CHAPTER 9 ALDEHYDES AND KETONES

9.1 Nomenclature of Aldehydes and Ketones

→ Aldehydes are named by replacing the -e of the corresponding parent alkane with -al

- P The aldehyde functional group is always carbon 1 and need not be numbered
- Some of the common names of aldehydes are shown in parenthesis



- → Aldehyde functional groups bonded to a ring are named using the suffix carbaldehyde
 - P Benzaldehyde is used more commonly than the name benzenecarbaldehyde







Benzenecarbaldehyde (benzaldehyde)

Cyclohexanecarbaldehyde

2-Naphthalenecarbaldehyde

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- → Ketones are named by replacing the -e of the corresponding parent alkane with -one
 - P The parent chain is numbered to give the ketone carbonyl the lowest possible number
 - In common nomenclature simple ketones are named by preceding the word ketone with the names of both groups attached to the ketone carbonyl

Butanone (ethyl methyl ketone)

2-Pentanone (methyl propyl ketone)

Pent-4-en-2-one (*not* 1-penten-4-one) (allyl methyl ketone)

Common names of ketones that are also IUPAC names are shown below

Ö CH₃CCH₃

Acetone (propanone)

Ο CCH₂

Acetophenone (1-phenylethanone or methyl phenyl ketone)



Benzophenone (diphenylmethanone or diphenyl ketone)

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Synthesis of Aldehydes

Aldehydes by Oxidation of 1° Alcohols
 Primary alcohols are oxidized to aldehydes by PCC



Synthesis of Ketones

• Ketones from Alkenes, Arenes, and 2° Alcohols

→ Ketones can be made from alkenes by ozonolysis



→ Aromatic ketones can be made by Friedel-Crafts Acylation



→ Ketones can be made from 2° alcohols by oxidation



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• Ketones from Alkynes

→ Markovnikov hydration of an alkyne initially yields a vinyl alcohol (enol) which then rearranges rapidly to a ketone (keto)



➔ Terminal alkynes yield ketones because of the Markovnikov regioselectivity of the hydration

- P Ethyne yields acetaldehyde
- P Internal alkynes give mixtures of ketones unless they are symmetrical

$$CH_{3}C \equiv CH + H_{2}O \xrightarrow{Hg^{2+}} \begin{bmatrix} CH_{3} \\ C = CH_{2} \end{bmatrix} \xrightarrow{CH_{3}} C = CH_{3}$$

Acetone

$$CH_{3}CH_{2}CH_{2}CH_{2}C \equiv CH + H_{2}O \xrightarrow[H_{2}SO_{4}]{H_{2}SO_{4}} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3}$$

$$O$$
(80%)



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9.4 Aldehydes and Ketones in Nature



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9.5 the Carbonyl Group



Molecules of aldehyde (or ketone) cannot hydrogen bond to each other

P They rely only on intermolecular dipole-dipole interactions and therefore have lower boiling points than the corresponding alcohols



Aldehydes and ketones can form hydrogen bonds with water and therefore low molecular weight aldehydes and ketones have appreciable water solubility

Formula	Name	mp (°C)	bp (°C)	Solubility in Water
НСНО	Formaldehyde	-92	-21	Very soluble
CH₃CHO	Acetaldehyde	-125	21	∞
CH₃CH₂CHO	Propanal	-81	49	Very soluble
CH ₃ (CH ₂) ₂ CHO	Butanal	-99	76	Soluble
CH ₃ (CH ₂) ₃ CHO	Pentanal	-91.5	102	Slightly soluble
CH ₃ (CH ₂) ₄ CHO	Hexanal	-51	131	Slightly soluble
C ₆ H ₅ CHO	Benzaldehyde	-26	178	Slightly soluble
C ₆ H ₅ CH ₂ CHO	Phenylacetaldehyde	33	193	Slightly soluble
CH ₃ COCH ₃	Acetone	-95	56.1	∞
CH ₃ COCH ₂ CH ₃	Butanone	-86	79.6	Very soluble
CH ₃ COCH ₂ CH ₂ CH ₃	2-Pentanone	-78	102	Soluble
CH ₃ CH ₂ COCH ₂ CH ₃	3-Pentanone	-39	102	Soluble
$C_6H_5COCH_3$	Acetophenone	21	202	Insoluble
$C_6H_5COC_6H_5$	Benzophenone	48	306	Insoluble

9.6 Nucleophilic Addition to the Carbonyl Groups

→ Addition of a nucleophile to a carbonyl carbon occurs because of the δ + charge at the carbon

General Reaction





(R or R' may be H)

The nucleophile may attack from above or below.

- Addition of strong nucleophiles result in formation of a tetrahedral alkoxide intermediate
 - \mathcal{P} The carbonyl π electrons shift to oxygen to give the alkoxide
 - P The carbonyl carbon changes from trigonal planar to tetrahedral



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→ An acid catalyst is used to facilitate reaction of weak nucleophiles with carbonyl groups

Protonating the carbonyl oxygen enhances the electrophilicity of the carbon

Step 1



acid)

In this step an electron pair of the carbonyl oxygen accepts a proton from the acid (or associates with a Lewis acid), producing an oxonium cation. The carbon of the oxonium cation is more susceptible to nucleophilic attack than the carbonyl of the starting ketone.

Step 2



In the first of these two steps, the oxonium cation accepts the electron pair of the nucleophile. In the second step, a base removes a proton from the positively charged atom, regenerating the acid.

9.7 The Addition of Alcohols: Hemiacetals and Acetals

- Hemiacetals
 - → An aldehyde or ketone dissolved in an alcohol will form an equilibrium mixture containing the corresponding hemiacetal
 - A hemiacetal has a hydroxyl and alkoxyl group on the same carbon
 - Acylic hemiacetals are generally not stable, however, cyclic five- and sixmembered ring hemiacetals are



Cylic hemiacetals









(R" may be H) **Protonation of the** aldehyde or ketone oxygen atom makes the carbonyl carbon more susceptible to nucleophilic attack. [The protonated alcohol results from reaction of the alcohol (present in excess) with the acid catalyst, e.g., HCl.]

An alcohol molecule adds to the carbon of the oxonium cation.



The transfer of a proton from the positive oxygen to another molecule of the alcohol leads to the hemiacetal.

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(R" may be H) An alkoxide anion acting as a nucleophile attacks the carbonyl carbon atom. An electron pair shifts onto the oxygen atom, producing a new alkoxide anion. The alkoxide anion abstracts a proton from an alcohol molecule to produce the hemiacetal and regenerates an alkoxide anion.



→ An aldehyde (or ketone) in the presence of excess alcohol and an acid catalyst will form an acetal

P Formation of the acetal proceeds via the corresponding hemiacetal

An acetal has two alkoxyl groups bonded to the same carbon





Attack on the carbon of the oxonium ion by a second molecule of the alcohol, followed by removal of a proton, leads to the acetal.

Acetals are stable when isolated and purified

→Acetal formation is reversible

An excess of water in the presence of an acid catalyst will hydrolyze an acetal to the corresponding aldehyde (or ketone)



Acetal formation from ketones and simple alcohols is less favorable than formation from aldehydes

- Formation of cyclic 5- and 6- membered ring acetals from ketones is, however, favorable
- Such cyclic acetals are often used as protecting groups for aldehydes and ketones
- P These protecting groups can be removed using dilute aqueous acid



Deprotection



- Acetals as Protecting Groups
 - → Acetal protecting groups are stable to most reagents except aqueous acid
 - Example: An ester can be reduced in the presence of a ketone protected as an acetal



9.8 Dissolving aldehydes (or ketones) in water causes formation of an equilibrium between the carbonyl compound and its hydrate

- The hydrate is also called a *gem*-diol (*gem i.e.* geminal, indicates the presence of two identical substituents on the same carbon)
- The equilibrum favors a ketone over its hydrate because the tetrahedral ketone hydrate is sterically crowded





the negative oxygen atom.