SLE155 Chemistry for the Professional Sciences

Burwood and Geelong

DEAKIN COLLEGE

Class 9

Amines
Reactions of Amines
Aldehydes and Ketones

References

Blackman A, Bottle S, Schmid G, Mocerino M and Wille U (2019a), *Chemistry*, 4th edn, John Wiley & Sons, Milton, Qld.

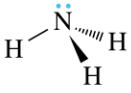
Blackman A, Southam D, Lawrie G, Williamson N, Thompson C and Bridgeman A (2019b), *Chemistry: core concepts*, 2nd edn, John Wiley & Sons, Milton, Qld.

DEAKIN COLLEGE

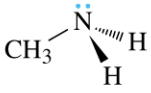
Amines

Amines are derivatives of NH_3

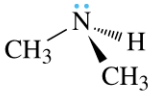
Amines are classified as 1°, 2° or 3° based on the number of alkyl groups replacing hydrogen atoms of ammonia, NH_3, i.e., the number of C atoms bonded to the N atom.



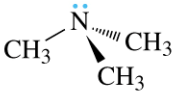
ammonia



methylamine
(a 1° amine)



dimethylamine
(a 2° amine)



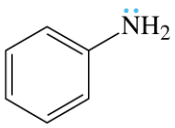
trimethylamine
(a 3° amine)

Source: Blackman et al. (2019:929).

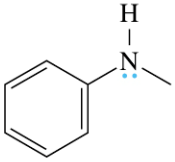
Amines

Amines are further divided into aliphatic, aromatic and heterocyclic

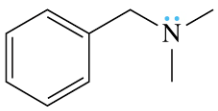
- **An aliphatic amine is an amine in which nitrogen is bonded only to alkyl groups**
- **An aromatic amine is an amine in which nitrogen is bonded to aryl groups**



aniline
(a 1° aromatic amine)



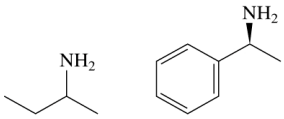
N-methylaniline
(a 2° aromatic amine)



benzyldimethylamine
(a 3° aliphatic amine)

Amines

Aliphatic amines have the suffix –e of the parent alkane replaced by –amine.



butan-2-amine

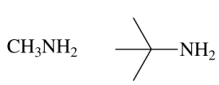
(*S*)-1-phenylethanamine

$H_2N(CH_2)_6NH_2$

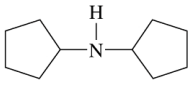
hexane-1,6-diamine

Source: Blackman et al. (2019:929).

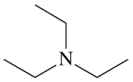
Common names list the alkyl groups bonded to nitrogen in alphabetical order ending in the suffix –amine.



methylamine *tert*-butylamine



dicyclopentylamine



triethylamine

Naming Amines

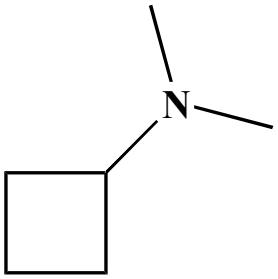
1. Name the Parent Chain

2. Add the Suffix
longest carbon chain followed by 'amine'

3. Add the Prefix
name the substituents

4. Include the Locant
numbers for substituents on carbon
'N' for substituents on nitrogen

Naming Amines



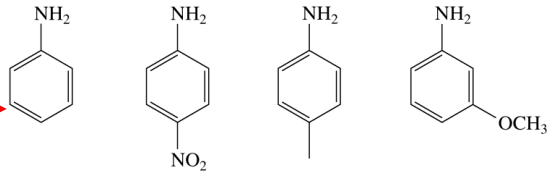
N,N-dimethylcyclobutanamine

N,N-dimethylcyclobutylamine

Amines

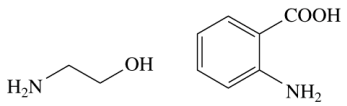
IUPAC nomenclature retains the common name aniline.

Remember this structure!



aniline | 4-nitroaniline (*p*-nitroaniline) | 4-methylaniline (*p*-toluidine) | 3-methoxyaniline (*m*-anisidine)

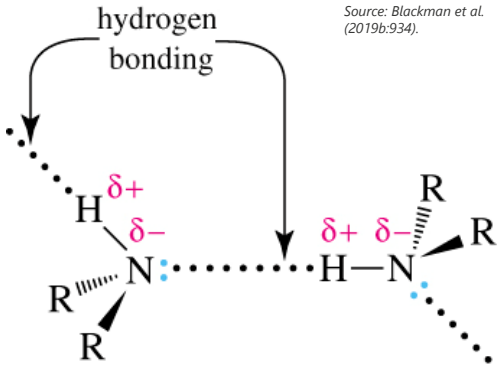
The functional group -NH_2 has one of the lowest priorities.



2-aminoethanol (ethanolamine) | 2-aminobenzoic acid (anthranilic acid)

Amines

Amines are polar compounds and both 1° and 2° amines form intermolecular hydrogen bonds.



Source: Blackman et al. (2019b:934).

Amines

N-H- - - -N hydrogen bonds are weaker than O-H- - - -O hydrogen bonds because the difference in electronegativity between N and H is less than that between O and H.

Source: Blackman et al. (2019b:934).

	CH_3NH_2	CH_3OH
number of electrons	18	18
boiling point (°C)	–6.3	65.0

Methanol will have a higher boiling point than methanamine because there is stronger hydrogen bonding between molecules.

Physical Properties of Amines

Name	Structural formula	Melting point (°C)	Boiling point (°C)	Solubility in water
ammonia	NH_3	–78	–33	very soluble
Primary amines				
methylamine	CH_3NH_2	–95	–6	very soluble
ethylamine	$CH_3CH_2NH_2$	–81	17	very soluble
propylamine	$CH_3CH_2CH_2NH_2$	–83	48	very soluble
cyclohexylamine	$C_6H_{11}NH_2$	–17	135	slightly soluble
Secondary amines				
diethylamine	$(CH_3CH_2)_2NH$	–48	56	very soluble
Tertiary amines				
triethylamine	$(CH_3CH_2)_3N$	–114	89	slightly soluble
Aromatic amines				
aniline	$C_6H_5NH_2$	–6	184	slightly soluble
Heterocyclic aromatic amines				
pyridine	C_5H_5N	–42	116	very soluble

Source: Blackman et al. (2019b:934).

Preparation of Amines

Preparation from haloalkanes

Amines can be prepared from haloalkanes by nucleophilic substitution reactions (chapter 18).

Ammonia is used as the nucleophile.

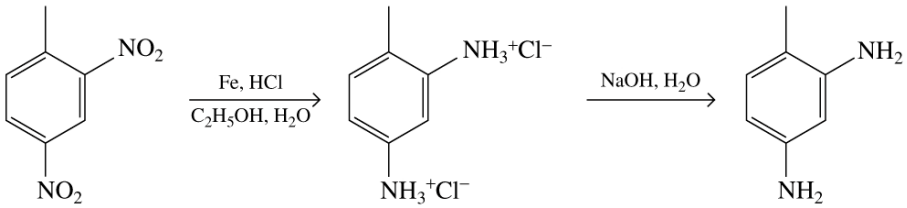
Mixtures of 1°, 2° and 3° amines are usually obtained.

$$\underset{\text{1-bromopropane}}{CH_3CH_2CH_2Br} + :NH_3 \longrightarrow \underset{\text{propylammonium}}{CH_3CH_2CH_2\overset{+}{N}H_3} + \underset{\text{bromide}}{Br^-}$$

$$CH_3CH_2CH_2\overset{+}{N}H_3 + {}^-OH \longrightarrow \underset{\text{propylamine}}{CH_3CH_2CH_2NH_2} + H_2O$$

Preparation of Amines

A nitro group can be reduced to a primary amino group by a metal in acid.



2,4-dinitrotoluene

2,4-diaminotoluene

Reactions of Amines

Amines have an unshared pair of electrons on the nitrogen atom.

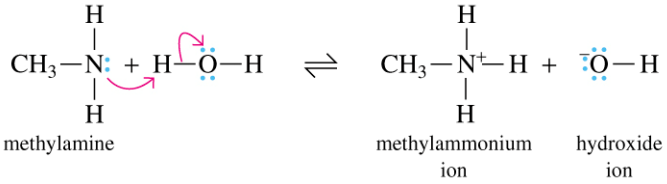
Amines are both basic and nucleophilic.

Hence, amines react readily:

- **With acids to form salts,**
- **With electrophilic species like haloalkanes, acyl halides and many others.**

Reactions of Amines

All amines are weak bases, and aqueous solutions of amines are basic.

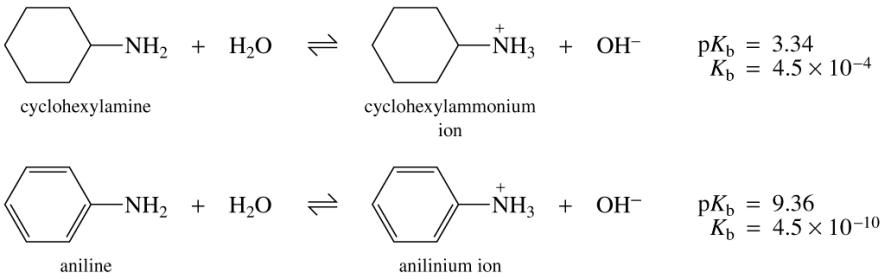


$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = 4.37 \times 10^{-4}$$

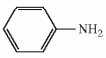
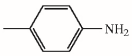
Reactions of Amines

Aromatic amines are much weaker bases than are aliphatic amines.

Source: Blackman et al. (2019b:940).



Reactions of Amines - basicity

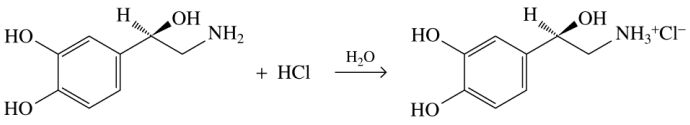
Amine	Structure	pK_b	pK_a
ammonia	NH_3	4.74	9.26
Primary amines			
ethylamine	$CH_3CH_2NH_2$	3.19	10.81
cyclohexylamine	$C_6H_{11}NH_2$	3.34	10.66
Secondary amines			
diethylamine	$(CH_3CH_2)_2NH$	3.02	10.98
Tertiary amines			
triethylamine	$(CH_3CH_2)_3N$	3.25	10.75
Aromatic amines			
aniline		9.36	4.64
4-methylaniline		8.92	5.08
4-nitroaniline		13.0	1.0
Heterocyclic aromatic amines			
pyridine		8.82	5.18

Source: Blackman et al. (2019b:939).

Reactions of Amines

Reaction with acids to form salts

Amines, whether soluble or insoluble in water, react quantitatively with strong acids to form water-soluble salts



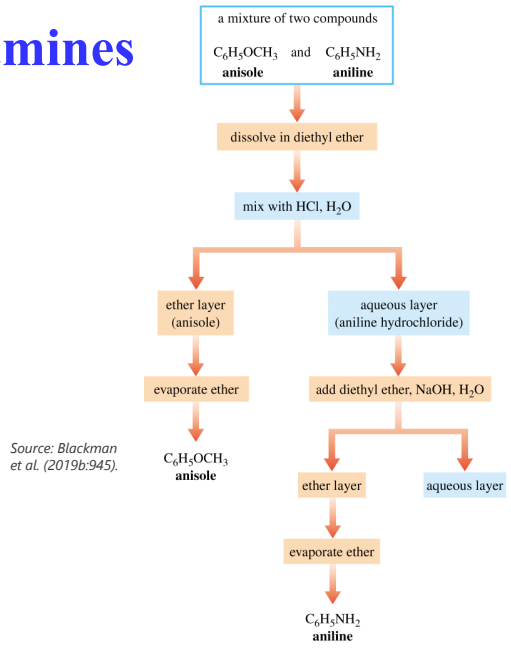
(*R*)-norepinephrine
(only slightly soluble in water)

(*R*)-norepinephrine hydrochloride
(a water-soluble salt)

This property can be used to separate amines from water-insoluble, nonbasic compounds.

Basicity of amines

The basicity of amines can be used to separate amines from water-insoluble, nonbasic compounds, for instance, ethers.

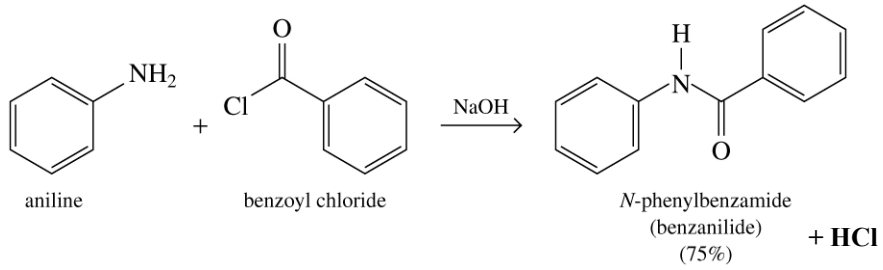


Source: Blackman et al. (2019b:945).

Reactions of Amines

Amide formation

Amines will react with acid chlorides or carboxylic anhydrides to form amides.



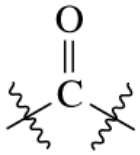
aniline + benzoyl chloride → *N*-phenylbenzamide (benzanilide) (75%) + **HCl**

Aldehydes and Ketones

- The carbonyl group is the most important functional group in organic chemistry.
- The majority of biologically important compounds contain the carbonyl group.
- It has a carbon - oxygen double bond.
- The formation of a bond to the carbonyl carbon is an important step in many synthetic and biological reactions.

DEAKIN COLLEGE

Aldehydes and ketones contain the carbonyl group, C=O

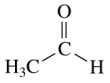


a carbonyl group

An aldehyde has a C=O bonded to an H atom and a hydrocarbon group

an aldehyde group

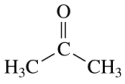
formaldehyde (methanal)



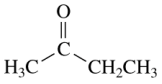
acetaldehyde (ethanal)

A ketone has a C=O group bonded to two hydrocarbon groups

a ketone group



acetone (propanone)



methyl ethyl ketone (butanone)

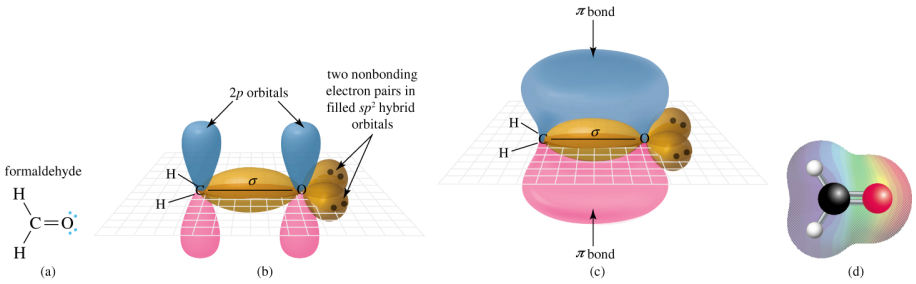
Source: Blackman et al. (2019b:1291).

DEAKIN COLLEGE

Structure and bonding

The carbonyl group is a planar group.

There is an angle of approximately 120° between the three atoms bonded to the carbonyl carbon atom.



Source: Blackman et al. (2019b:1291).

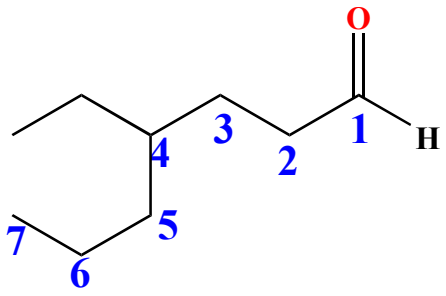
Nomenclature

The IUPAC system is used when naming

- **The parent chain is the longest chain that contains the carbonyl group.**
- **The –e of the alkane is replaced with the suffix –al for an aldehyde.**
- **The carbonyl group of an aldehyde can appear only at the end of a parent chain, there is no need to use a number to locate it.**

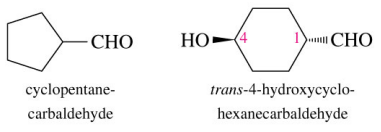
Nomenclature

1. Name the Parent Chain
heptane
2. Add the Suffix
heptanal
3. Add the Prefix
ethylheptanal
4. Include the Locant
4-ethylheptanal



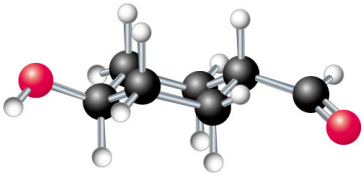
Nomenclature

A cyclic molecule with -CHO bonded to the ring has the suffix –carbaldehyde.



cyclopentane-carbaldehyde

trans-4-hydroxycyclo-hexanecarbaldehyde



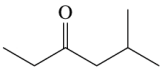
Common names of aldehydes are derived from the carboxylic acid.

O ‖ HCH	O ‖ HCOH	O ‖ CH_3CH	O ‖ CH_3COH
formaldehyde	formic acid	acetaldehyde	acetic acid

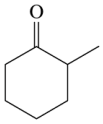
Source: Blackman et al. (2019b:1292).

Nomenclature

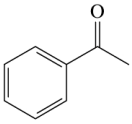
Ketones have the suffix –one



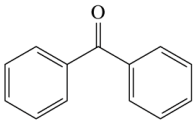
5-methylhexan-3-one



2-methyl-cyclohexanone

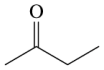


acetophenone

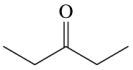


benzophenone

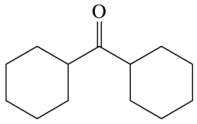
Common names use a separate word for each alkyl or aryl group.



methyl ethyl ketone (MEK) (butanone)



diethyl ketone (pentan-3-one)

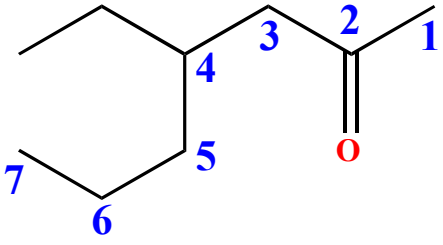


dicyclohexyl ketone

Source: Blackman et al. (2019b:1291).

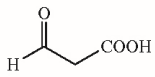
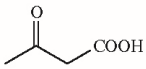
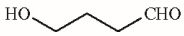
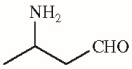
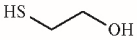
Nomenclature

1. Name the Parent Chain
heptane
2. Add the Suffix
heptanone
3. Add the Prefix
ethylheptanone
4. Include the Locant
4-ethylheptan-2-one



Nomenclature

IUPAC names for complex aldehydes and ketones

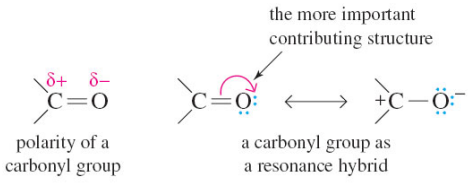
Functional group	Suffix	Prefix	Example of when the functional group is not highest priority and is used as a prefix	
carboxyl group	-oic acid	—		
aldehyde group	-al	oxo-	3-oxopropanoic acid	
ketone group	-one	oxo-	3-oxobutanoic acid	
alcohol group	-ol	hydroxy-	4-hydroxybutanal	
amino group	-amine	amino-	3-aminobutanal	
sulfhydryl	-thiol	mercapto-	2-mercaptoethanol	

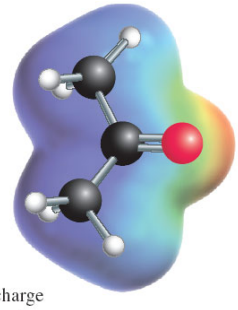
Source: Blackman et al. (2019b:1295).

Physical properties of carbonyl compounds

Oxygen is more electronegative than carbon (3.5 compared with 2.5)

Therefore, a C=O group is polar





The electron density model shows that the partial positive charge on an acetone molecule is distributed both on the carbonyl carbon and on the two attached methyl groups.

Source: Blackman et al. (2019b:1291).

Physical properties of carbonyl compounds

Aldehydes and ketones are polar

They interact in the pure state by dipole–dipole interactions.

They have higher boiling points and higher water solubility than alkanes and ethers of similar molar mass.

Name	Structural formula	Number of electrons	Boiling point (°C)
diethyl ether	$CH_3CH_2OCH_2CH_3$	42	34
pentane	$CH_3CH_2CH_2CH_2CH_3$	42	36
butanal	$CH_3CH_2CH_2CHO$	40	76
butanone	$CH_3CH_2COCH_3$	40	80
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	42	117
propanoic acid	CH_3CH_2COOH	40	141

Source: Blackman et al. (2019b:1297).

DEAKIN COLLEGE

Physical properties of carbonyl compounds

Aldehydes and ketones are polar

They interact in the pure state by dipole–dipole interactions.

They have higher boiling points and higher water solubility than alkanes and ethers of similar molar mass.

IUPAC name	Common name	Structural formula	Boiling point (°C)	Solubility (g/100 g water)
methanal	formaldehyde	HCHO	−21	infinite
ethanal	acetaldehyde	CH_3CHO	20	infinite
propanal	propionaldehyde	CH_3CH_2CHO	49	16
butanal	butyraldehyde	$CH_3CH_2CH_2CHO$	76	7
hexanal	caproaldehyde	$CH_3(CH_2)_4CHO$	129	slight
propanone	acetone	CH_3COCH_3	56	infinite
butanone	methyl ethyl ketone	$CH_3COCH_2CH_3$	80	26
pentan-3-one	diethyl ketone	$CH_3CH_2COCH_2CH_3$	101	5

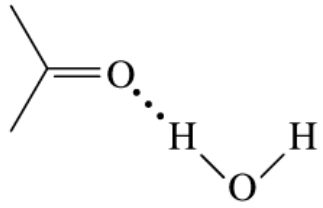
Source: Blackman et al. (2019b:1297).

DEAKIN COLLEGE

Physical properties of carbonyl compounds

The electronegative O atom of the carbonyl group in aldehydes and ketones forms hydrogen bonds with water.

Low-molar-mass aldehydes and ketones are more soluble in water than nonpolar compounds of similar molar mass.



Preparation of aldehydes and ketones

They can be prepared from many functional groups using various reactions

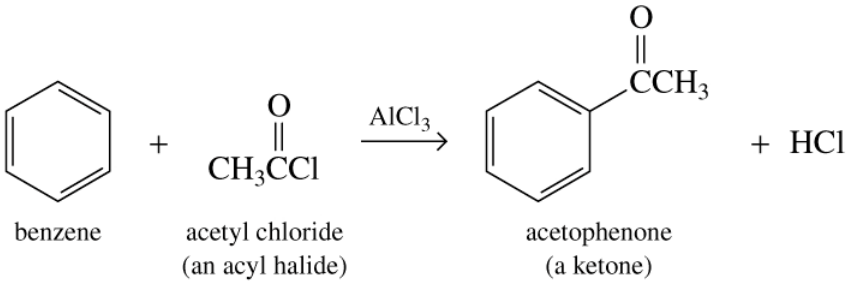
Reactions discussed here are:

- **Friedel-Crafts acylation**
- **Oxidation of alcohols**
- **Ozonolysis of alkenes**
- **Hydration of alkynes**

Preparation of aldehydes and ketones

Friedel–Crafts acylation

Ketones can be prepared by Friedel–Crafts acylation of aromatic compounds.



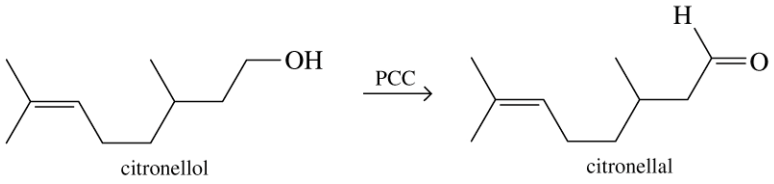
Source: Blackman et al. (2019b:1299).

Preparation of aldehydes and ketones

Oxidation of alcohols

Primary alcohols can be oxidised under mild conditions to give aldehydes.

(PCC is pyridinium chlorochromate.)



Secondary alcohols can be oxidised to give ketones.

Source: Blackman et al. (2019b:1299).

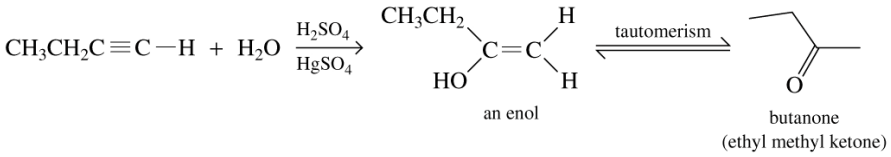
Preparation of aldehydes and ketones

Hydration of alkynes

Water added to alkenes gives an alcohol

Water added to alkynes gives an enol.

Enols undergo tautomerism (rearrangement of atoms and bonds) to give a ketone.



Source: Blackman et al. (2019b:1300).

Summary

Amines

Amines can be classified as 1°, 2° or 3°.

An aliphatic amine is an amine in which nitrogen is bonded only to alkyl groups.

An aromatic amine is an amine in which nitrogen is bonded to a C atom of an aromatic ring.

Amines are polar compounds.

They have lower boiling points than alcohols of similar molar mass and structure.

Summary

Reactions of amines

Amines are weak bases.

Aqueous solutions of amines are basic.

It is common to discuss acid-base properties of amines by reference to the acid ionisation constant, K_a, for the conjugate acid of the amine.

Acid-base ionisation constants for amines in water are related by

$$pK_a + pK_b = 14.0$$

Summary

- **Aldehydes and ketones contain the carbonyl group, C=O.**
- **They are polar compounds.**
- **They have higher boiling points and water solubility.**
- **They can be prepared from various functional groups.**
- **They are very reactive due to the polarity and structure of the C=O group.**

Summary

The key reactions are:

Preparation of aldehydes and ketones:

- **Oxidation of 1° alcohols to give aldehydes.**
- **Oxidation of 2° alcohols to give ketones.**
- **Ozonolysis of alkenes.**

Preparation of ketones:

- **Friedel-Crafts acylation of aromatic compounds.**
- **Hydration of alkynes under appropriate conditions.**