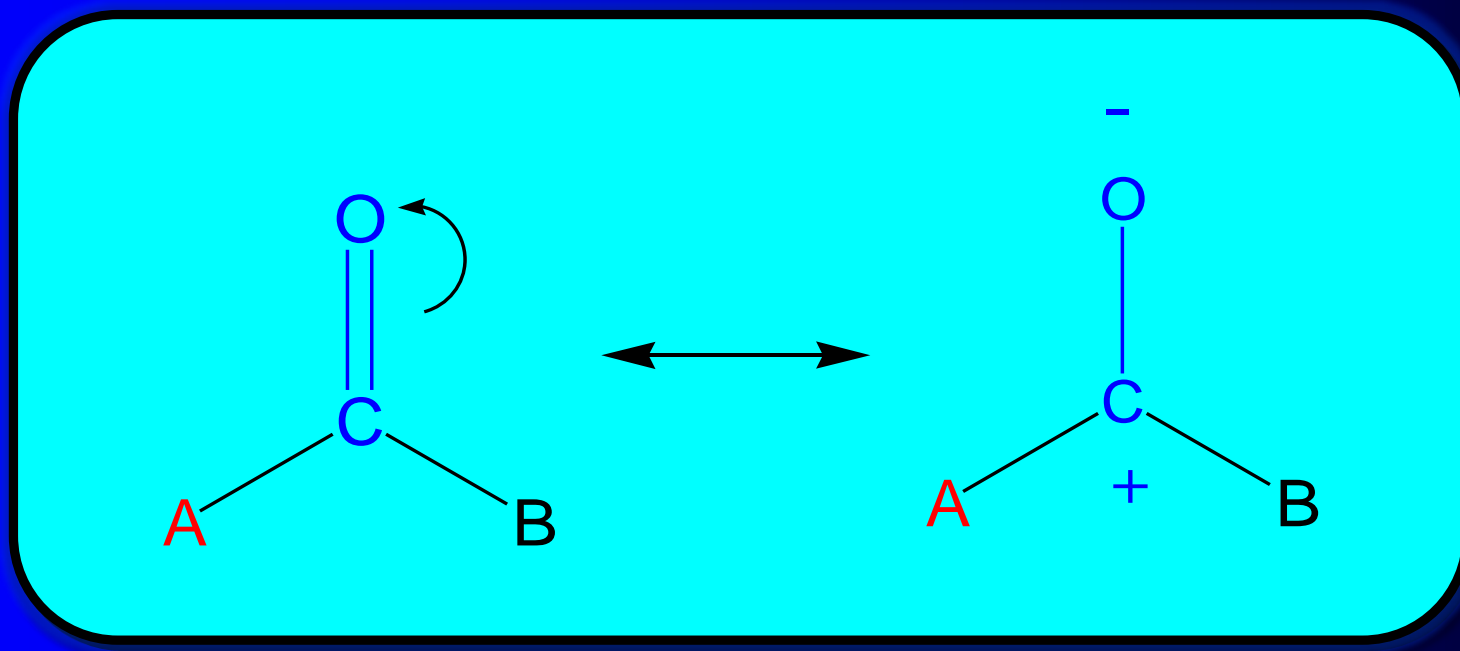


Lecture 13

Carbonyl Chemistry



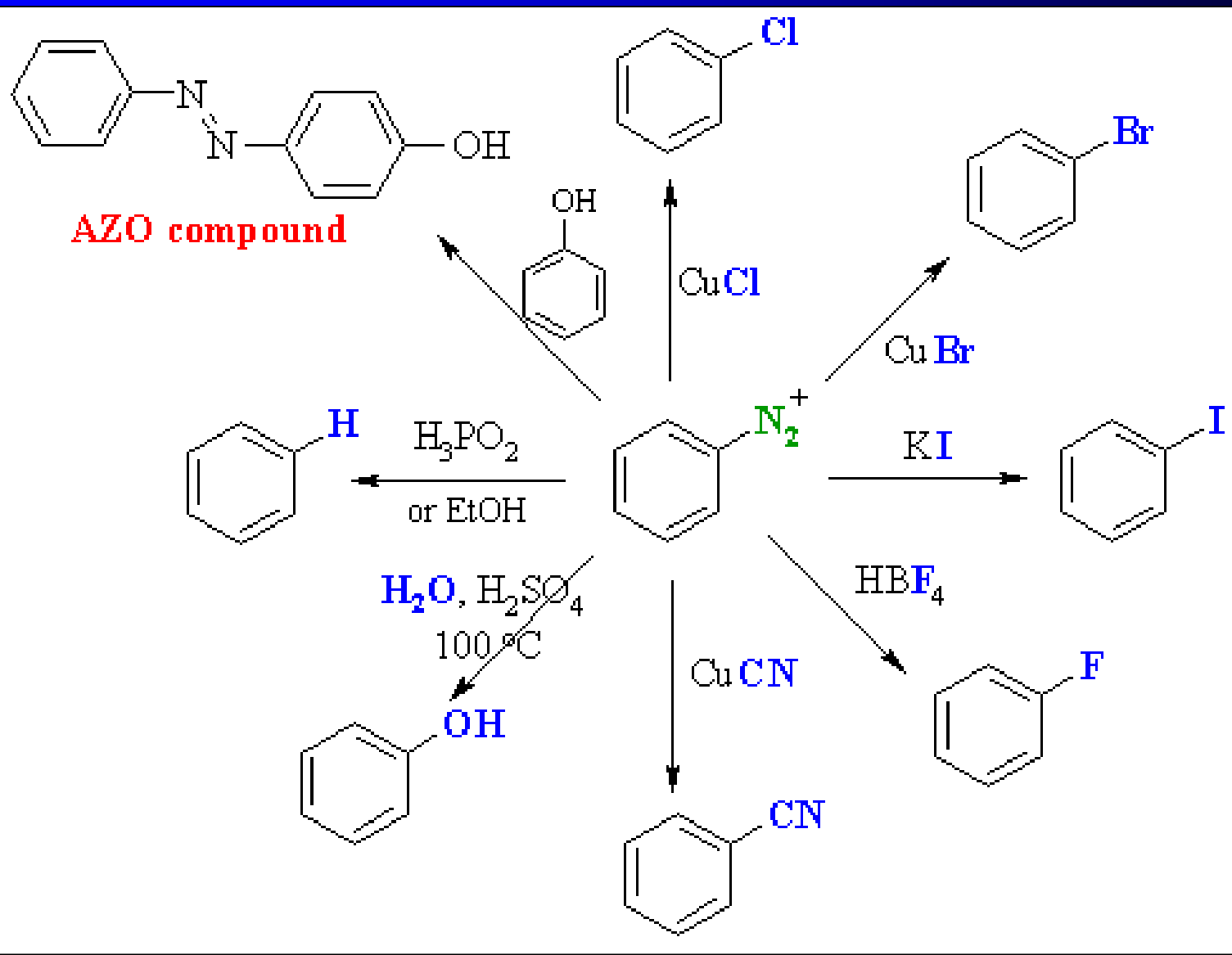
Help!!!

If you play a musical instrument, please see me after class... we need you.

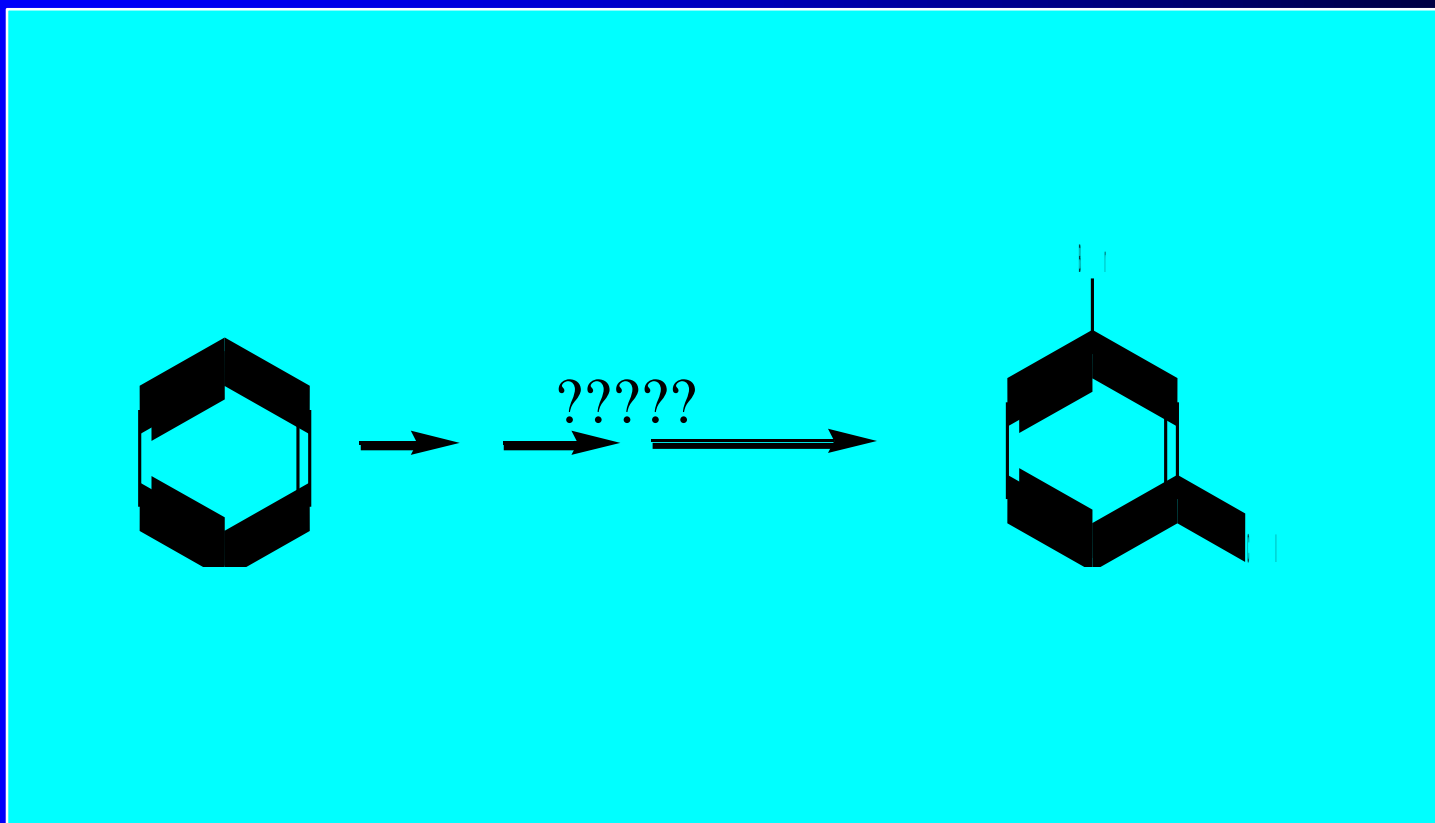
Thanks, GW



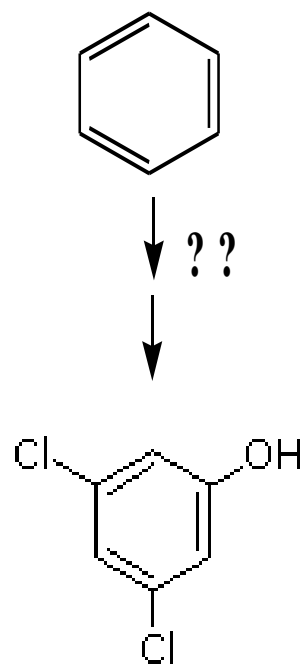
Reactions of Diazonium Salts



Practice...work backwards



Synthesis Strategy



Substitution in Heterocyclic Aromatic Compounds



Generalization

There is none.

There are so many different kinds of heterocyclic aromatic compounds that no generalization is possible.

Some heterocyclic aromatic compounds are very reactive toward electrophilic aromatic substitution, others are very unreactive..



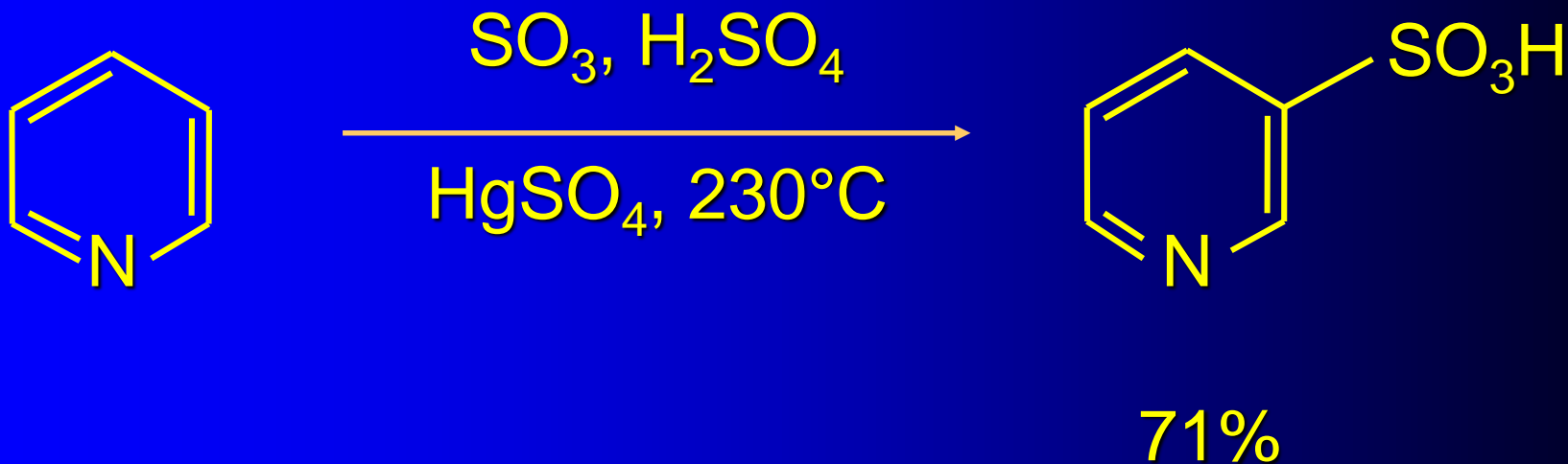
Pyridine



- Pyridine is very unreactive; it resembles nitrobenzene in its reactivity.
- Presence of electronegative atom (N) in ring causes p electrons to be held more strongly than in benzene.



Pyridine

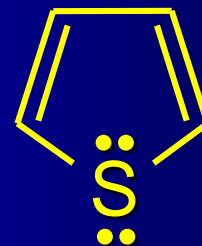
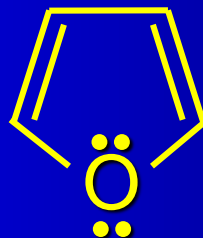
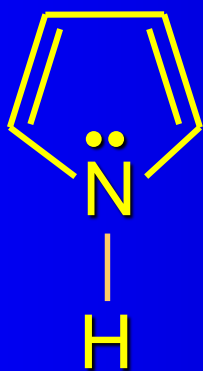


Pyridine can be sulfonated at high temperature.

EAS takes place at C-3.



Pyrrole, Furan, and Thiophene



Have 1 less ring atom than benzene or pyridine to hold same number of p electrons (6).

p electrons are held less strongly.

These compounds are quite reactive toward EAS..



Example: Furan



75-92%

undergoes EAS readily
C-2 is most reactive position



Substitution Reactions

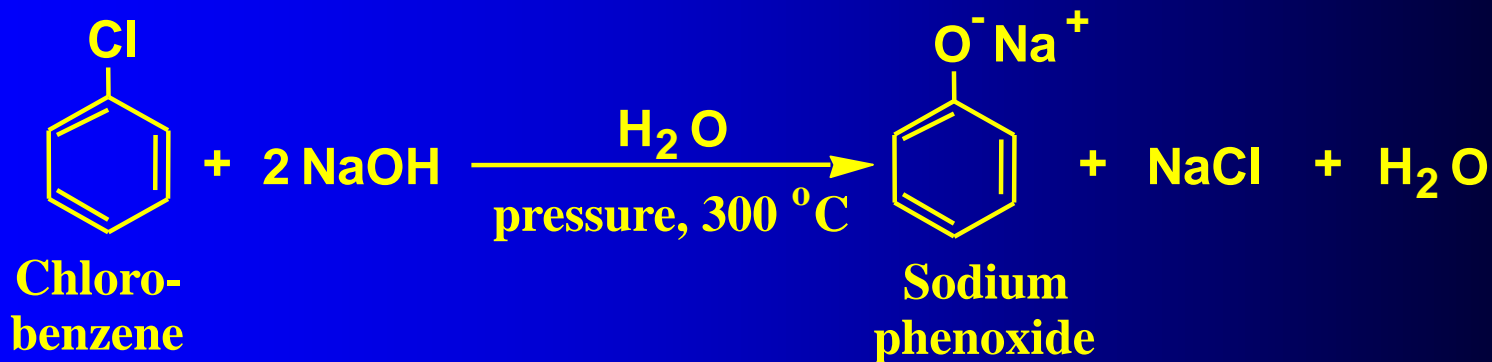
- Aryl halides do not undergo nucleophilic substitution by either S_N1 or S_N2 pathways!

But.....



But....this is fact

- When heated under pressure with aqueous NaOH, chlorobenzene is converted to sodium phenoxide

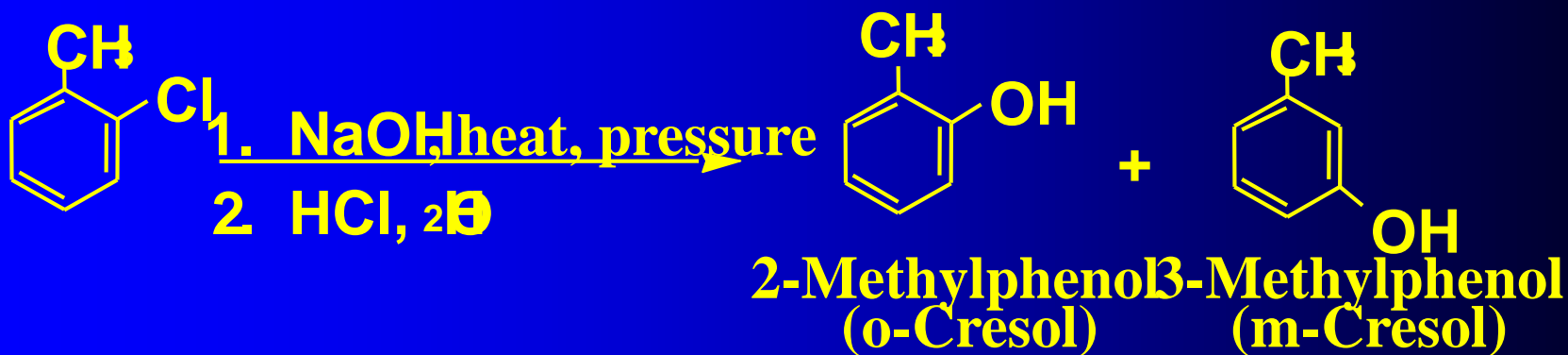


- neutralization with HCl gives phenol????? What is this??



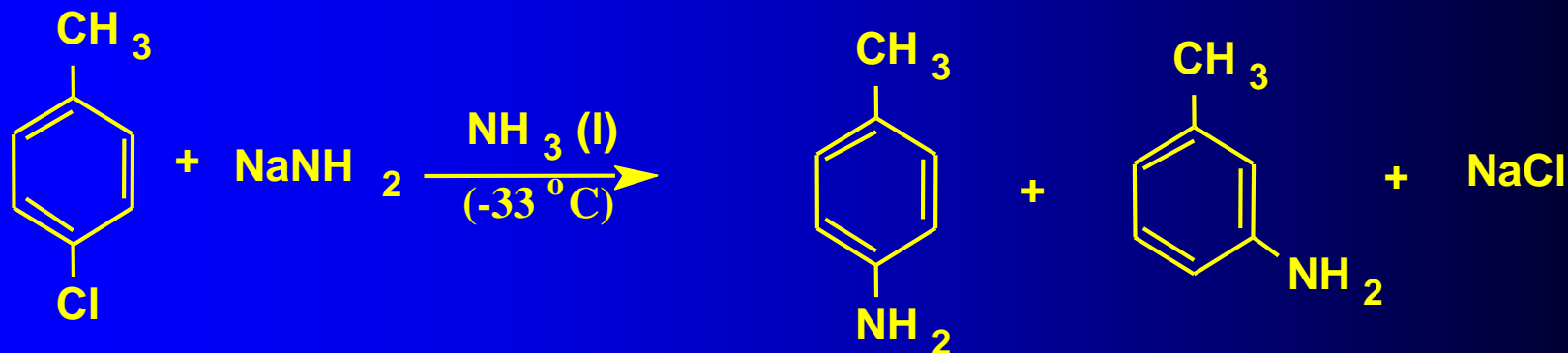
Also fact....

- The same reaction with 2-chlorotoluene gives a mixture of ortho- and meta-cresol???? Ortho and meta....huh????



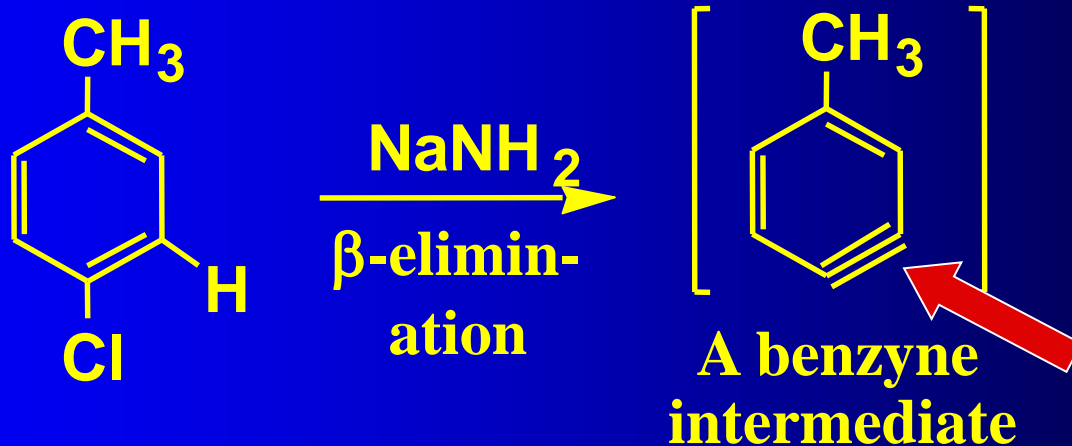
Also true

- The same type of reaction can be brought about by the use of sodium amide in liquid ammonia

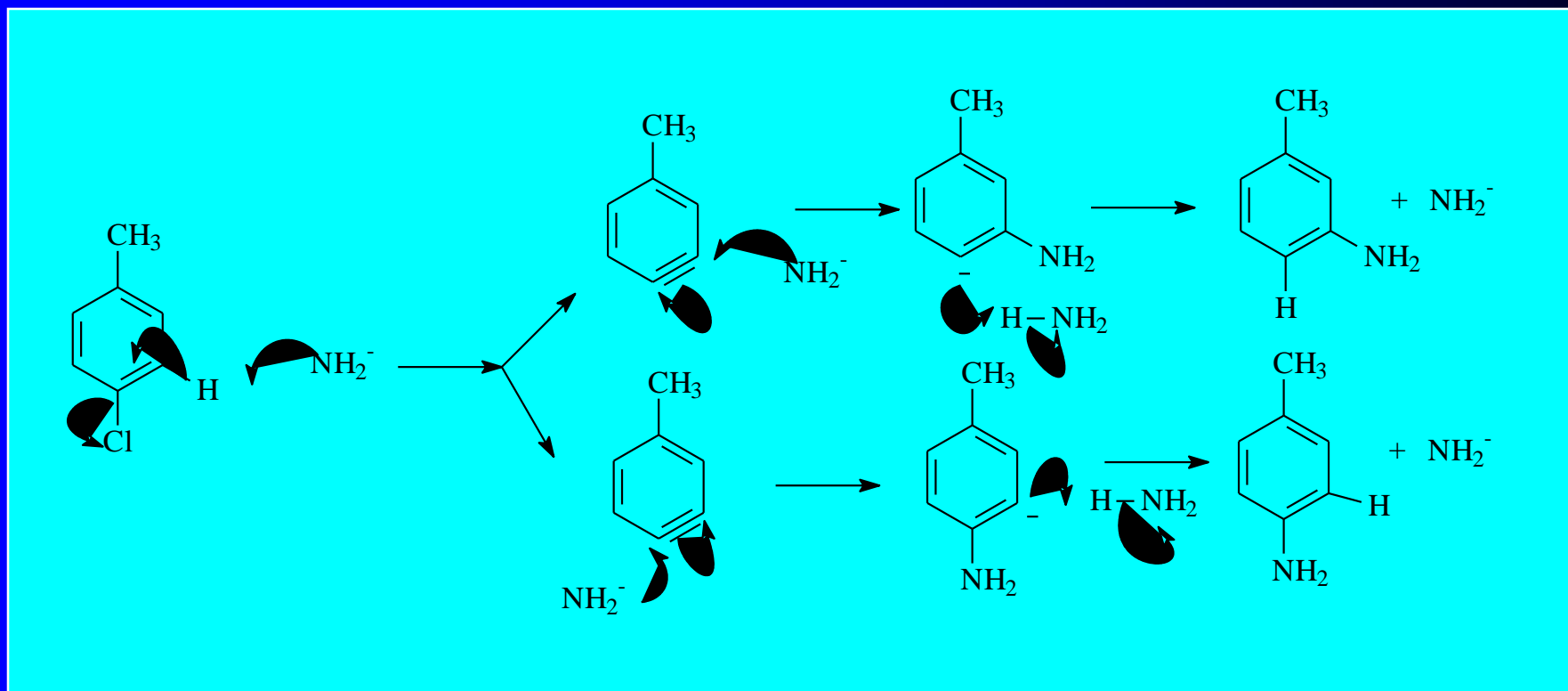


Proposed Benzyne Intermediate

- β -elimination of HX gives a “benzyne” intermediate, that then adds the nucleophile to give products

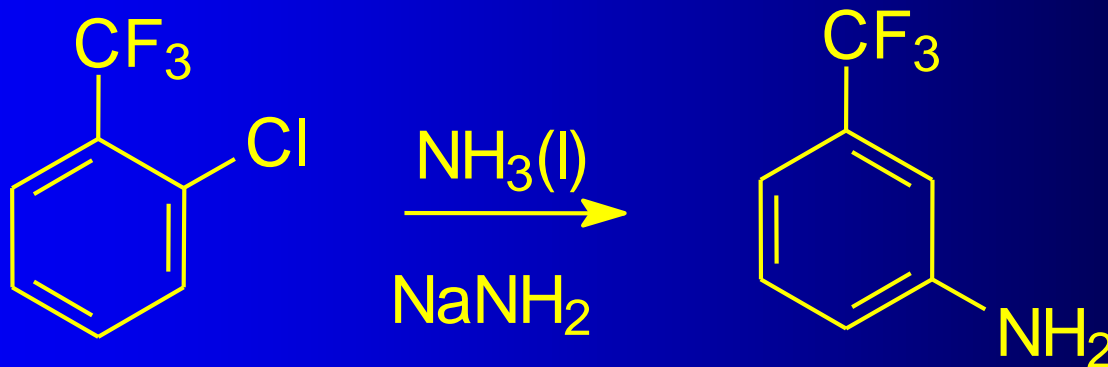


Proposed Benzyne Intermediate



Proposed Benzyne Intermediate

Another Mystery??

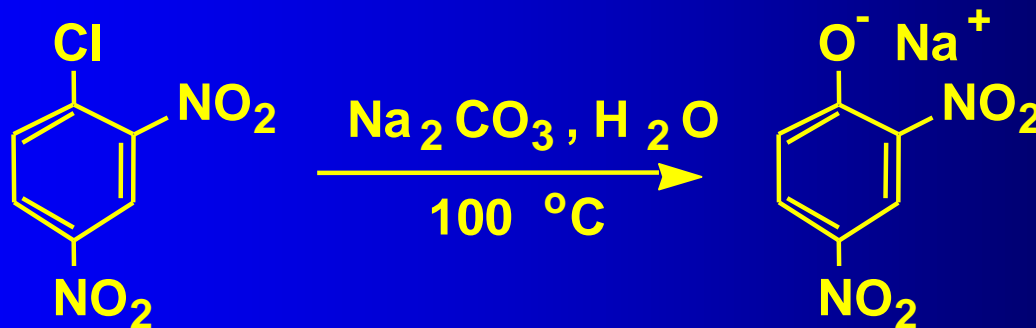


More than 95% of the product is the meta isomer??



Nucleophilic Addition-Elimination

- When an aryl halide contains strongly electron-withdrawing $-\text{NO}_2$ groups ortho and/or para to X, nucleophilic aromatic sub. takes place readily



1-Chloro-2,4- dinitrobenzene

Sodium 2,4-dinitrophenoxide



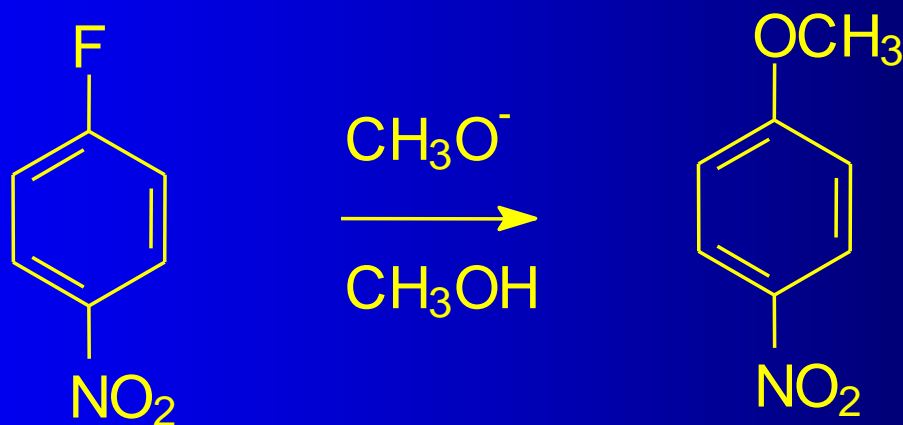
Meisenheimer Complex



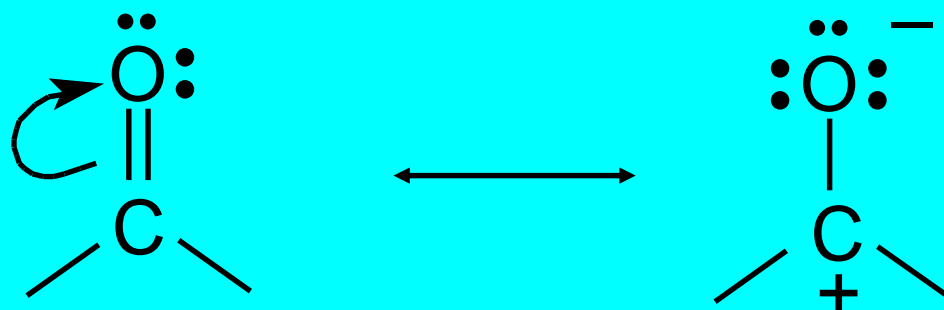
A Meisenheimer complex



Addition Elimination



Resonance Description of Carbonyl Group



nucleophiles attack carbon;

electrophiles attack oxygen

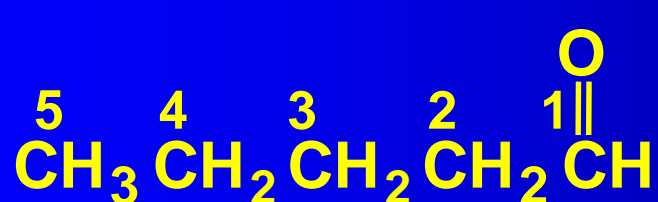


Nomenclature-Aldehydes

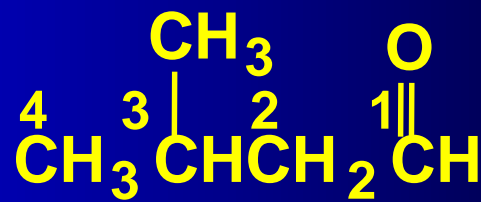
- **IUPAC names:** select as the parent alkane the longest chain of carbon atoms that contains the carbonyl group..**subtract e and add al**
 - because the carbonyl group of the aldehyde must be on carbon 1, there is no need to give it a number
- For unsaturated aldehydes, show the presence of the C=C by changing **-an-** to **-en-**
 - the location of the suffix determines the numbering pattern



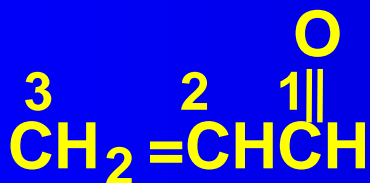
Nomenclature-Aldehydes



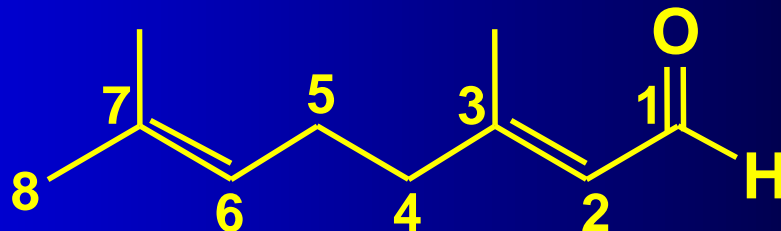
Pentane → Pentanal



3-Methylbutanal



2-Propenal
(Acrolein)



(2E)-3,7-Dimethyl-2,6-octadienal
(Geranial)



Formaldehyde

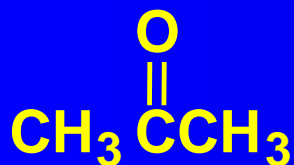
- “Formalin” is an aqueous solution of a mixture of formaldehyde derived species
- Used for embalming and preservation of tissue samples, bugs, etc.
- Widely used in melamine resins for plywood, flooring, etc...
- Naturally occurring at 0.1mm in blood derived from metabolism of amino acids
- Toxicity is an issue and level set at 0.016ppm in air.



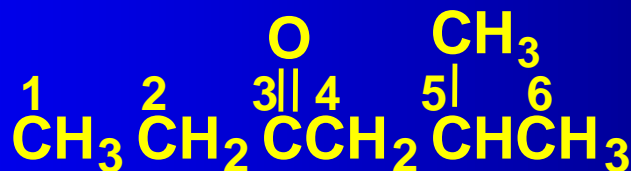
Nomenclature-Ketones

- **IUPAC names:**

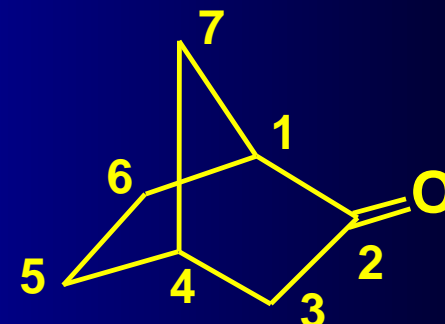
- select as the parent alkane the longest chain that contains the carbonyl group,
- number to give C=O the smaller number and then subtract e and add one



Propanone
(Acetone)



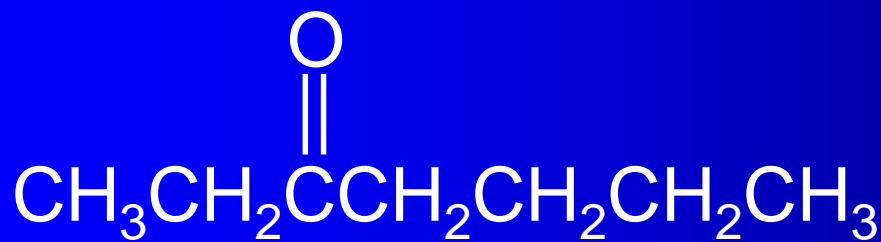
5-Methyl-3-hexanone



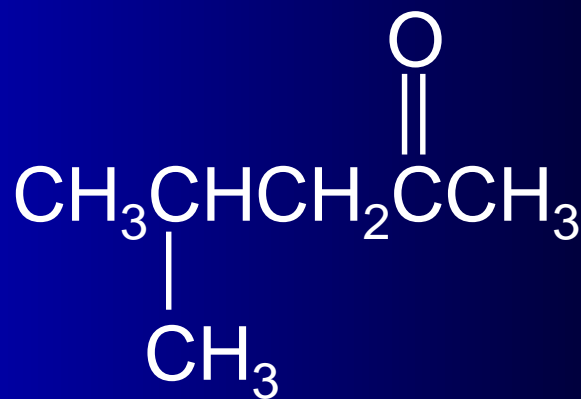
Bicyclo[2.2.1]-2-heptanone



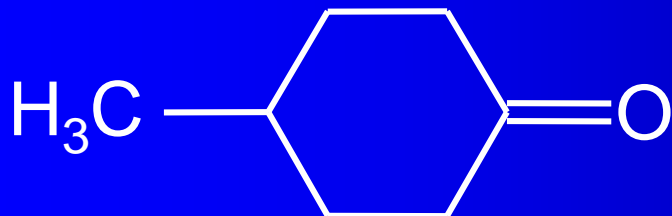
IUPAC Nomenclature of Ketones



3-heptanone



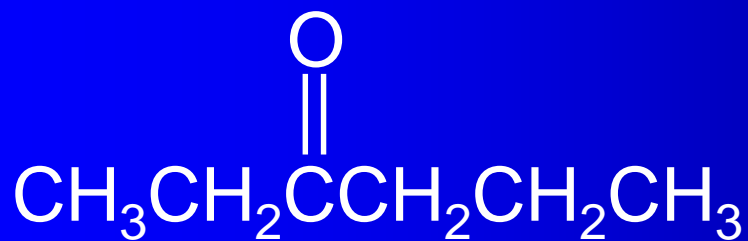
4-methyl-2-pentanone



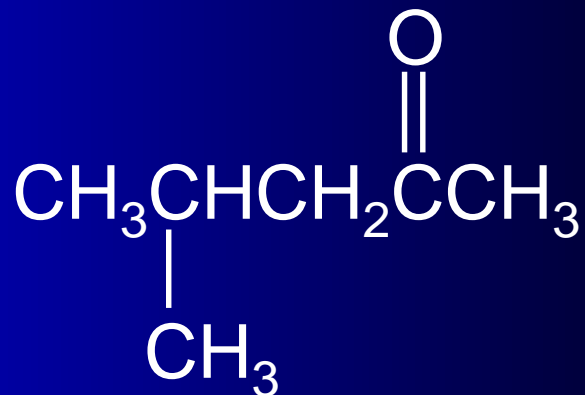
4-methylcyclohexanone



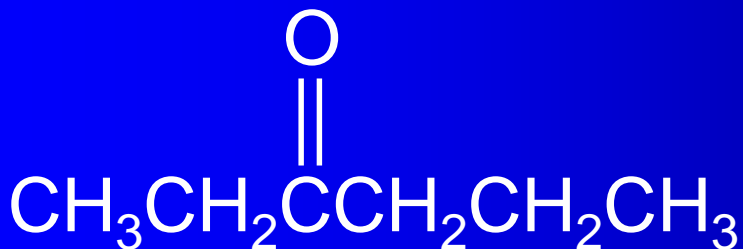
IUPAC Nomenclature of Ketones



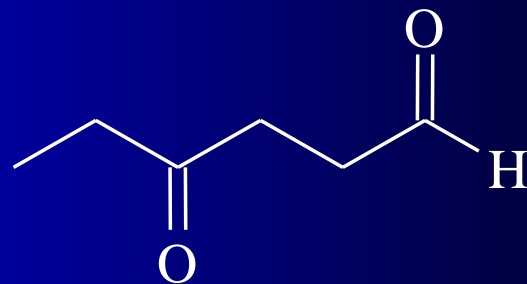
3-hexanone



4-methyl-2-pentanone



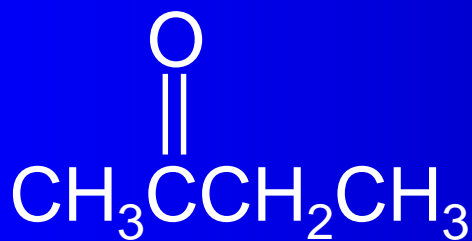
ethyl propyl ketone (trivial)



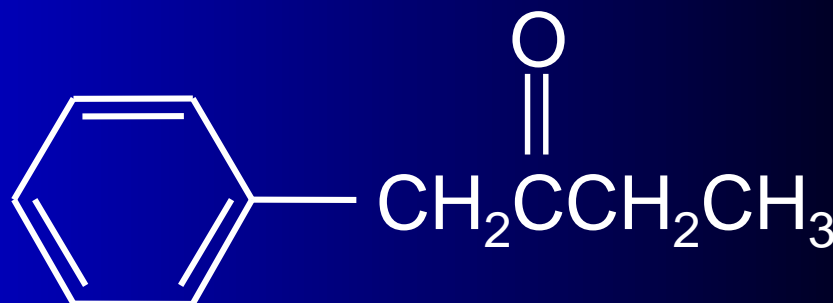
4-oxohexanal



Trivial Nomenclature of Ketones



Methyl ethyl ketone



benzyl ethyl ketone



divinyl ketone



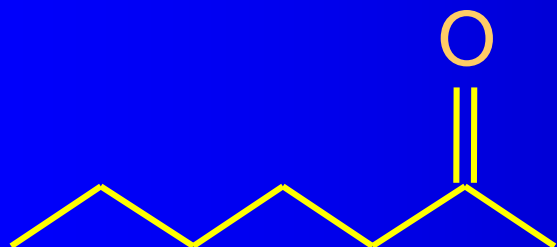
Order of Precedence (Pecking order)

- For compounds that contain more than one functional group indicated by a suffix

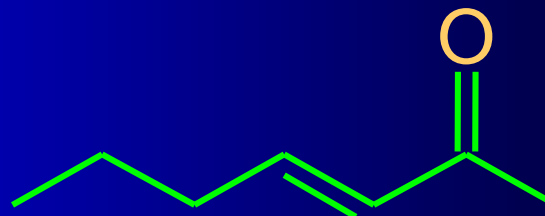
	Functional Group	Suffix if Higher in Precedence	Prefix if Lower in Precedence
↑ Precedence	$-\text{CO}_2\text{H}$	-oic acid	_____
	$-\text{CHO}$	-al	oxo-
	>C=O	-one	oxo-
	$-\text{OH}$	-ol	hydroxy-
	$-\text{NH}_2$	-amine	amino-
	$-\text{SH}$	-thiol	mercapto-



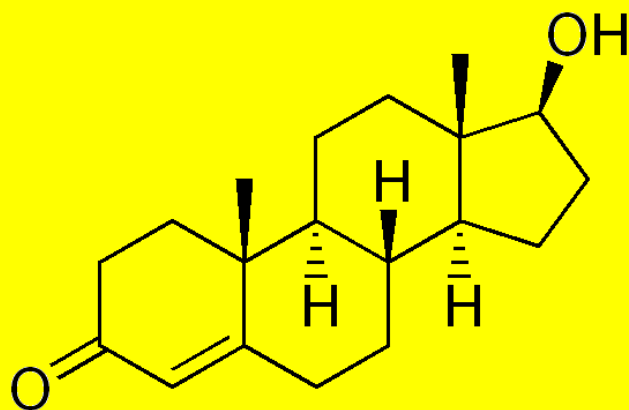
Many aldehydes and ketones occur naturally



2-heptanone
(component of alarm
pheromone of bees)

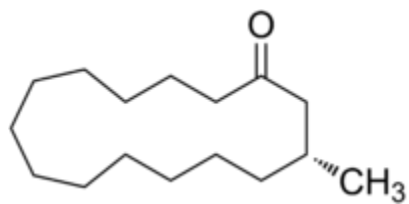


trans-2-hexenal
(alarm pheromone
of myrmicine ant)

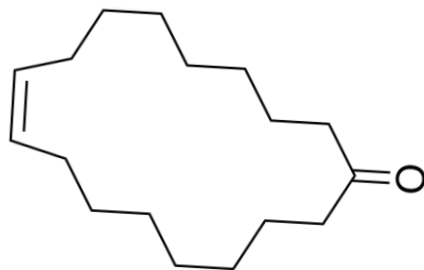


Testosterone

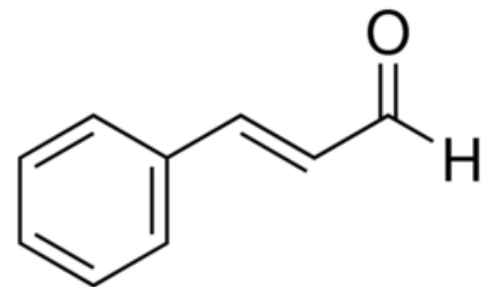




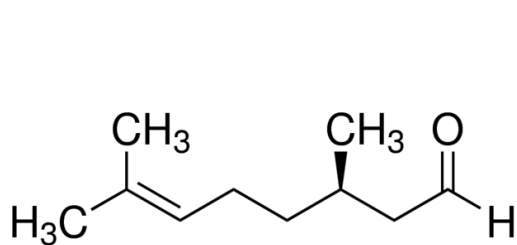
Muscone



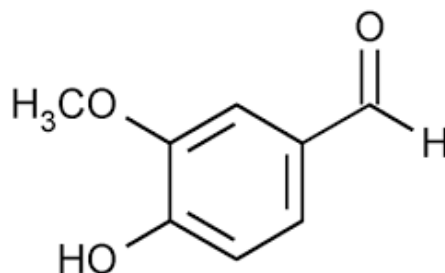
Civitone



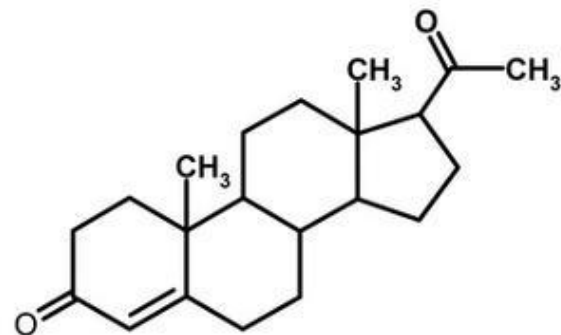
Cinnamaldehyde



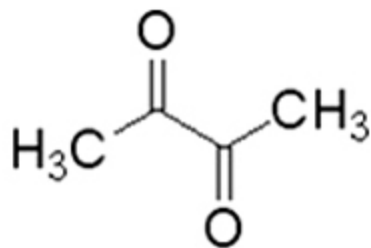
Citronellal



Vanillin



Progesterone



Diacetyl



Synthesis of Aldehydes and Ketones

A number of reactions already studied provide efficient synthetic routes to aldehydes and ketones.

- from alkenes
 - by ozonolysis (p252)
- from alkynes
 - by hydration (via enol)
- from arenes
 - via Friedel-Crafts acylation



Stock room inventory

