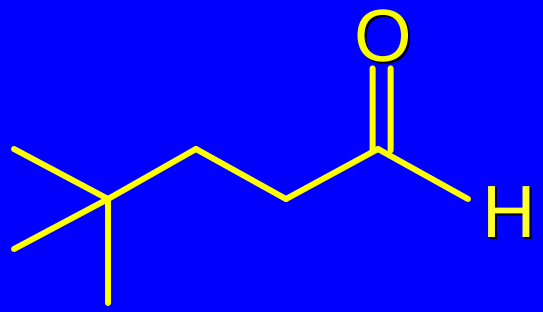
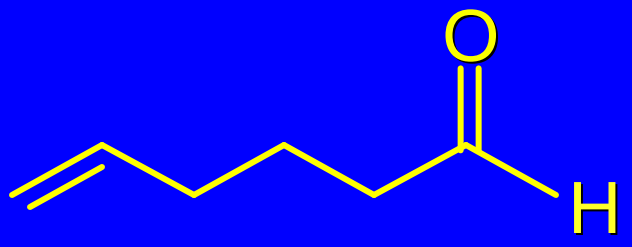
Chapter 17
Aldehydes and Ketones

17.1
Nomenclature

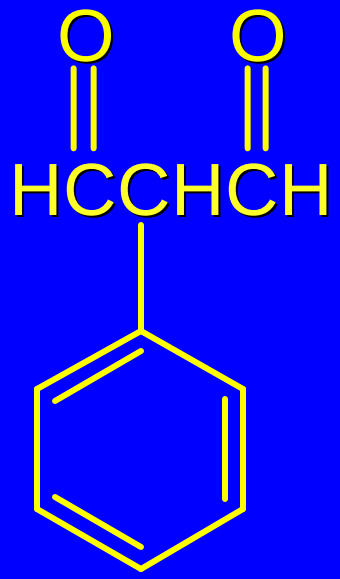
Nomenclature of Aldehydes



4,4-dimethylpentanal

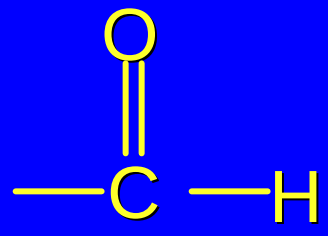


5-hexenal



2-phenylpropanedial

Nomenclature of Aldehydes



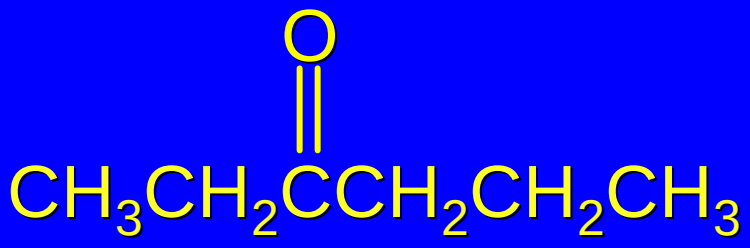
when named as a substituent

formyl group

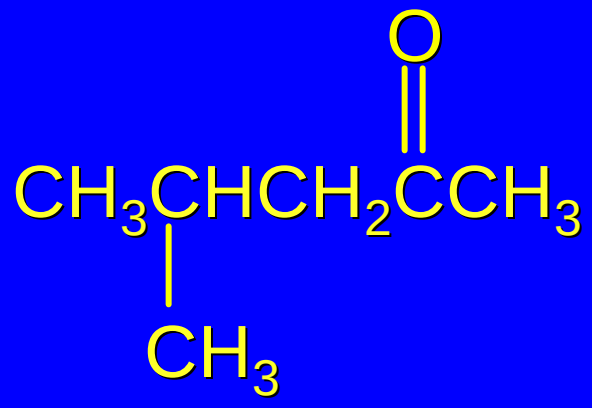
when named as a suffix

carbaldehyde
carboxaldehyde

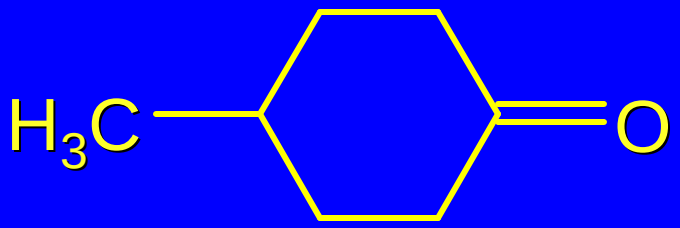
Substitutive Nomenclature of Ketones



3-hexanone

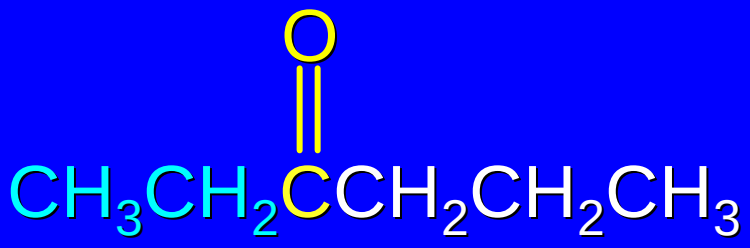


4-methyl-2-pentanone

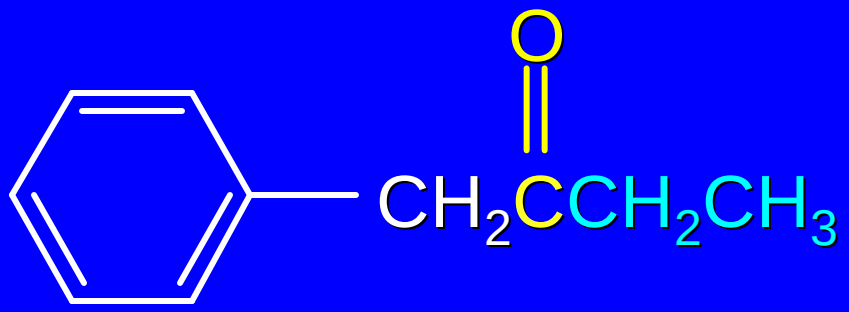


4-methylcyclohexanone

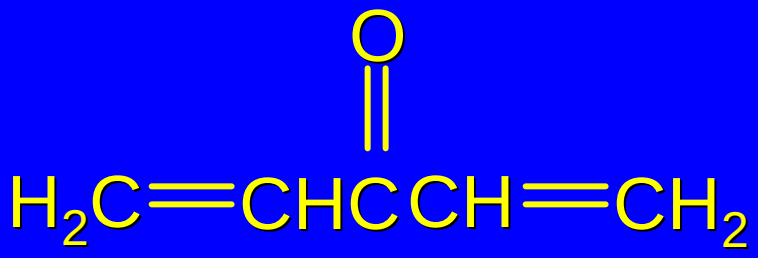
Functional Class Nomenclature of Ketones



ethyl propyl ketone



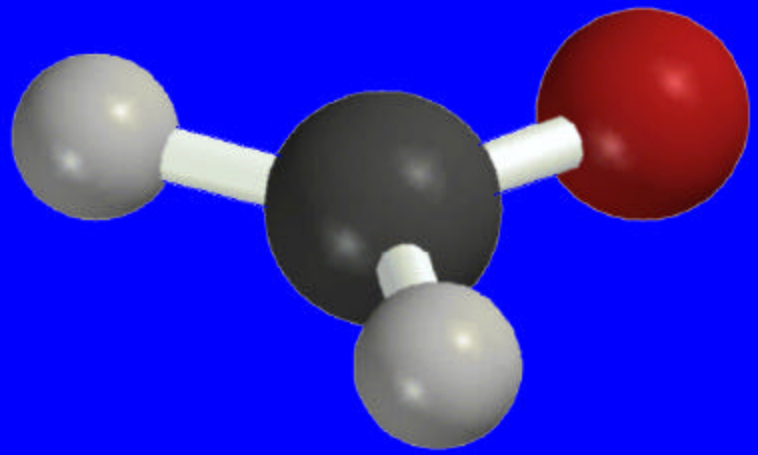
benzyl ethyl ketone



divinyl ketone

17.2
Structure and Bonding: The Carbonyl Group

Structure of Formaldehyde



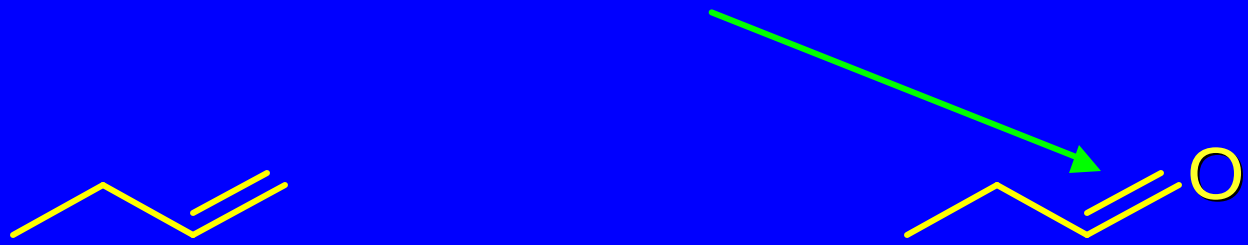
planar

bond angles: close to 120°

C=O bond distance: 122 pm

The Carbonyl Group

very polar double bond



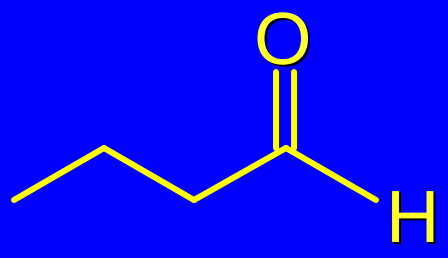
1-butene

propanal

dipole moment = 0.3D

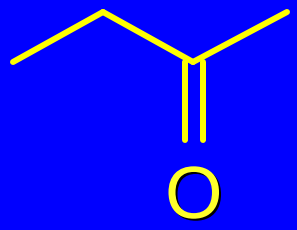
dipole moment = 2.5D

Carbonyl group of a ketone is more stable than that of an aldehyde



heat of combustion

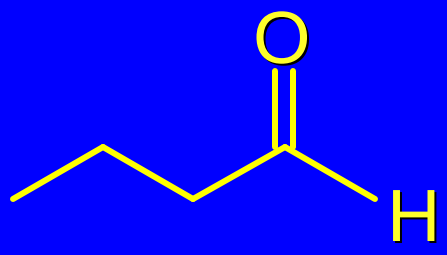
2475 kJ/mol



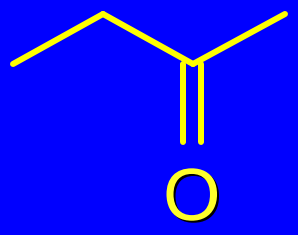
2442 kJ/mol

Alkyl groups stabilize carbonyl groups the same way they stabilize carbon-carbon double bonds, carbocations, and free radicals.

Spread is greater for aldehydes and ketones than for alkenes



2475 kJ/mol



2442 kJ/mol

Heats of combustion of C_4H_8 isomeric alkenes

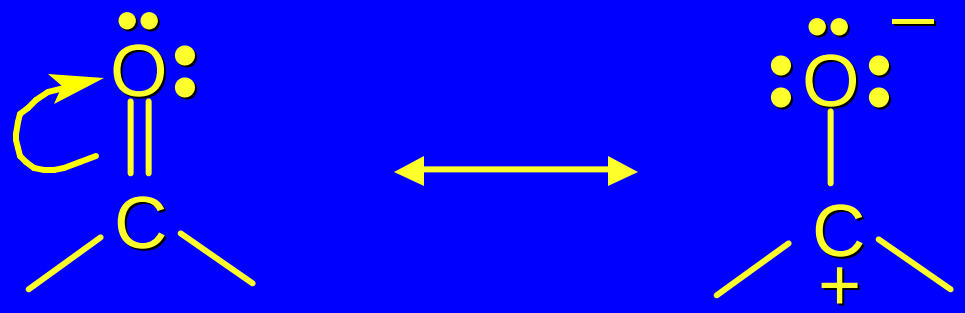
$CH_3CH_2CH=CH_2$
2717 kJ/mol

cis-$CH_3CH=CHCH_3$
2710 kJ/mol

trans-$CH_3CH=CHCH_3$
2707 kJ/mol

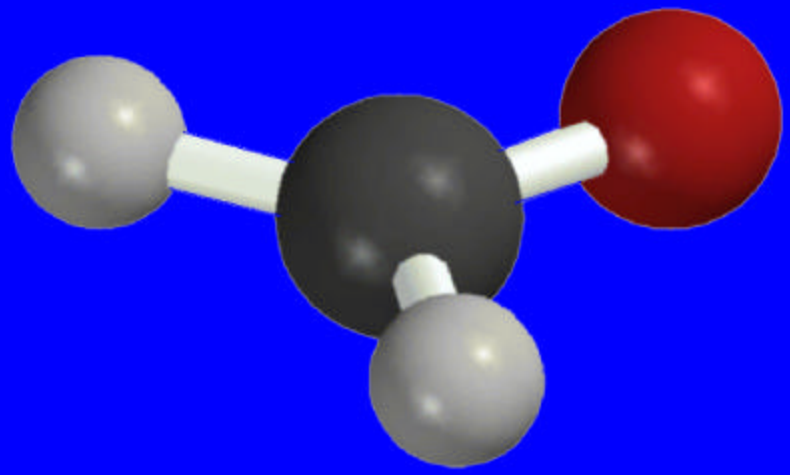
$(CH_3)_2C=CH_2$
2700 kJ/mol

Resonance Description of Carbonyl Group



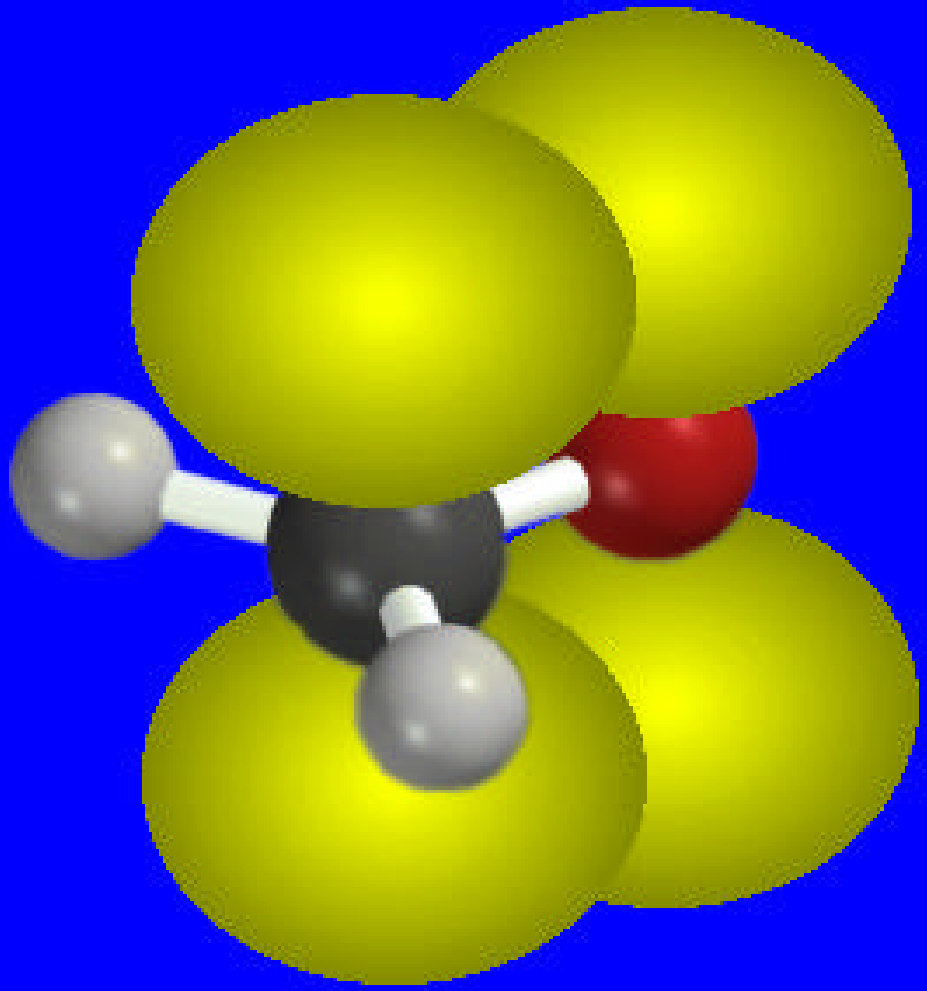
nucleophiles attack carbon;
electrophiles attack oxygen

Bonding in Formaldehyde



Carbon and oxygen are sp^2 hybridized

Bonding in Formaldehyde

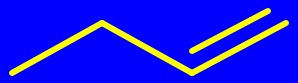


The half-filled *p* orbitals on carbon and oxygen overlap to form a π bond

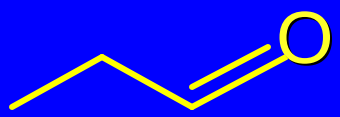
17.3
Physical Properties

Aldehydes and ketones have higher boiling than alkenes, but lower boiling points than alcohols.

boiling point



–6°C



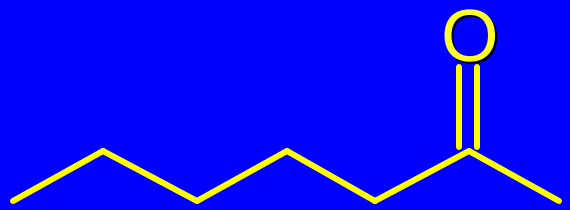
49°C

97°C

More polar than alkenes, but cannot form intermolecular hydrogen bonds to other carbonyl groups

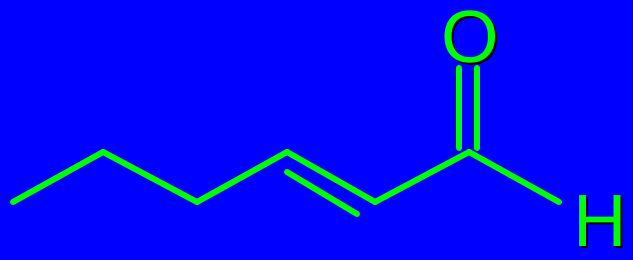
17.4
Sources of Aldehydes and Ketones

Many aldehydes and ketones occur naturally



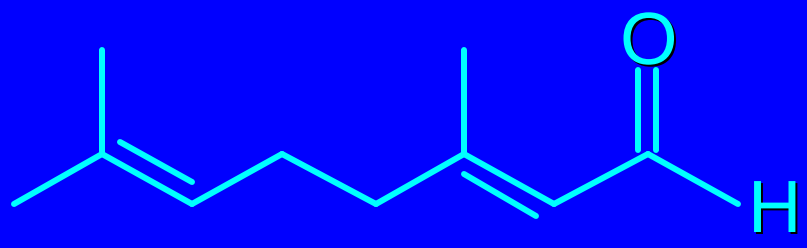
2-heptanone
(component of alarm pheromone of bees)

Many aldehydes and ketones occur naturally



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

Many aldehydes and ketones occur naturally



citral (from lemon grass oil)

Synthesis of Aldehydes and Ketones

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

from alkenes

ozonolysis

from alkynes

hydration (via enol)

from arenes

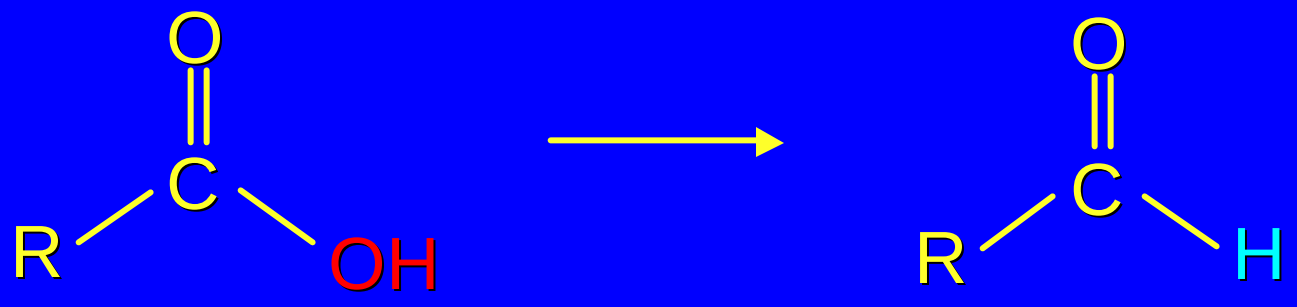
Friedel-Crafts acylation

from alcohols

oxidation

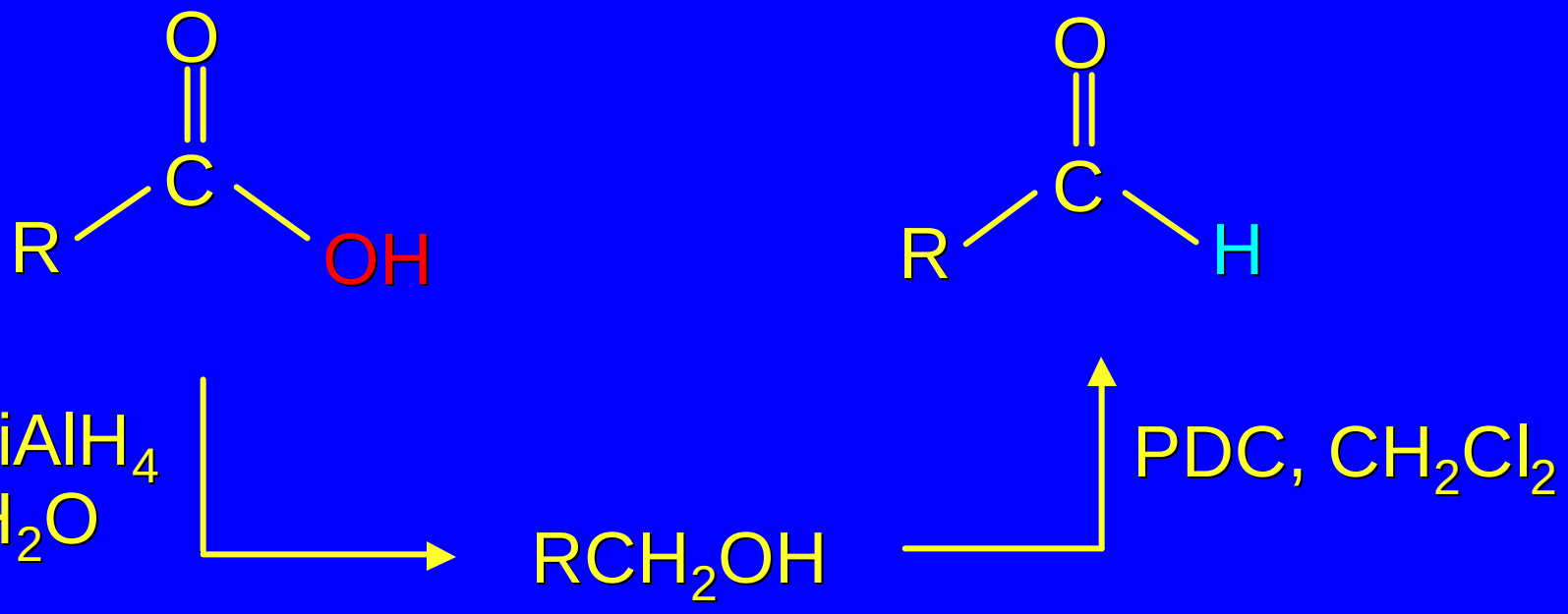
What about..?

aldehydes from carboxylic acids



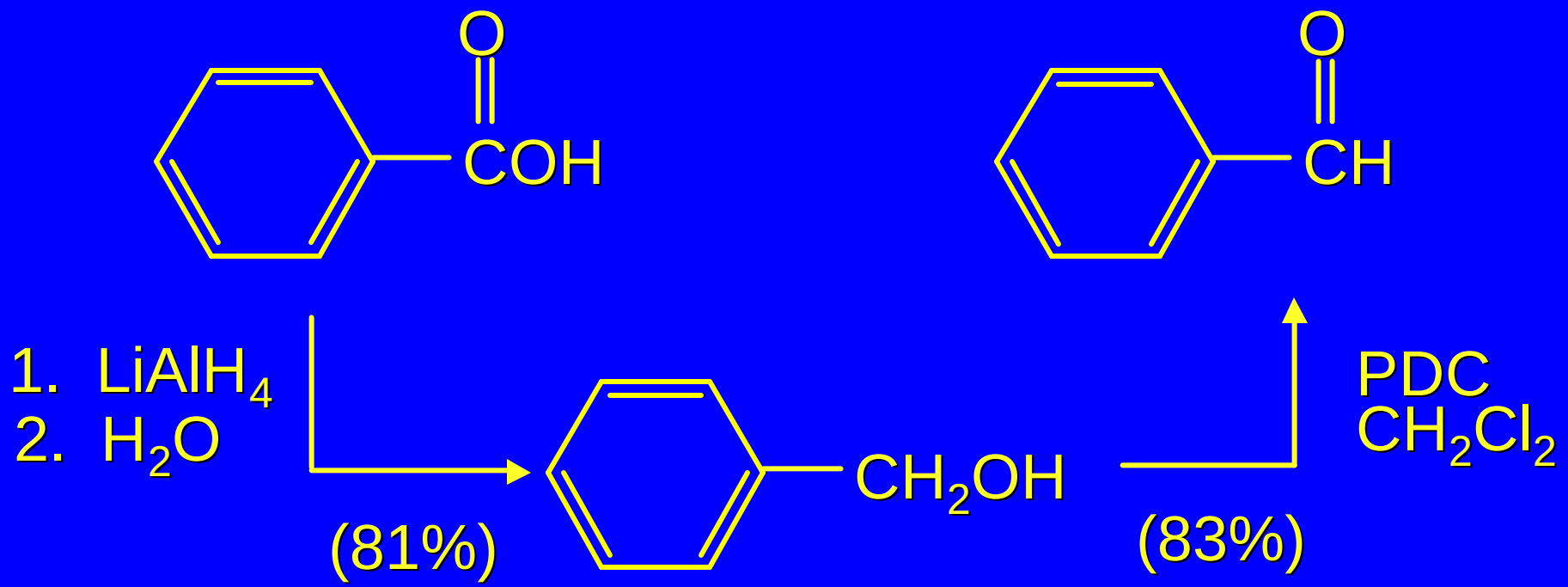
What about..?

aldehydes from carboxylic acids



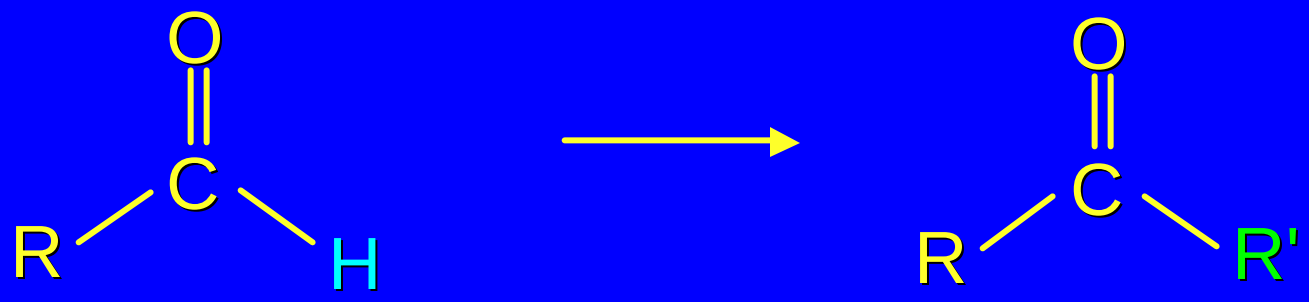
Example

benzaldehyde from benzoic acid



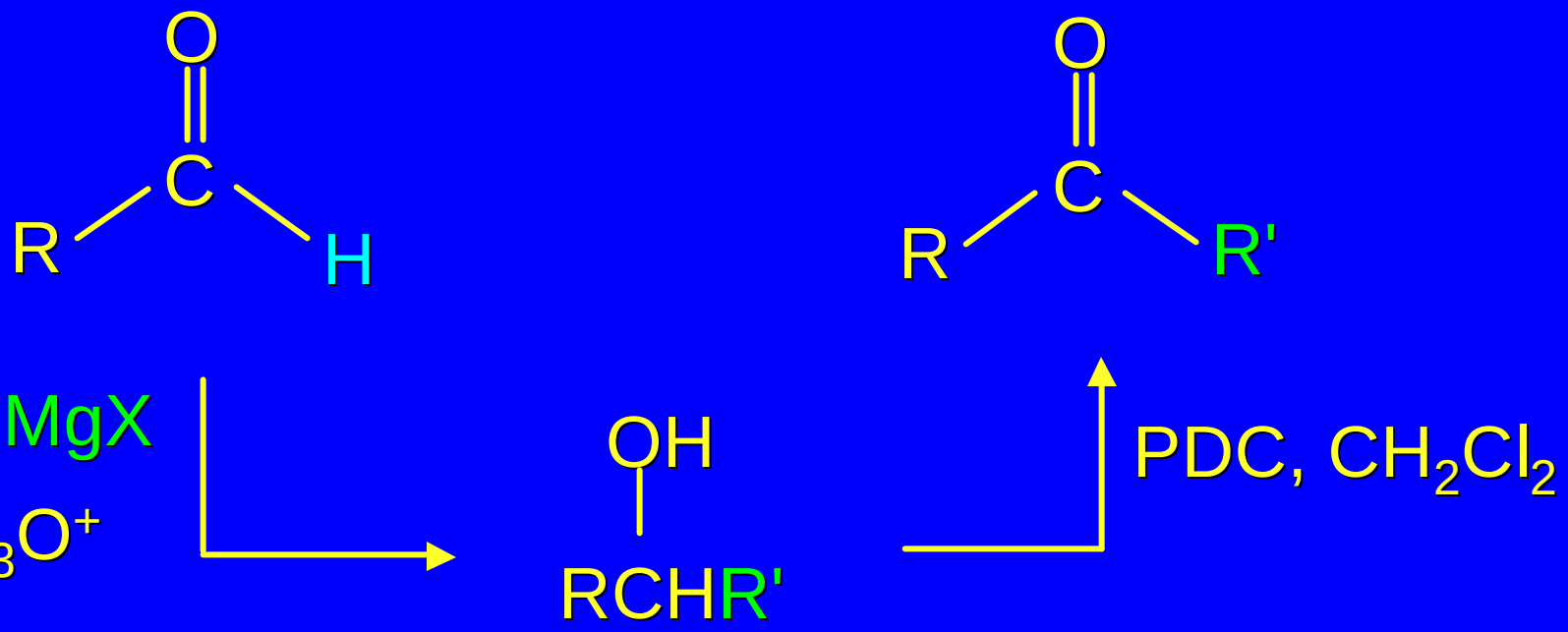
What about..?

ketones from aldehydes



What about..?

ketones from aldehydes



Example

3-heptanone from propanal