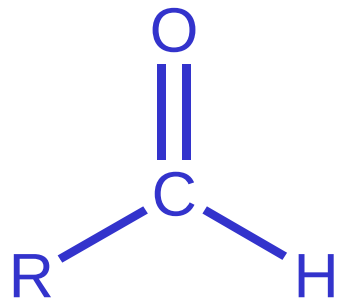
ALDEHYDES AND KETONES

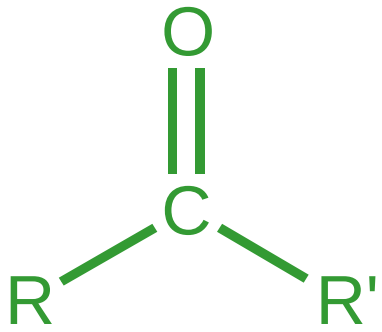
STRUCTURE

Aldehyde



R = H, alkyl, aryl

Ketone



R and R' = alkyl or aryl
R and R' cannot be hydrogen!

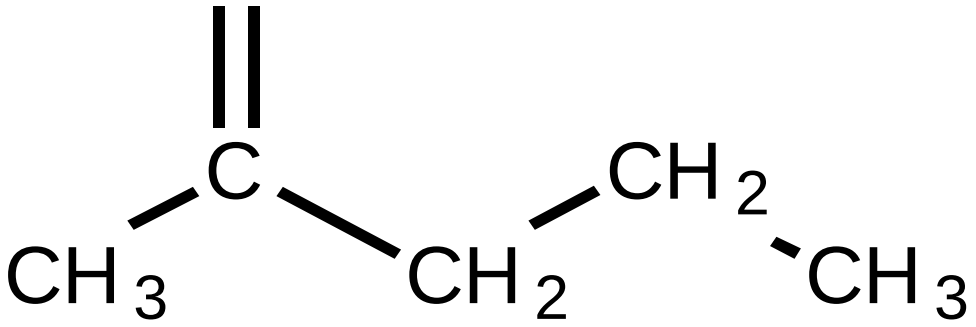
NOMENCLATURE

IUPAC Nomenclature of Ketones

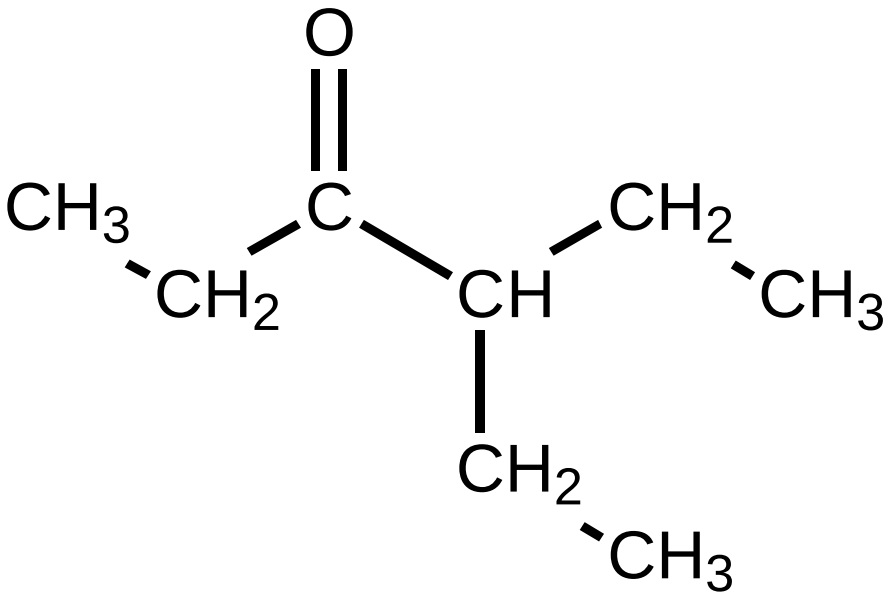
- Choose the longest continuous carbon chain that contains the carbonyl carbon
- Number from the end of the chain closest to the carbonyl carbon
- Ketone ending is ***-one***

Do the ***ketones*** section of Organic Nomenclature program!

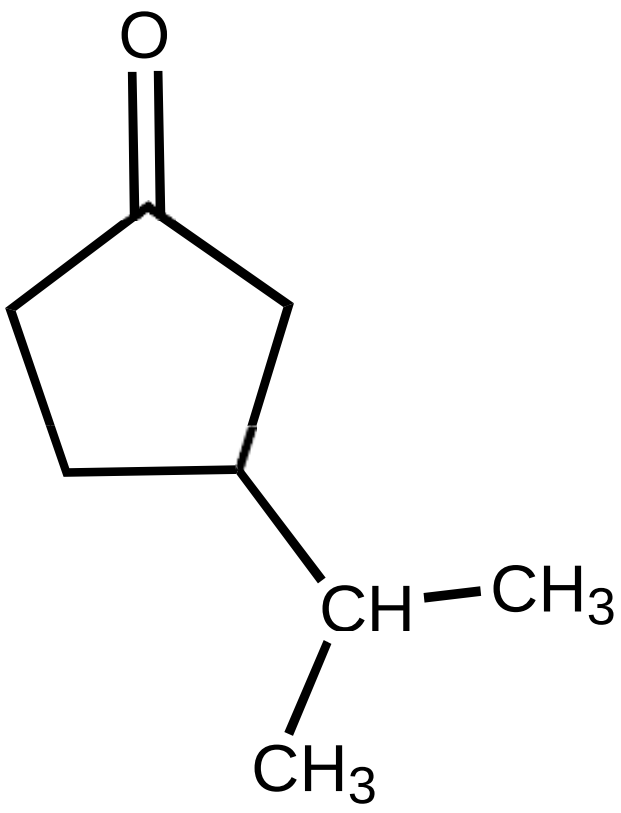
EXAMPLES



2-Pentanone



4-Ethyl-3-hexanone



3-Isopropylcyclopentanone

KETONES

Common, or Trivial, Names

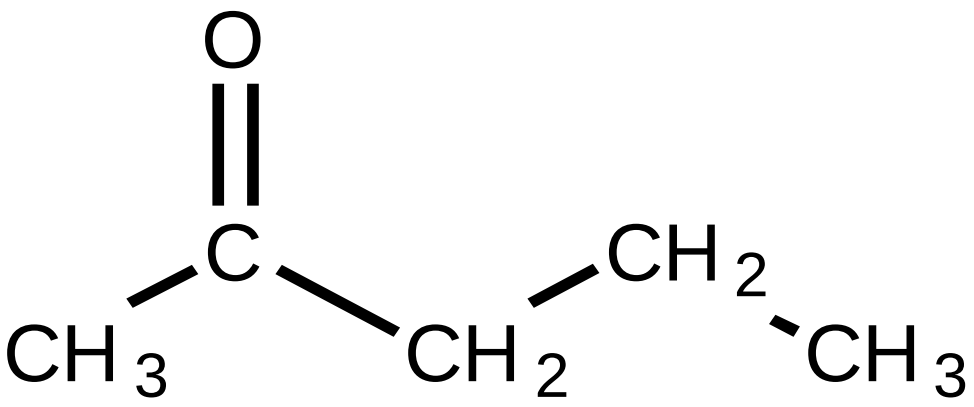
- Name each group attached to the carbonyl group as an alkyl group

- Combine into a name, according to the pattern:

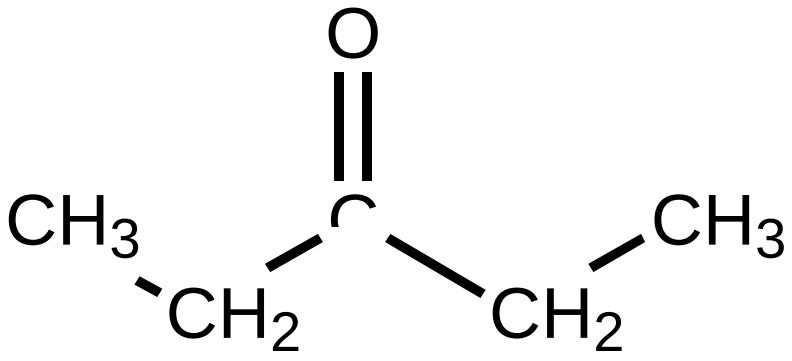
alkyl alkyl' ketone

NOTE: This is not all one word!

Example of Common Names

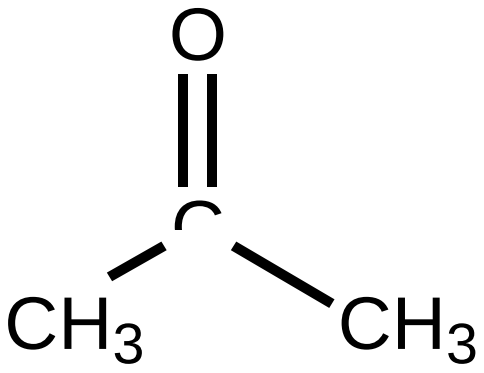


Methyl propyl ketone



Diethyl ketone

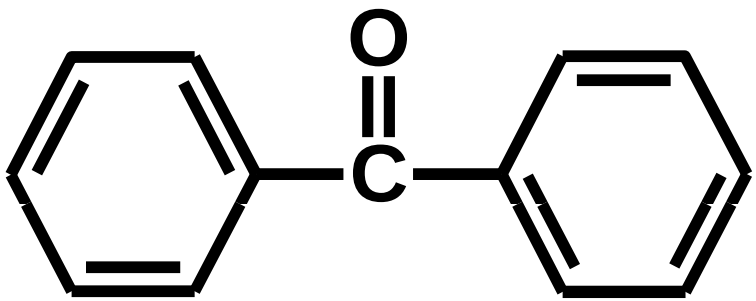
SPECIAL CASES



dimethyl ketone

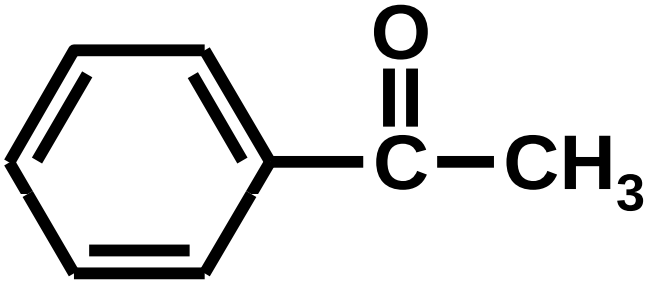
acetone

A common laboratory solvent and cleaning agent



diphenyl ketone

benzophenone



methyl phenyl ketone

acetophenone

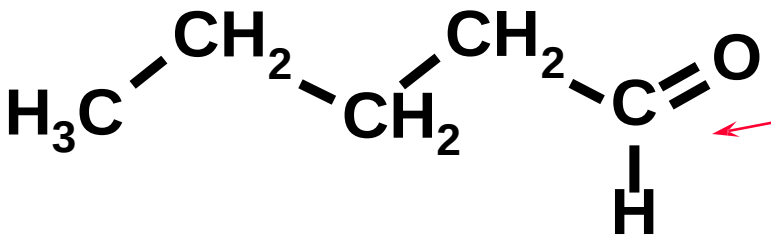
KNOW THESE

IUPAC Nomenclature of Aldehydes

- Choose the longest continuous carbon chain that contains the carbonyl carbon
- Number from the end of the chain closest to the carbonyl carbon (carbon #1!)
- Aldehyde ending is *-al*

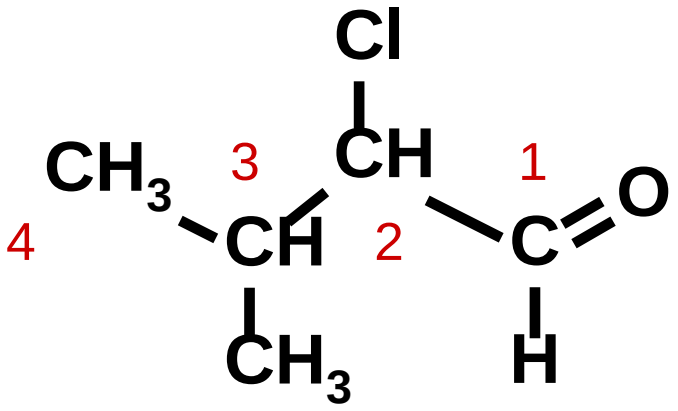
Do the *aldehydes* section of Organic Nomenclature program.

EXAMPLES



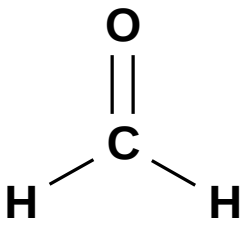
aldehyde group is always carbon 1

pentanal



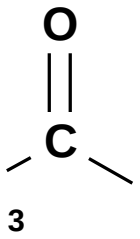
2-chloro-3-methylbutanal

Common Names of the Aldehydes



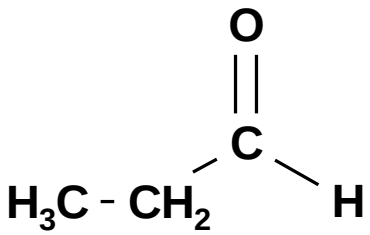
Formaldehyde

1



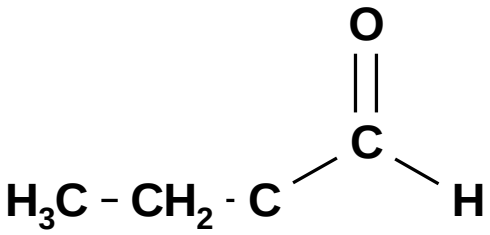
Acetaldehyde

2



Propionaldehyde

3

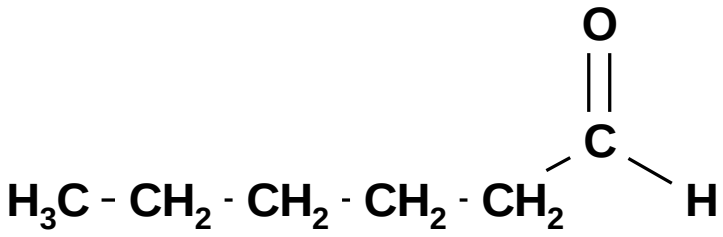


Butyraldehyde

4

Valeraldehyde

5

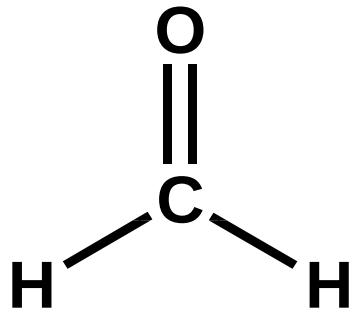


Caproaldehyde

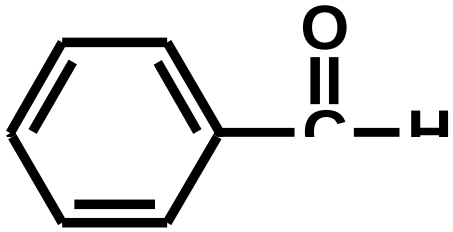
6

RECOGNIZE THESE

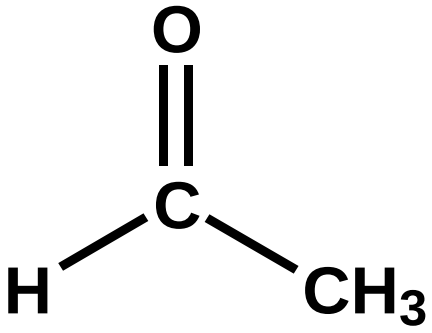
SPECIAL CASES



formaldehyde



benzaldehyde

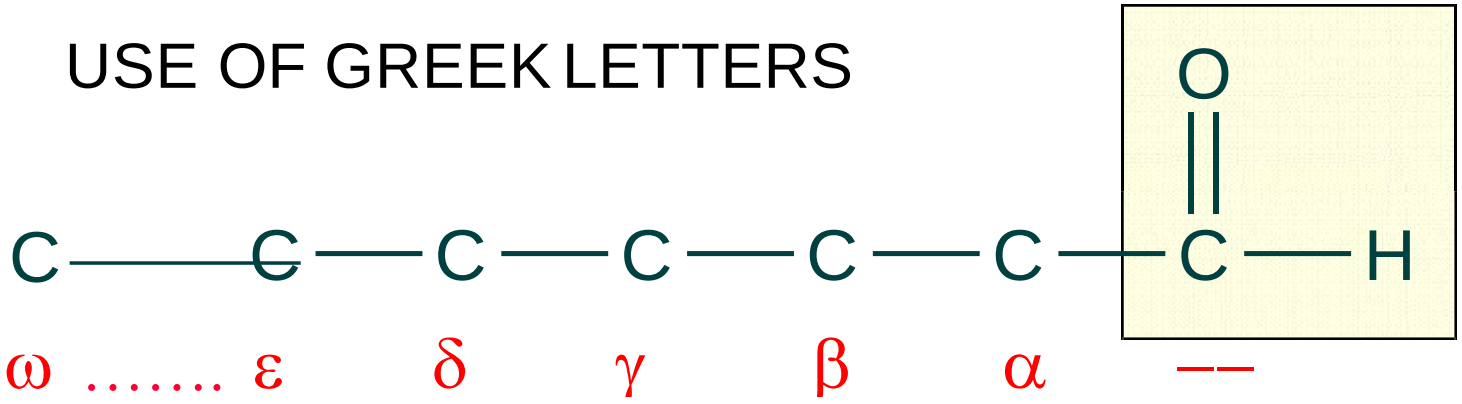


acetaldehyde

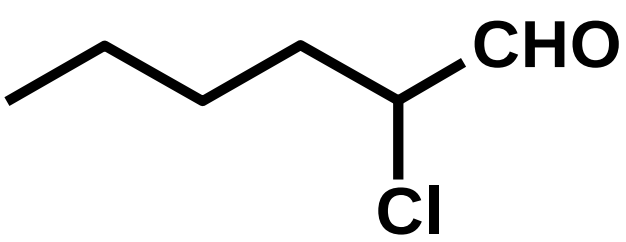
KNOW THESE

Forming Common Names of Aldehydes

USE OF GREEK LETTERS

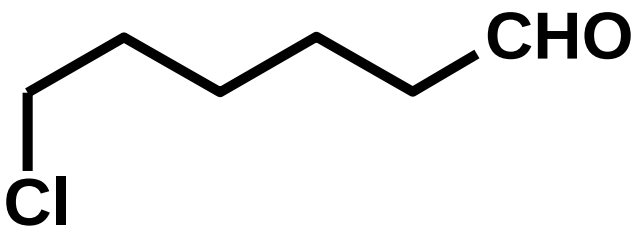


ω is always the end of the chain, no matter how long



α-chlorocaproaldehyde

(α-chlorohexanal)



ω-chlorocaproaldehyde

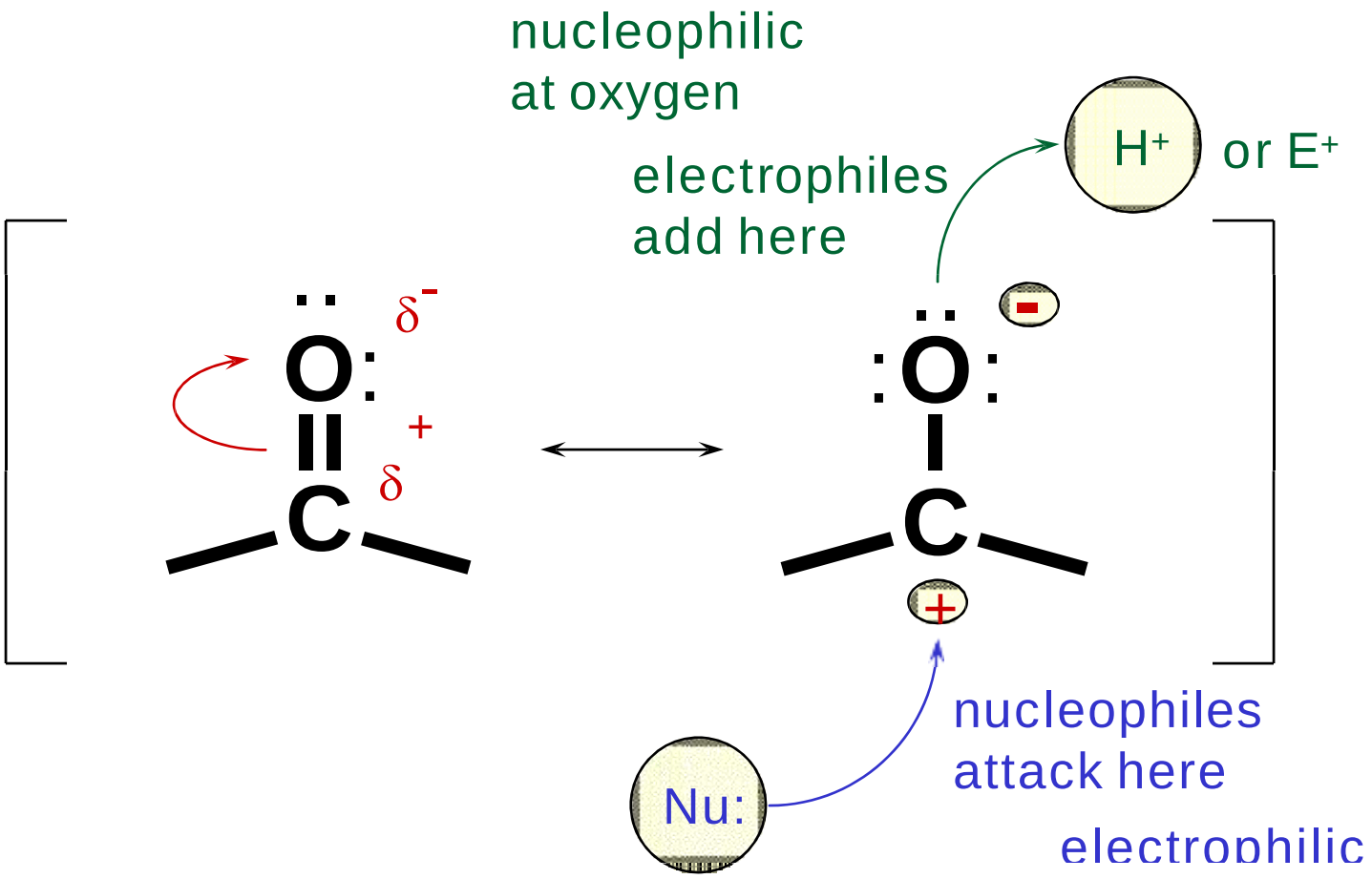
(ω-chlorohexanal)

REACTIVITY OF THE C=O GROUP

NUCLEOPHILIC ADDITION

GENERALIZED CHEMISTRY

THE CARBONYL GROUP

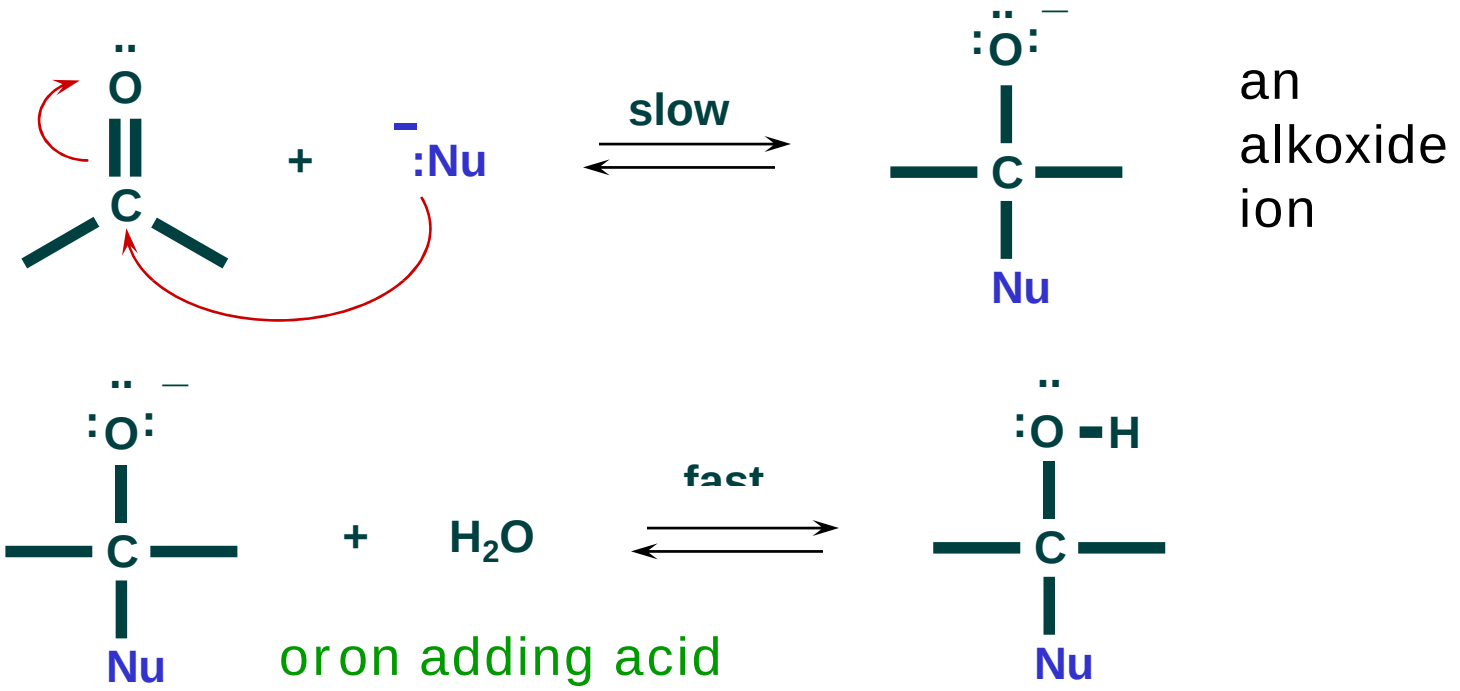


NUCLEOPHILIC ADDITION TO C=O

MECHANISMS

IN ACID AND IN BASE

Nucleophilic Addition to Carbonyl
Basic or Neutral Solution

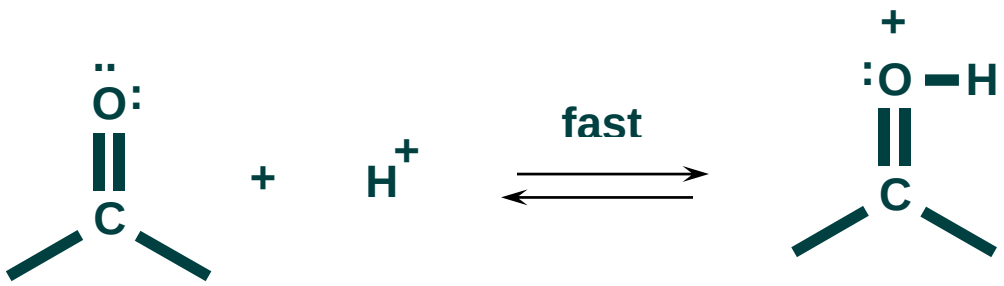


Good nucleophiles and strong bases (usually charged)

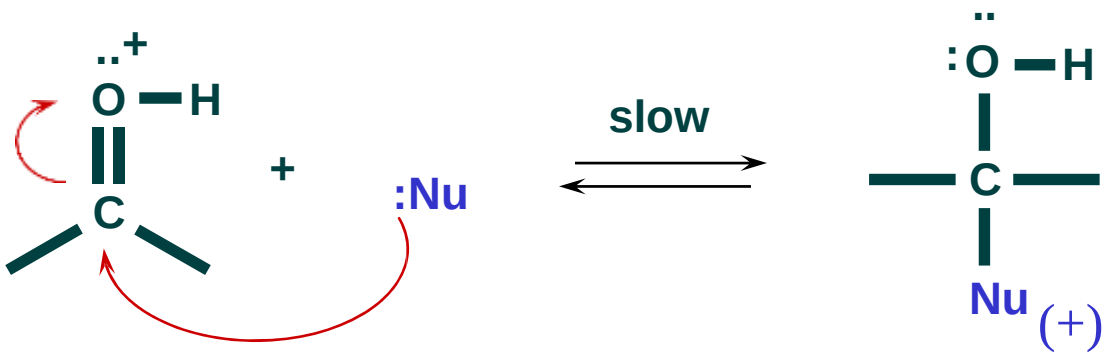
BASIC SOLUTION

Nucleophilic Addition to Carbonyl

Acid Catalyzed



more reactive to addition than the un-protonated precursor



Acid catalysis speeds the rate of addition of
- weak nucleophiles and
- weak bases (usually uncharged).

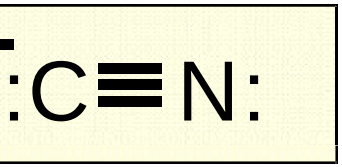
ACIDIC SOLUTION

pH 5-6

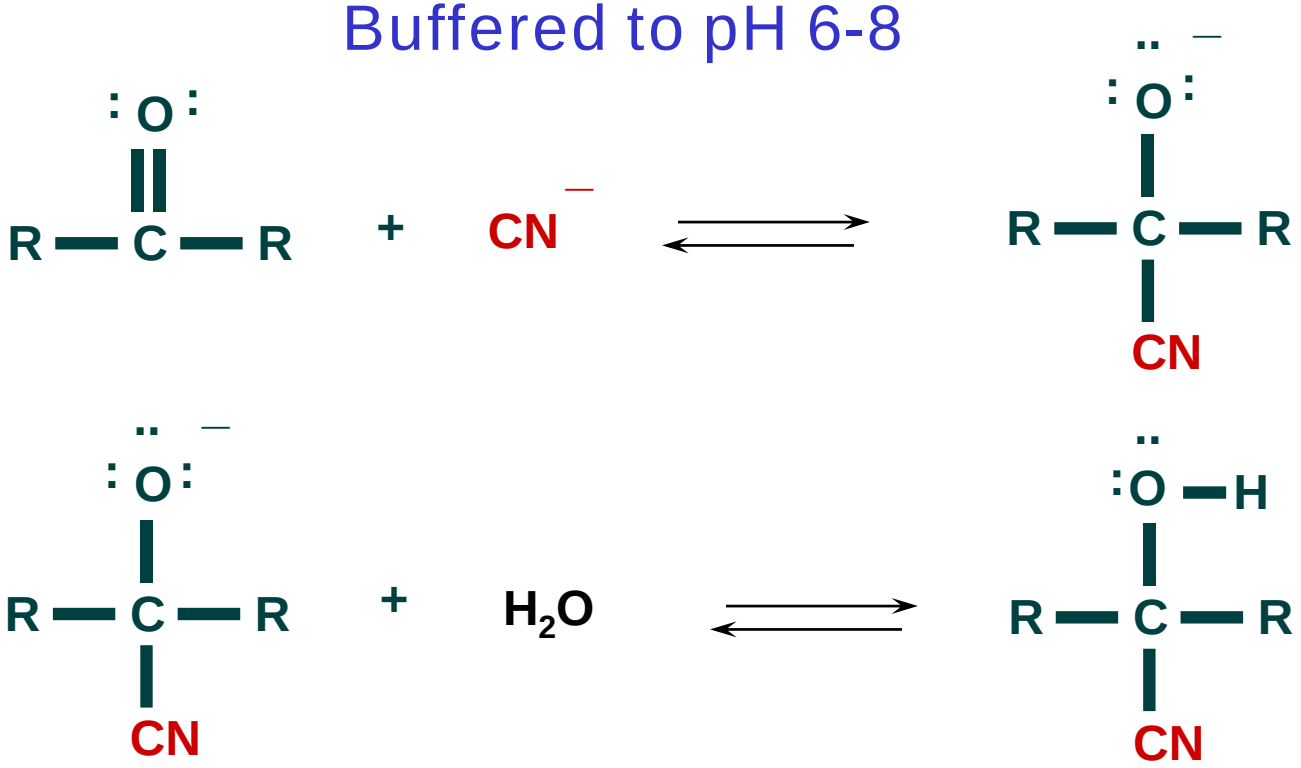
stronger acid protonates the nucleophile

CYANOHYDRINS

Addition of Cyanide



Buffered to pH 6-8

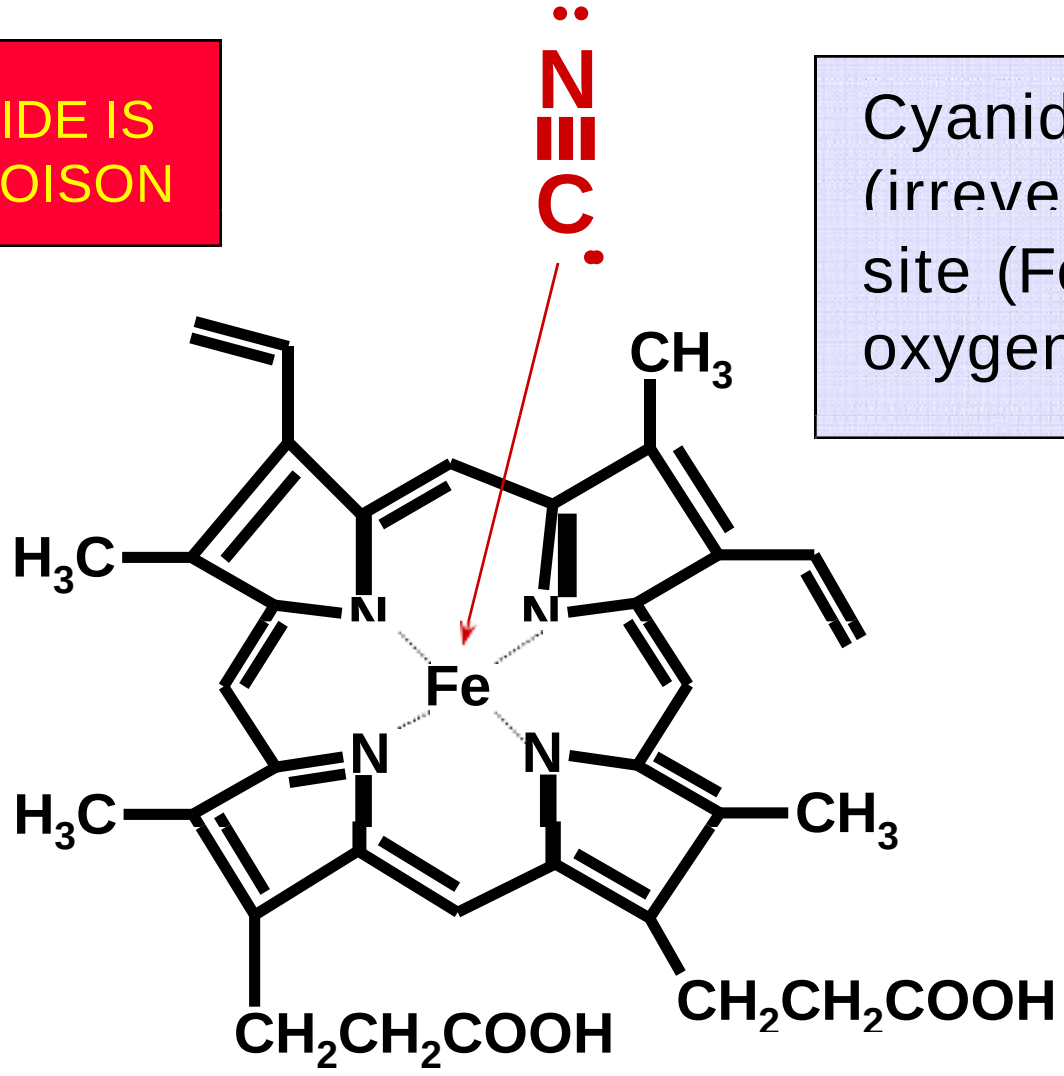


a cyanohydrin

In acid solution there would be little CN^-, and HCN (g) would be a problem (poison).

CYANIDE ION BONDS TO HEMOGLOBIN

CYANIDE IS IS A POISON



Cyanide bonds (irreversibly) to the site (Fe II) where oxygen usually bonds.

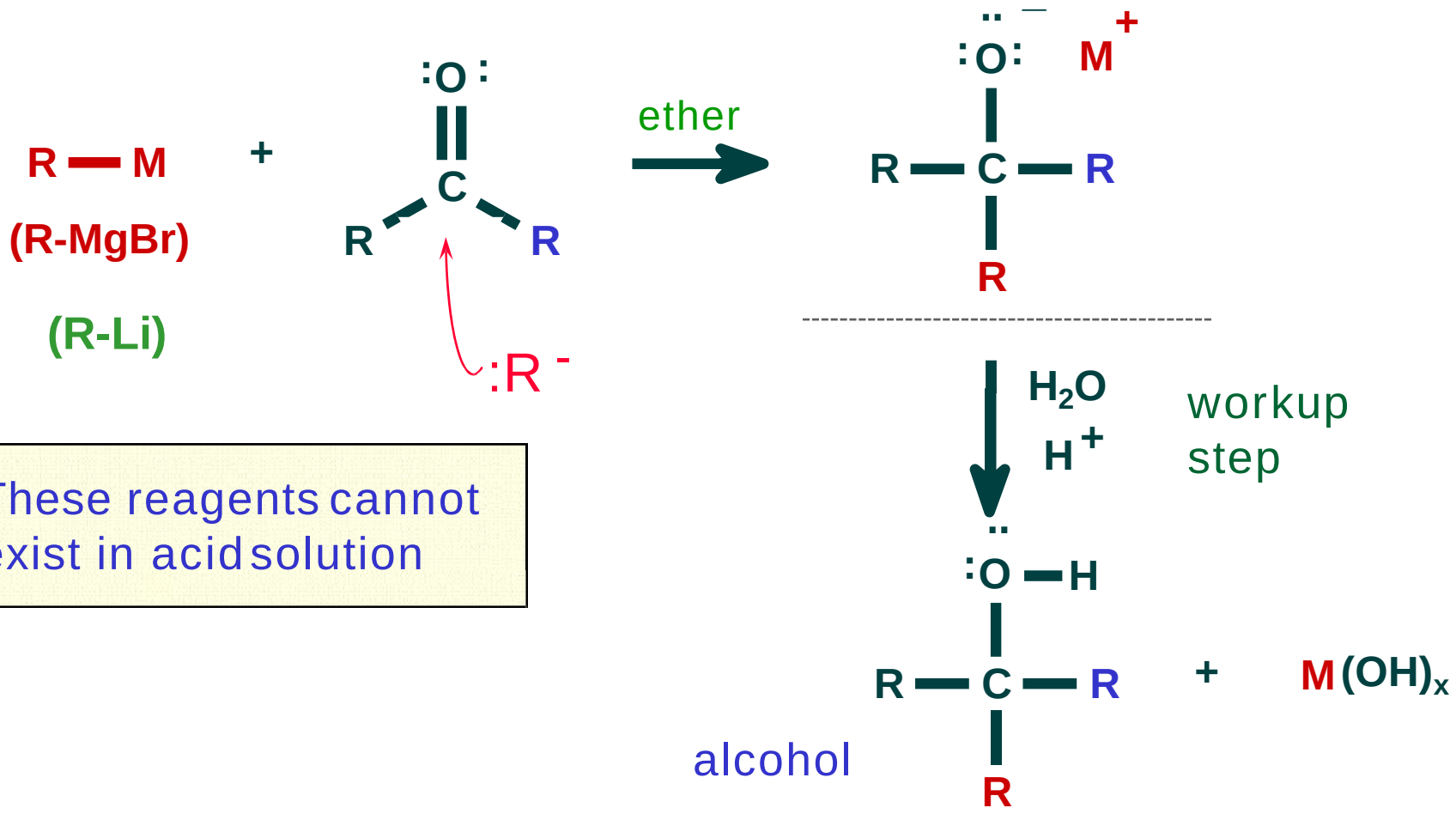
You die of suffocation - lack of oxygen.

HCN is a gas that you can easily breathe into your lungs.

ORGANOMETALLICS

Synthesis of Alcohols

Addition of Organometallic Reagents



These reagents cannot exist in acid solution

Summary of Reactions of Organometallics with Carbonyl Compounds

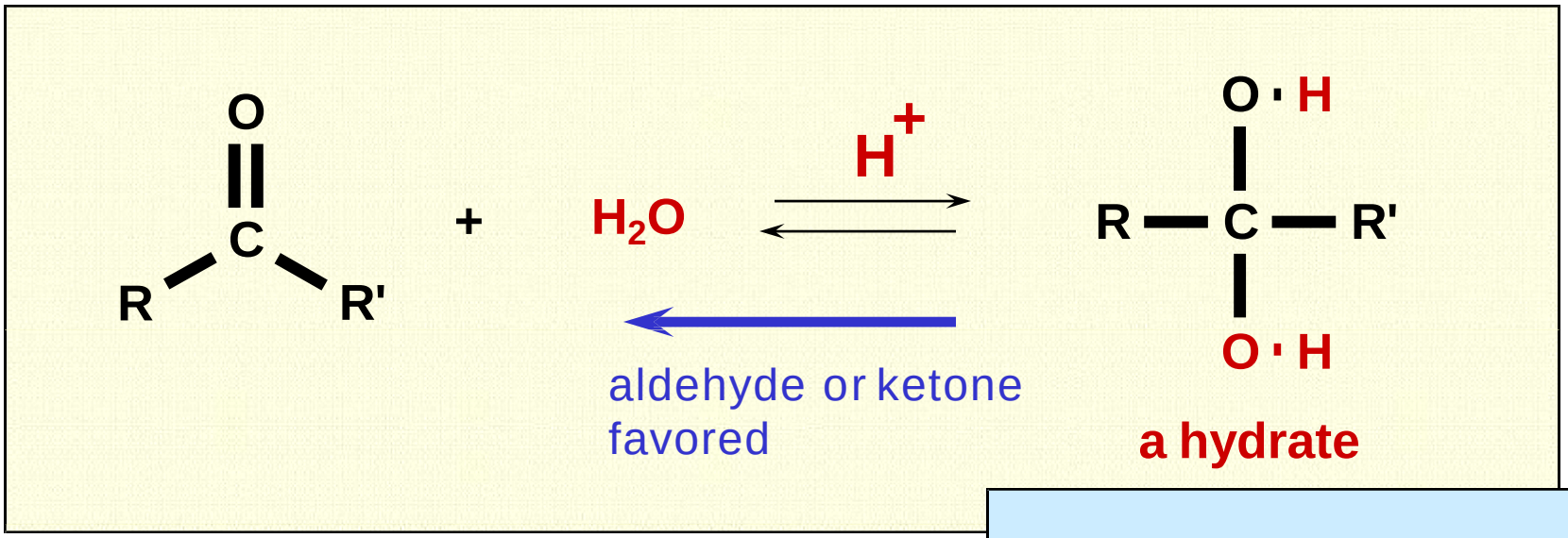
All review to you

- Organometallics with ketones yield *tertiary* alcohols
- Organometallics with aldehydes yield *secondary* alcohols
- Organometallics with formaldehyde yield *primary* alcohols.
- Organometallics with carbon dioxide yield carboxylic acids.

etc.

HYDRATES

Addition of Water

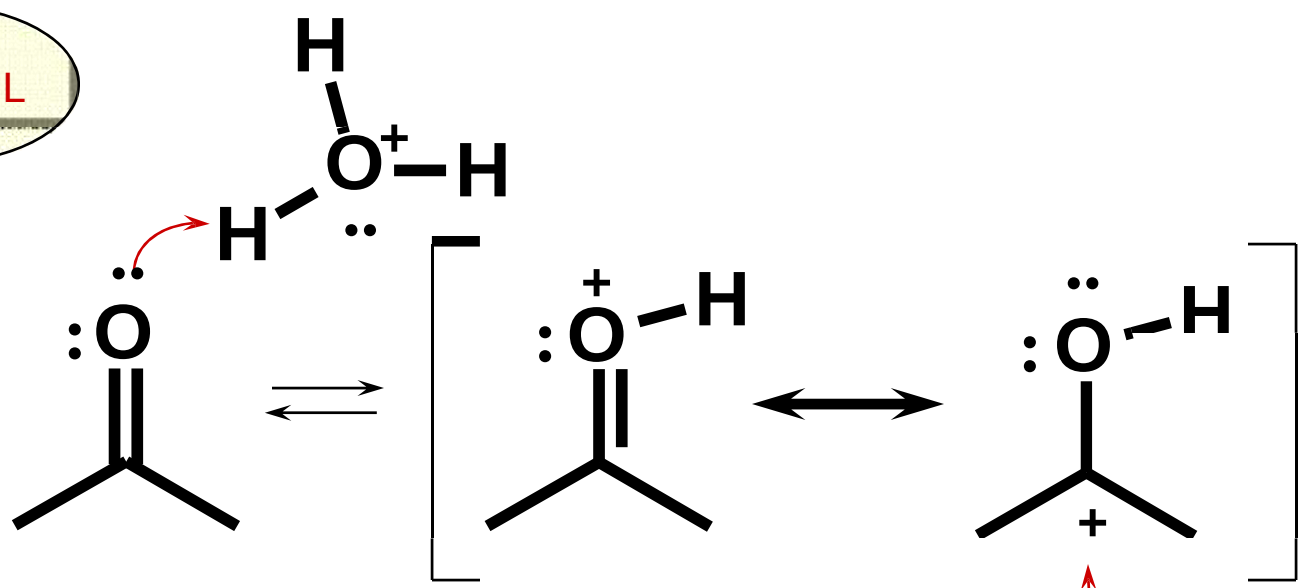


hydrates are unstable and cannot be isolated in most cases

most hydrates revert to an aldehyde or ketone as soon as they form

ACID CATALYSIS

RECALL



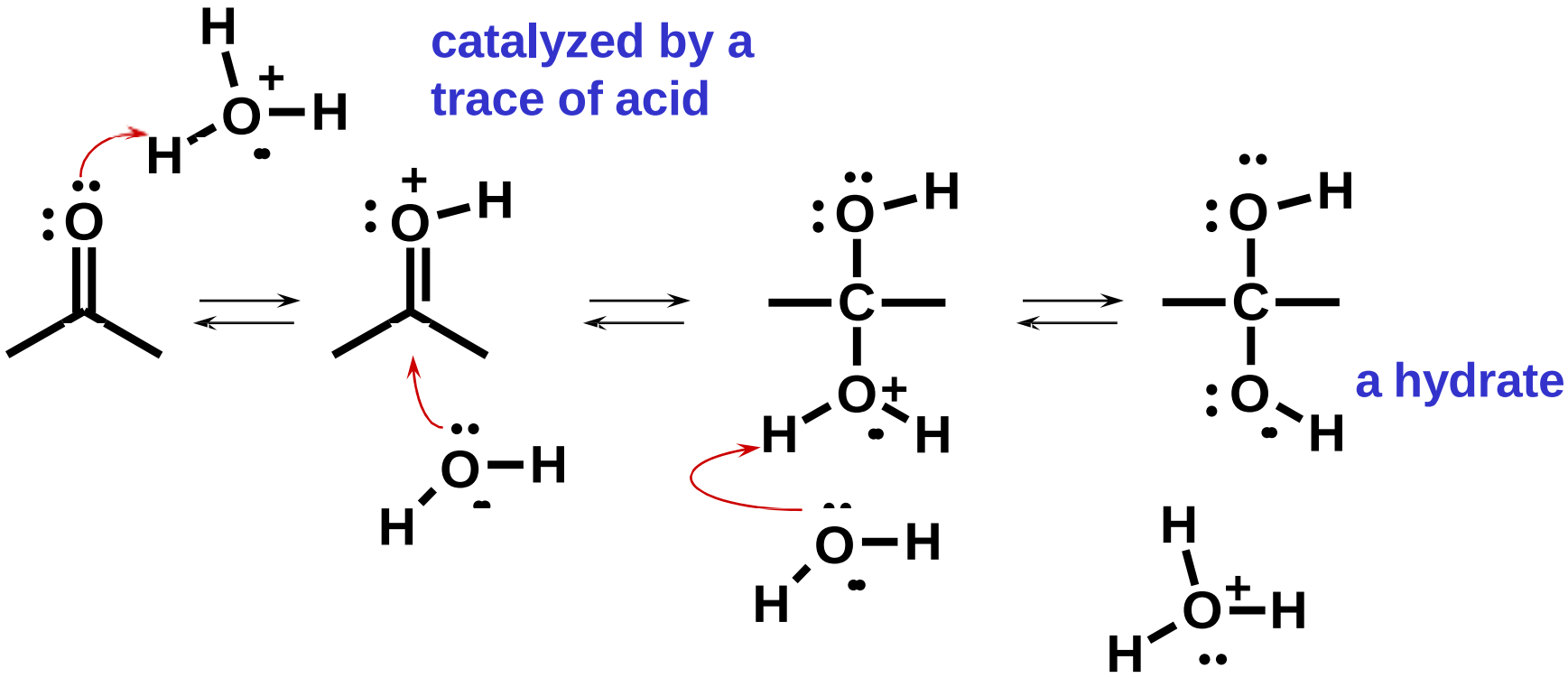
Acid catalysis enhances the reactivity of the carbonyl group - nucleophilic addition proceeds more easily.

:Nu

weak nucleophiles can react

Water is a weak nucleophile.

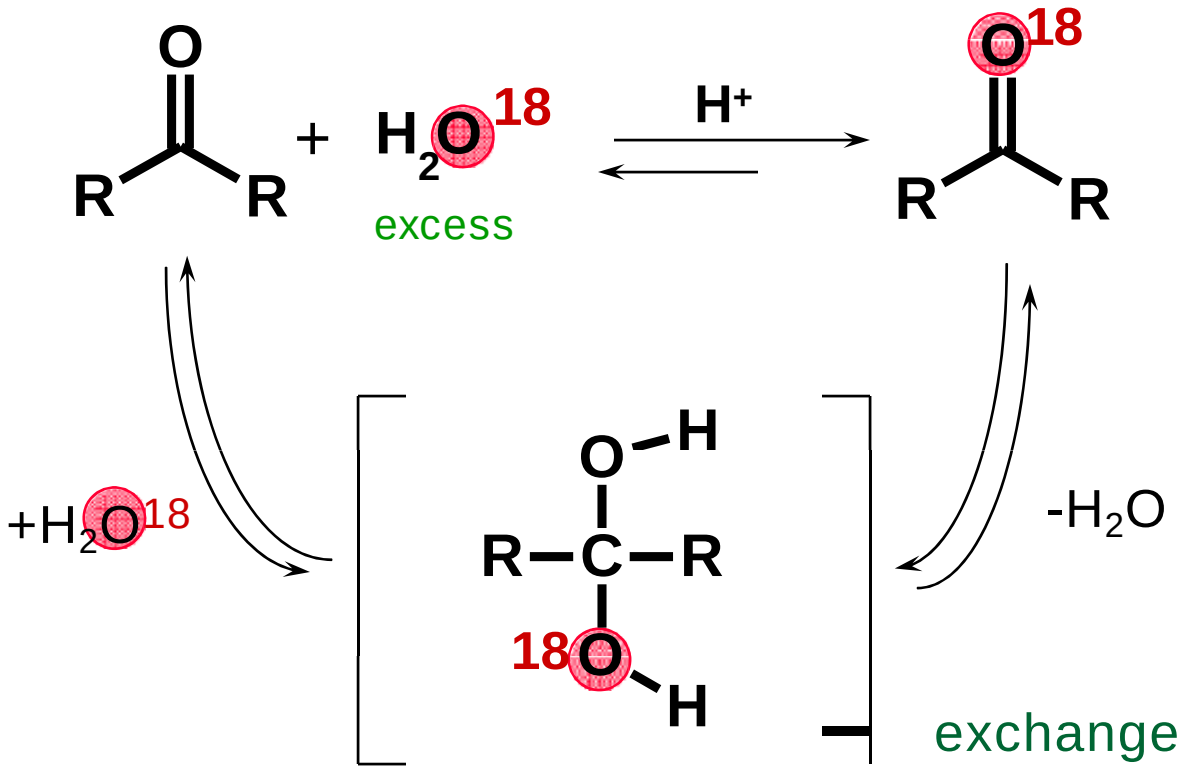
WATER ADDS TO THE CARBONYL GROUP OF ALDEHYDES AND KETONES TO FORM HYDRATES



for most compounds the equilibrium favors the starting materials and you cannot isolate the hydrate

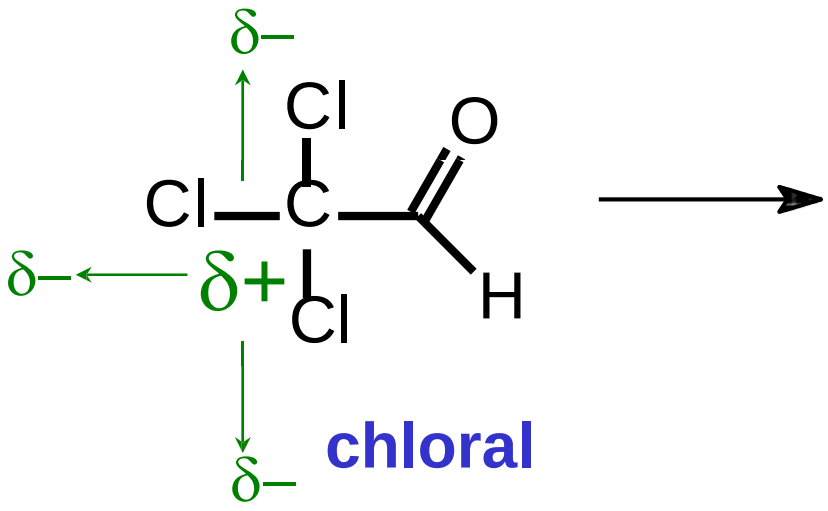
MICROREVERSIBILITY:
In a reaction where all steps are reversible, the steps in the reverse reaction are the same as those in the forward reaction, reversed!

ISOTOPE EXCHANGE REVEALS THE PRESENCE OF THE HYDRATE

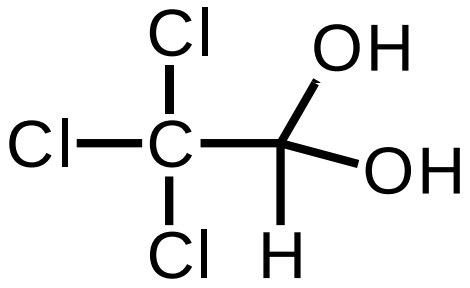


SOME STABLE HYDRATES

these also indicate that hydrates are possible

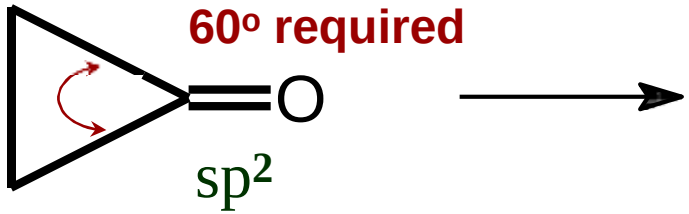


chloral

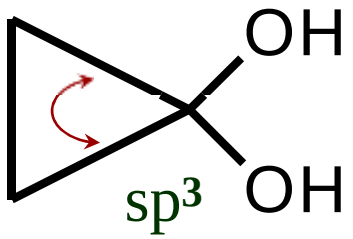


chloral hydrate

120° expected
60° required



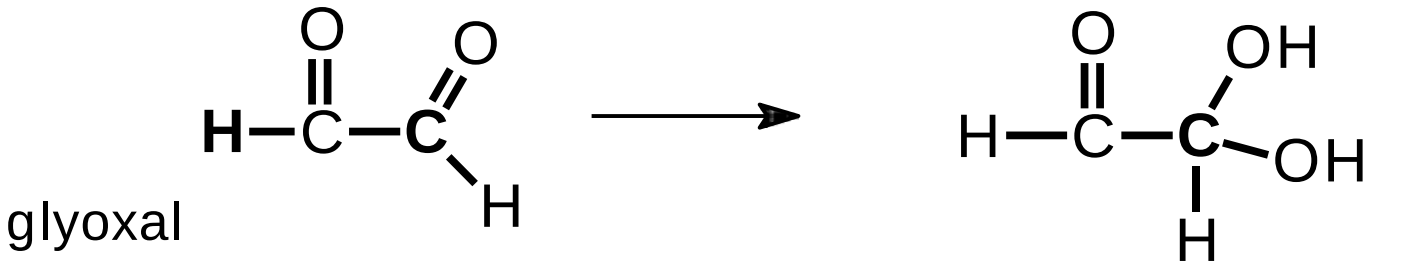
cyclopropanone



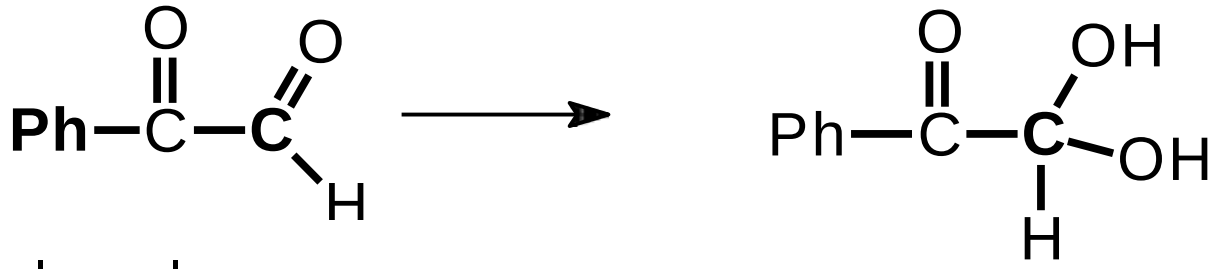
109° expected
60° required

cyclopropanone hydrate

SOME ADDITIONAL STABLE HYDRATES



glyoxal

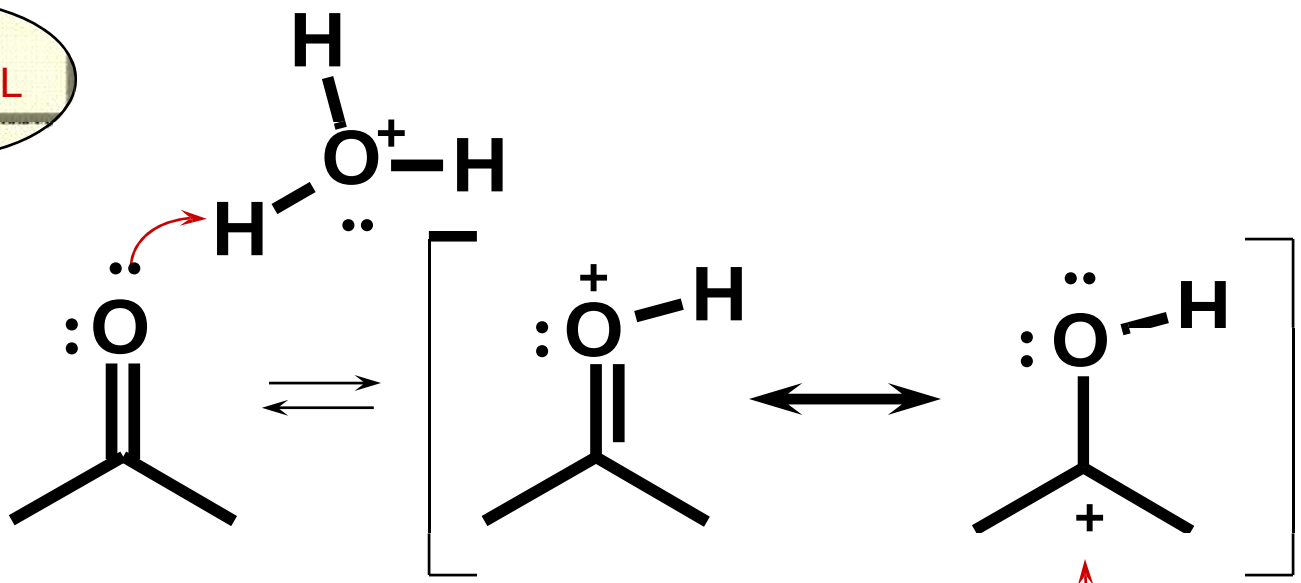


phenylglyoxal

ACETALS AND HEMIACETALS

ACID CATALYSIS

RECALL



Acid catalysis enhances the reactivity of the carbonyl group - nucleophilic addition proceeds more easily.

:Nu

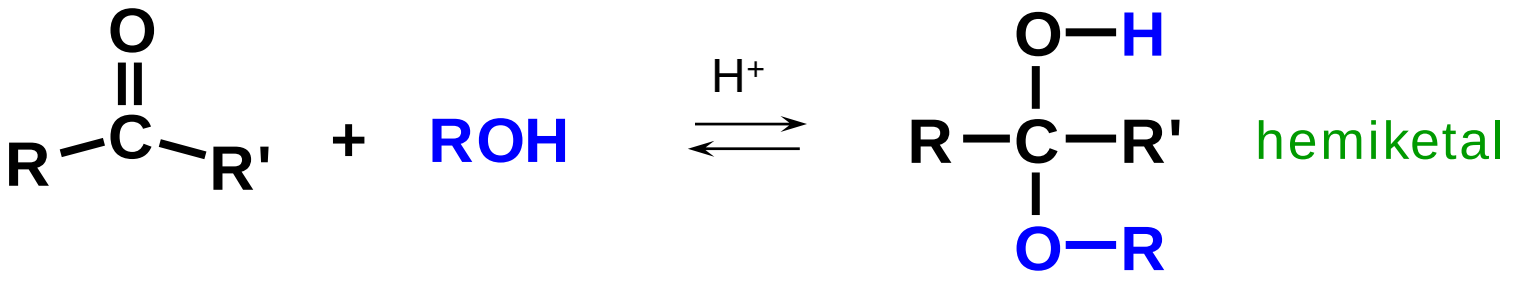
weak nucleophiles can react

Alcohols are weak nucleophiles.

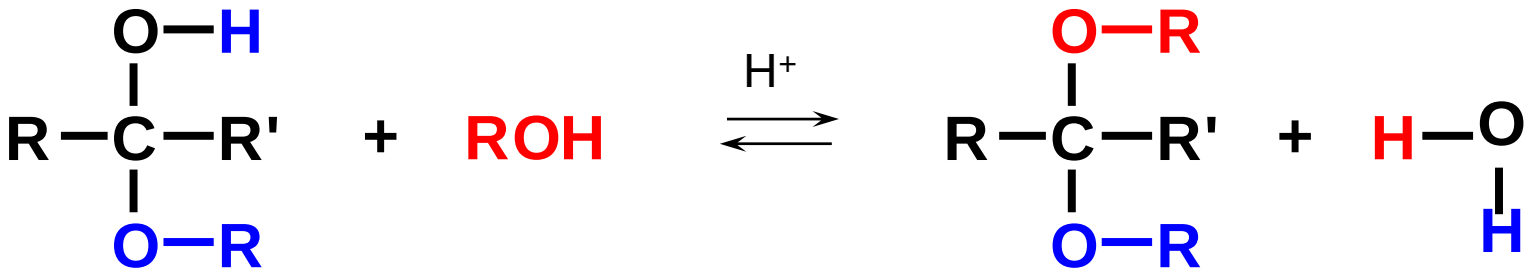
Addition of Alcohols

TWO MOLES OF ALCOHOL WILL ADD

addition of one mole



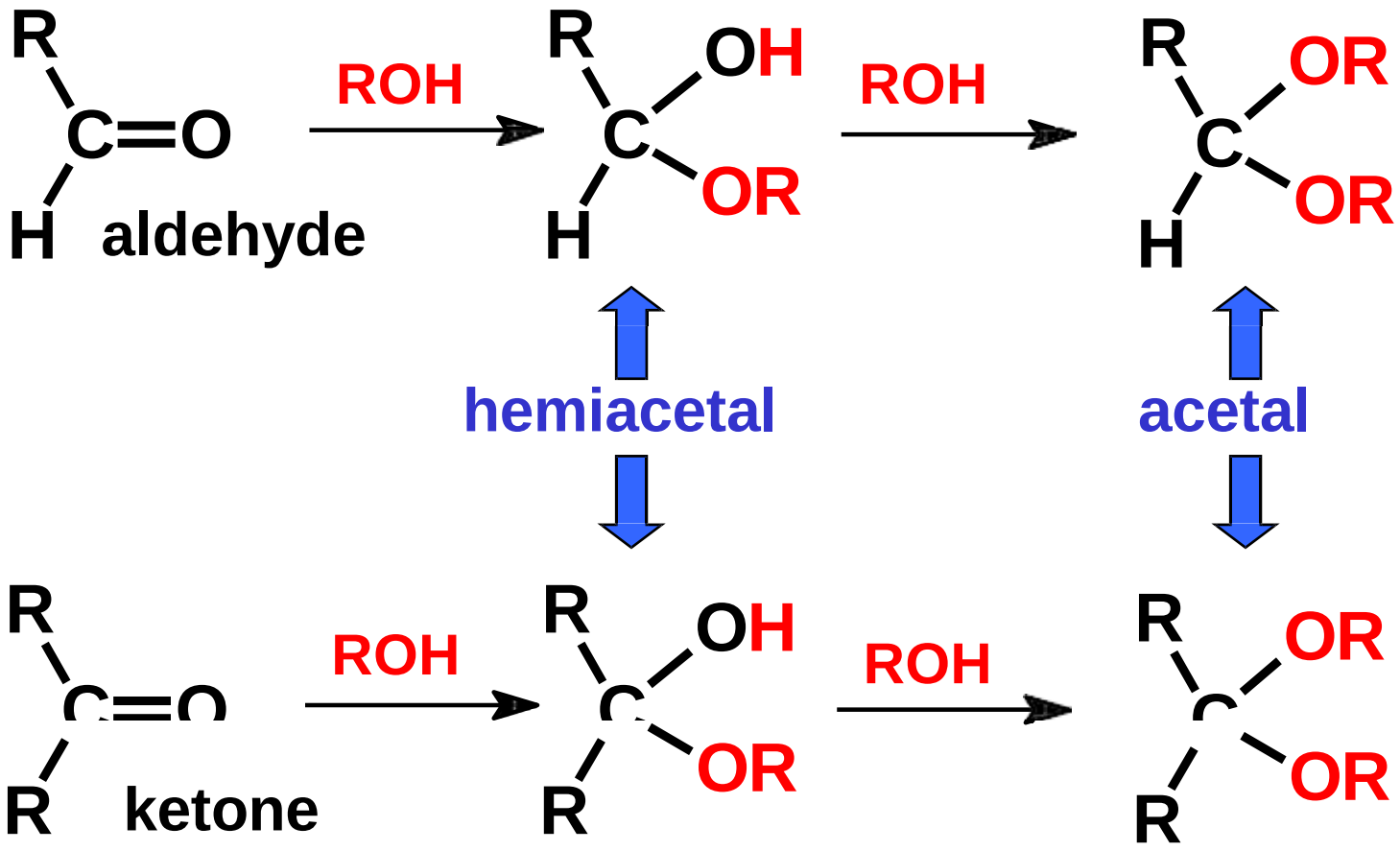
addition of second mole

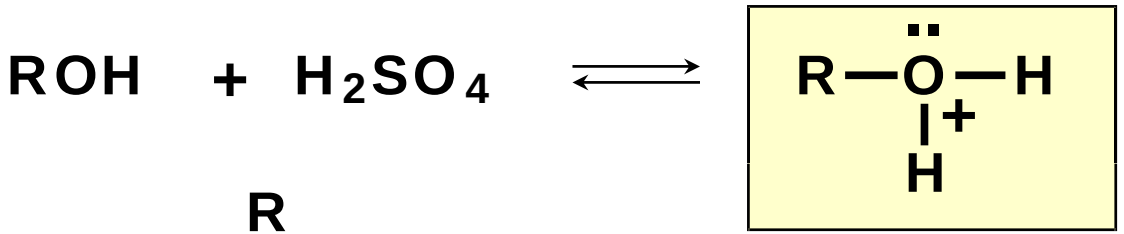


an aketal

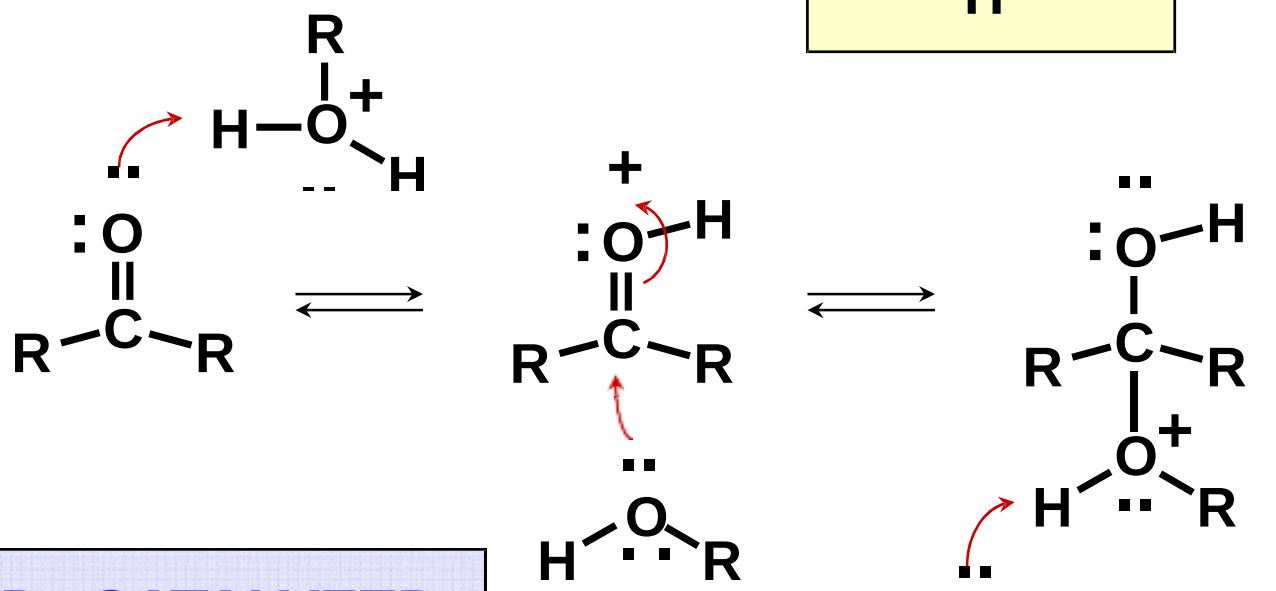
The equilibria normally favor the aldehyde or ketone starting material, but we will show how they can be made.

ACETALS AND HEMIACETALS





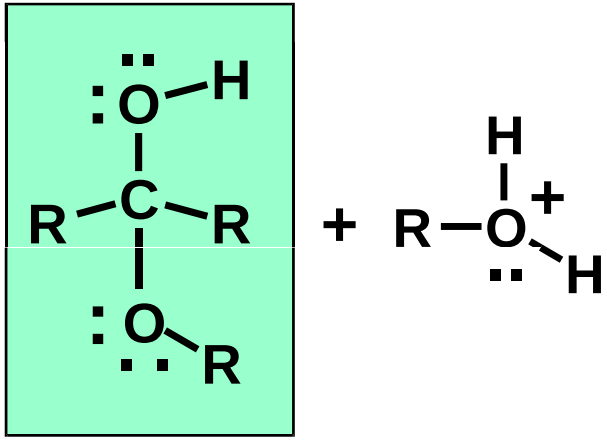
Like a hydronium ion



first addition

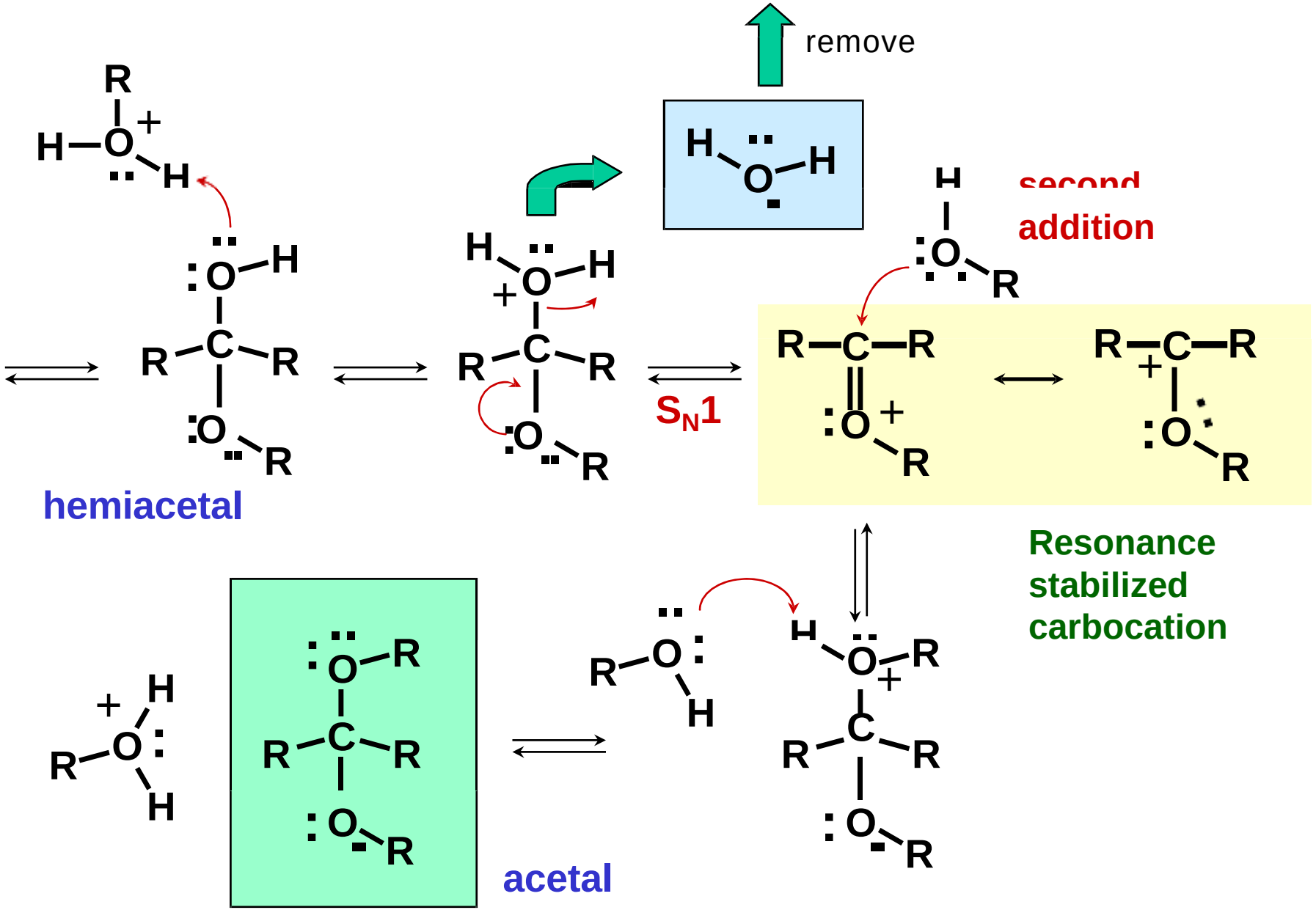
ACID CATALYZED FORMATION OF A HEMIACETAL

Normally the starting material is favored - but a second molecule of alcohol can react if in excess (next slide)



hemiacetal

FORMATION OF THE ACETAL (from the hemiacetal)

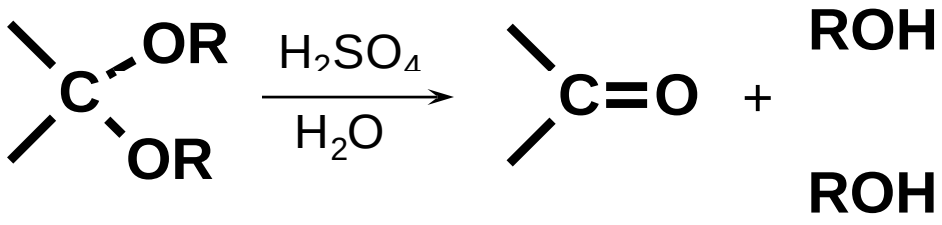


STABILITY OF ACETALS AND HEMIACETALS

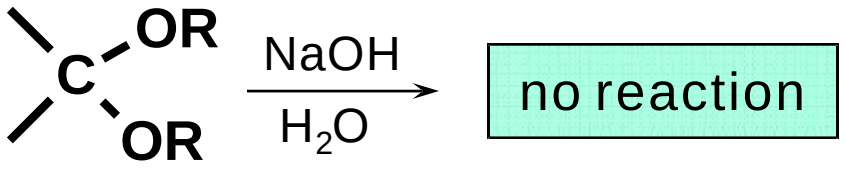
Most hemiacetals are not stable, except for those of sugars (see later).

Acetals are not stable in aqueous acid, but they are stable to aqueous base.

AQUEOUS ACID

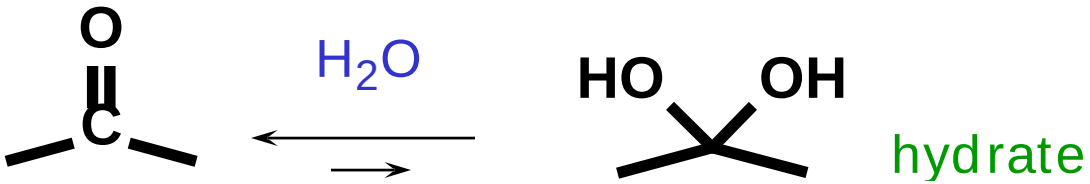


AQUEOUS BASE



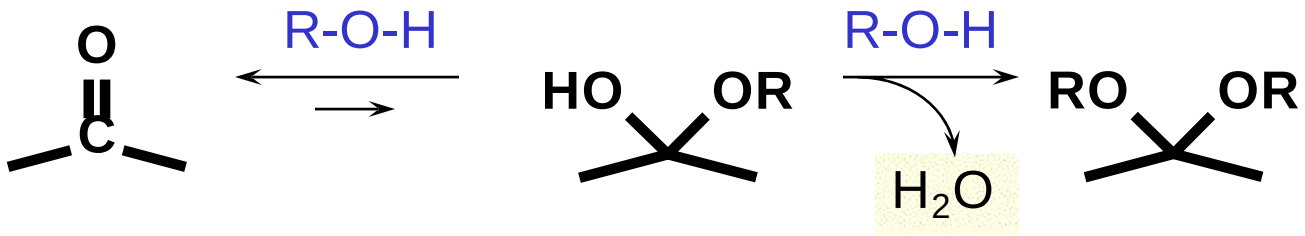
ADDITION OF WATER AND ALCOHOLS

WATER



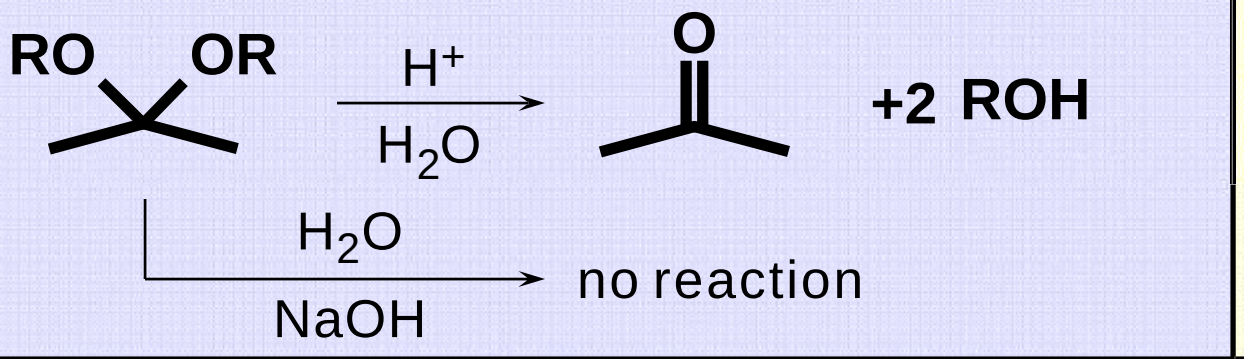
hydrate

ALCOHOLS



hemiacetal

acetal



acetals are stable to base but not to aqueous acid