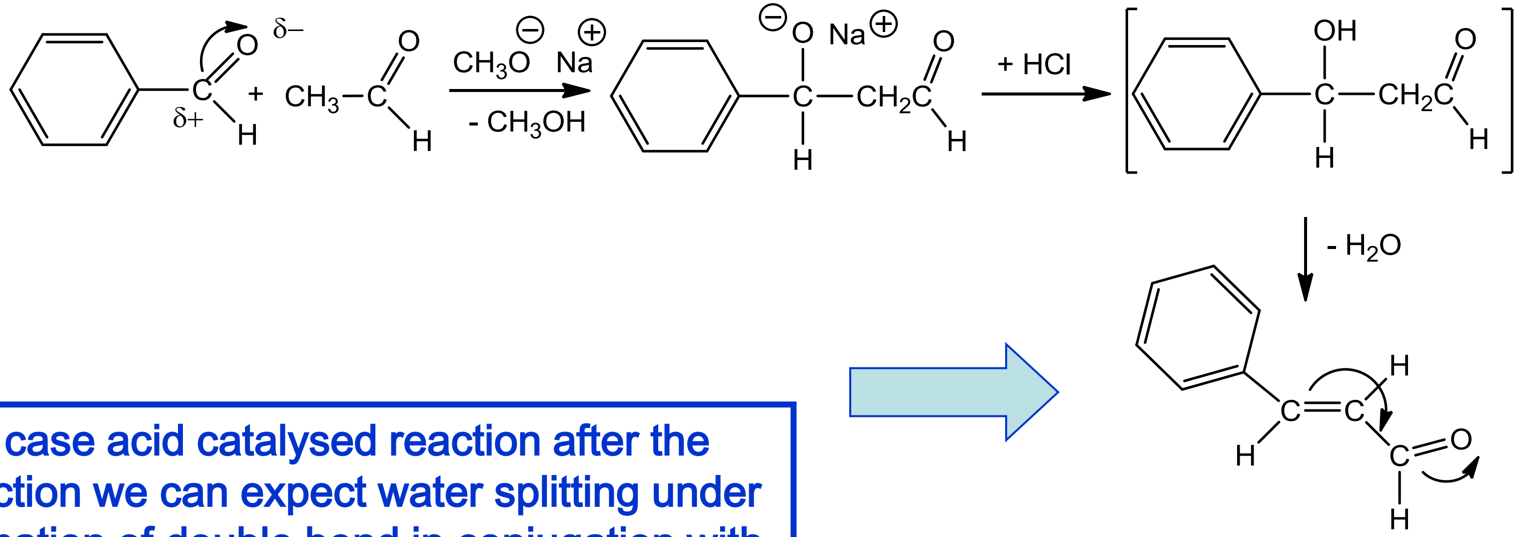
Aldolisation and aldol condensation– catalysed by a base

Acidity constants of various compounds

compound	structure	pK_a
karboxylová kyselina	CH_3CO_2H	5
1,3-diketon	$CH_2(COCH_3)_2$	9
1,3-ketoester	$CH_3COCH_2CO_2C_2H_5$	11
1,3-dinitril	$CH_2(CN)_2$	11
1,3-diester	$CH_2(CO_2C_2H_5)_2$	13
alkohol	CH_3CH_2OH	16
chlorid kyseliny	CH_3COCl	16
aldehyd	CH_3CHO	17
keton	CH_3COCH_3	19
ester	$CH_3CO_2C_2H_5$	25
nitril	CH_3CN	25
dialkylamid	$CH_3CON(CH_3)_2$	30
amoniak	NH_3	36
dialkylamin	$HN(iso\text{-}C_3H_7)_2$	40
alkyn	$HC?CH$	25
alken	$CH_2{=}CH_2$	44
alkan	CH_3CH_3	60

Aldolisation and aldol condensation– catalysed by a base

Mixed aldolisation – enol is prepared from compound with α–acidic hydrogen atom and that then adds to carbonyl group of othercarbonyl molecule without α–hydrogen atom.

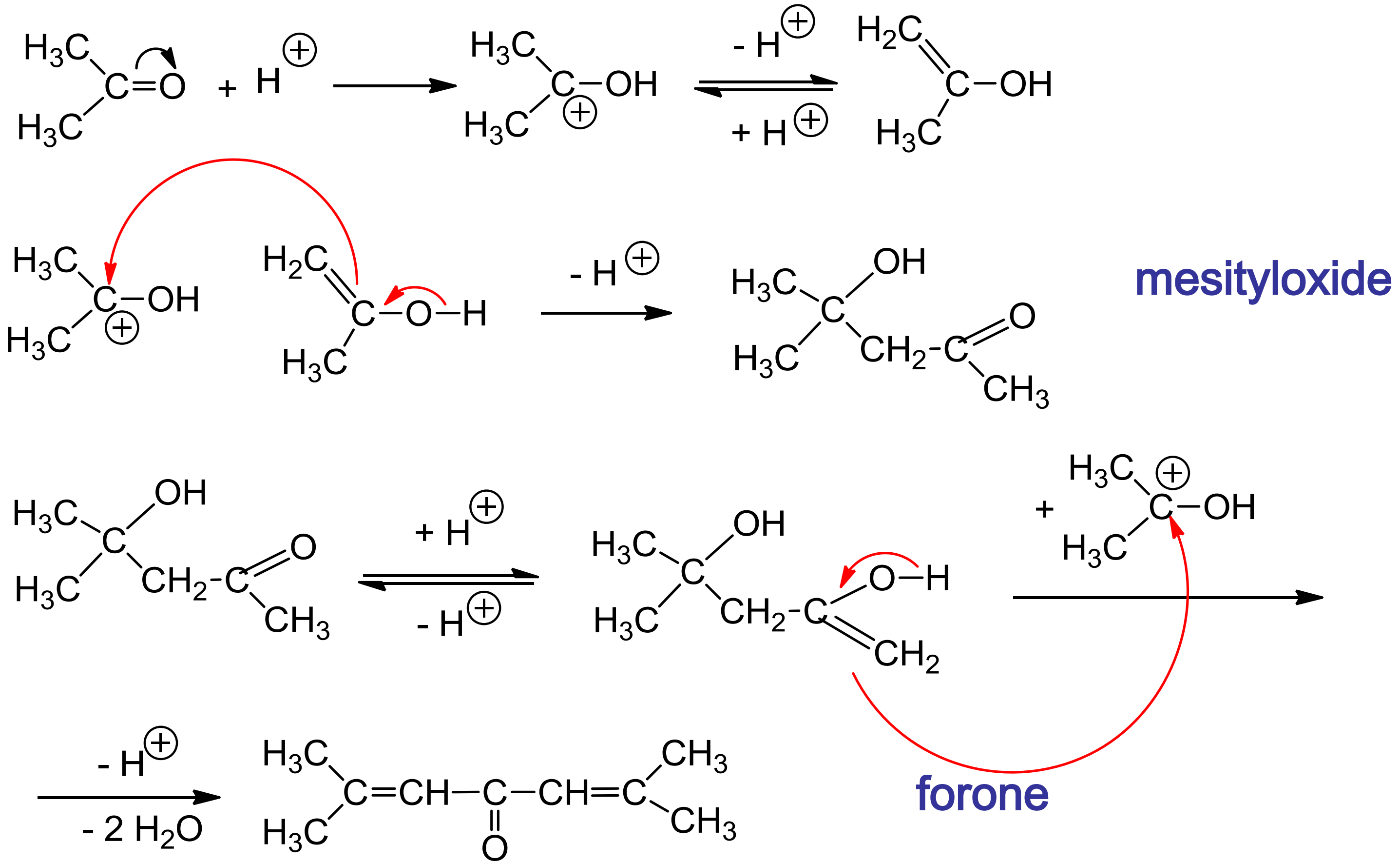


I case acid catalysed reaction after the reaction we can expect water splitting under formation of double bond in conjugation with carbonyle

aldol condensation

Aldolisation and aldol condensation– catalysed by a acid

Aldol condensation may be developed even by acid catalysis

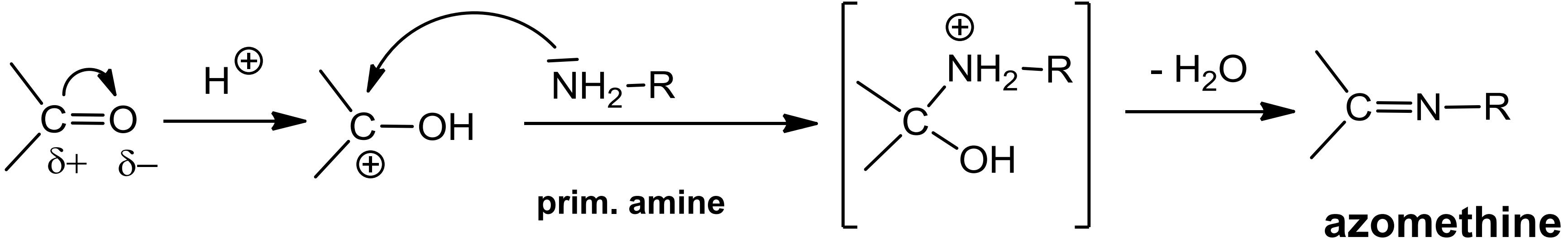


mesityloxide

forone

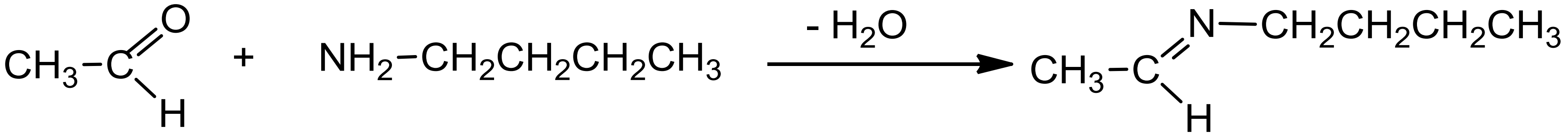
Reaction of aldehydes and ketones with N-nucleophiles

reaction is mostly catalysed by an acid – (pay attention to the strength and concentration of acid)

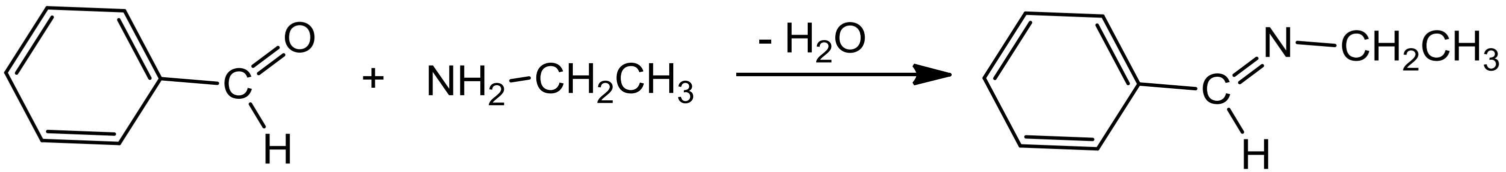


alkylidenalkylamine

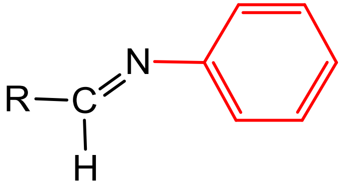
alifatic aldehydes do not need acid catalysis, but for aromatic is necessary



ethylidenbutylamine



benzylidenethylamine



azomethines with phenyl at N atom are named Schiff bases

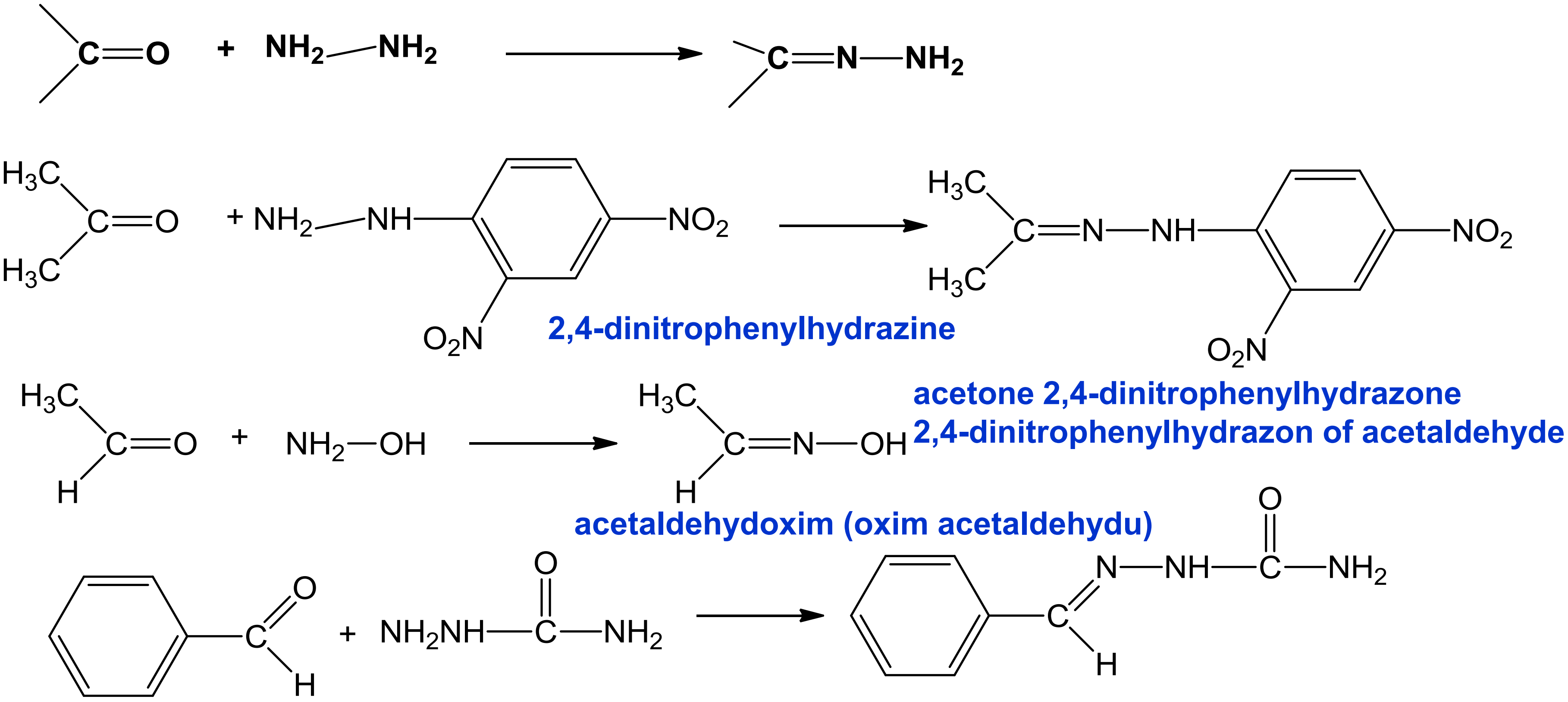
Reaction of aldehydes and ketones with N-nucleophiles

When acid is used, we must pay attention to concentration of acid:

with growing pH of the reaction medium is activated carbonyl group,
but in the same time is lowered concentration of non protonated amine for the reaction

Reaction of aldehydes and ketones with N-nucleophiles

Similarly are adding other nitrogen compounds:



2,4-dinitrophenylhydrazine

acetone 2,4-dinitrophenylhydrazone
2,4-dinitrophenylhydrazon of acetaldehyde

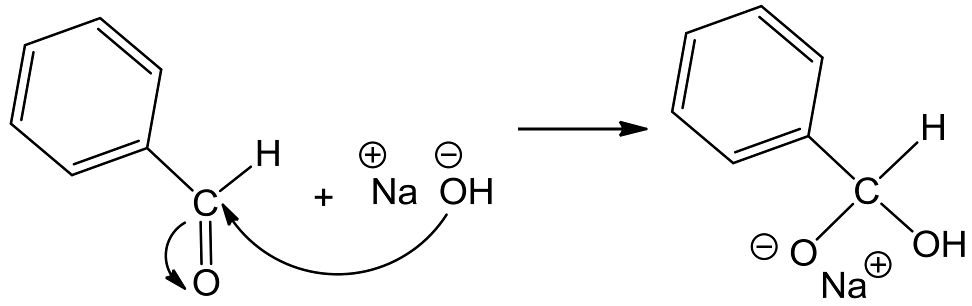
acetaldehydoxim (oxim acetaldehydu)

semikarbazide

benzaldehyde semikarbazone
semikarbazon of benzaldehyde

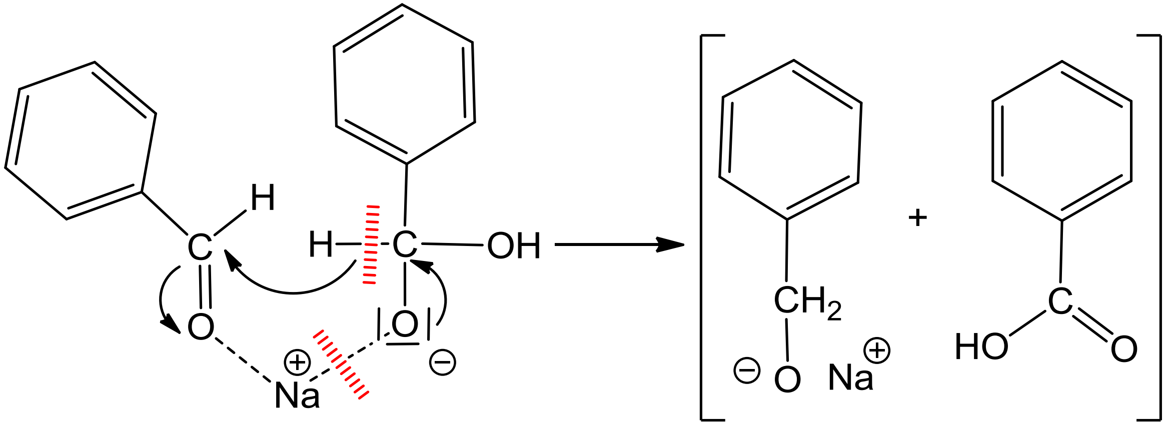
Reaction of carbonyl compounds without α–hydrogen atoms

by a treatment of a base they cannot undergo aldolization or aldol condensation

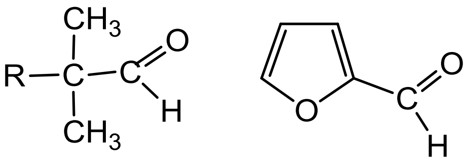


Cannizar reaction (disproporcionation):

from aldehyde alcohol and carboxylic acid are obtained



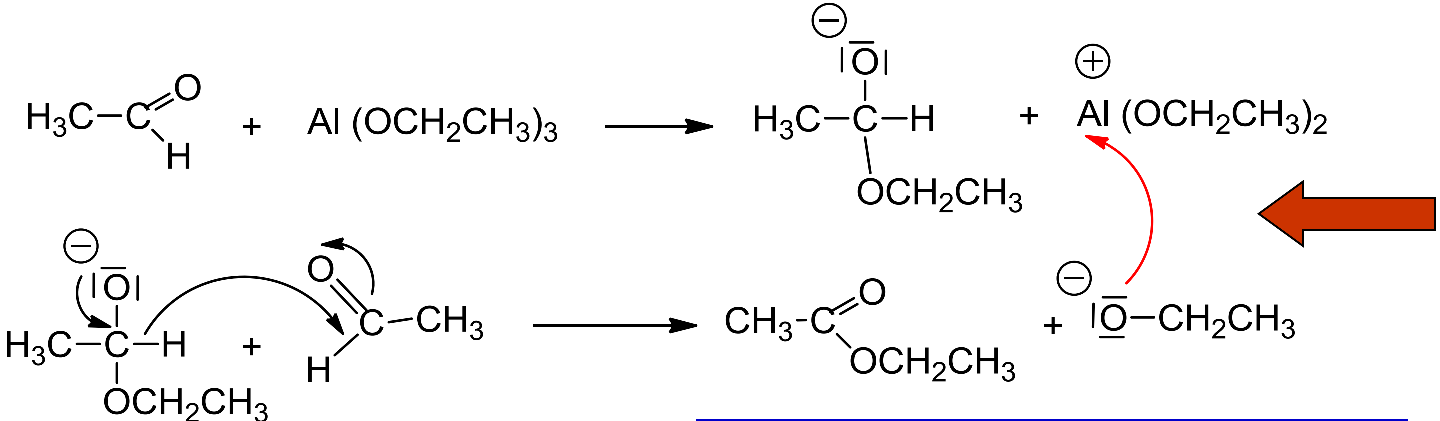
beside benzaldehyde also alifatic compounds with substituted α–carbon and other aromates can enter such a reaction:



Reactions of carbonyl compounds

Tiščenko reaction

aluminium alkoxide is used as catalyst

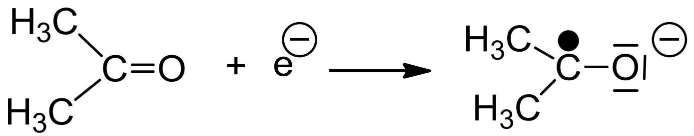


regeneration of catalyst

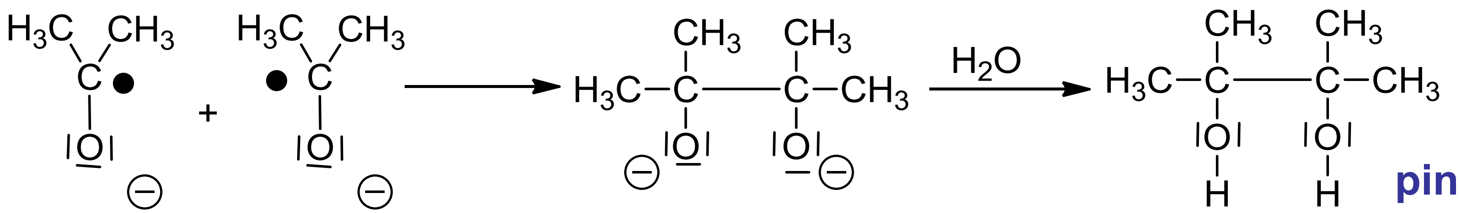
from aldehyde ester is prepared

Aluminium alcoholate as a weak base is not developing any aldolisation but adds to cabonyle to give ester

Reduction of carbonyl compounds



reduction in nonaqueous medium (benzene, toluene) by a metal (for example by magnesium) proceeds with a transfer of electrons by radical mechanism



pinakole

H^+

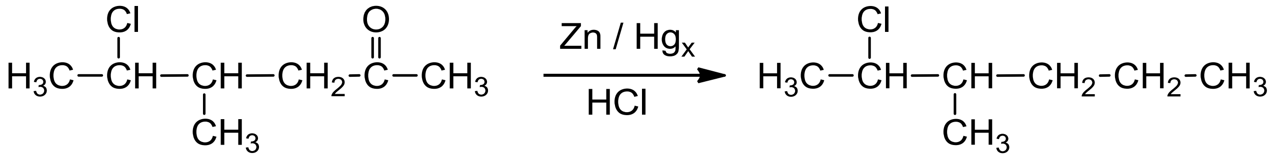
pinakoline rearrangement

Reduction of carbonyl compounds

Reduction of aldehydes and ketones to saturated alkanes

1. **Clemensen reduction** in acidic medium (reaction suitable for systems without groups sensitive to acidic medium)

Reaction is carried out in medium of hydrochloric acid, source of hydrogen amalgamed zinc



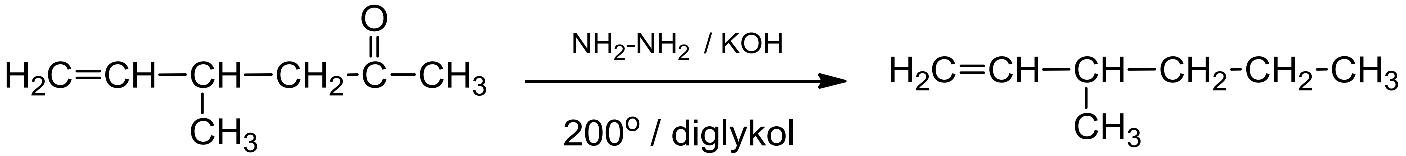
$$H_3C-\overset{Cl}{\overset{|}{C}H}-\underset{\overset{|}{CH_3}}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[HCl]{Zn / Hg_x} H_3C-\overset{Cl}{\overset{|}{C}H}-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_2-CH_3$$

in alkali medium substitution of halogen could take place

2. **Kižner – Wolff reduction** in a alkali medium

Reaction is suitable for systems without groups sensitive to alkali medium

Reaction is carried out at high temperature in a high boiling solvent as diglykol, triglykol in the presence of concentrated sodium hydroxide.



$$H_2C=CH-\underset{\overset{|}{CH_3}}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[200^o / diglykol]{NH_2\text{-}NH_2 \; / \; KOH} H_2C=CH-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_2-CH_3$$

In acidic medium would proceed addition of hydrogen to the double bond