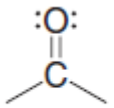
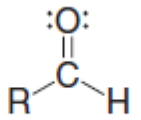
Aldehydes and Ketones 1

Based on Organic Chemistry, J. G. Smith 3rde.

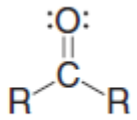
Introduction:



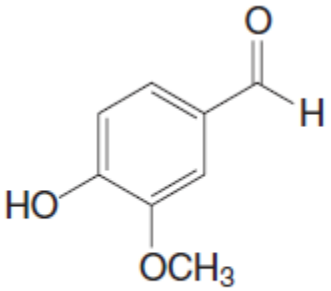
carbonyl group



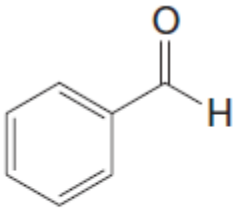
aldehyde



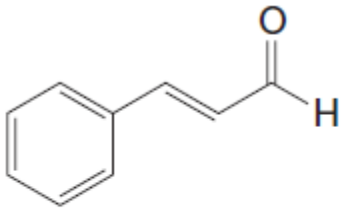
ketone



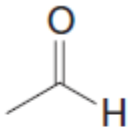
Vanillin



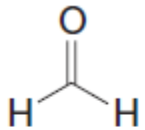
Benzaldehyde



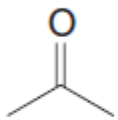
Cinnamaldehyde



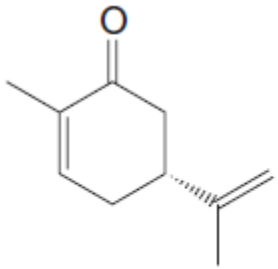
Acetaldehyde



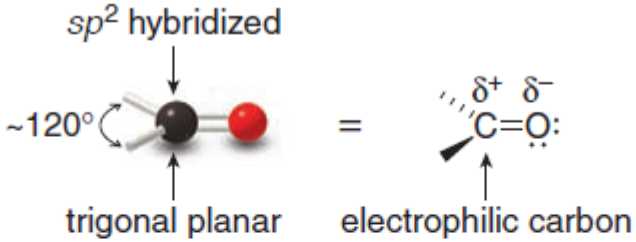
Formaldehyde



Acetone

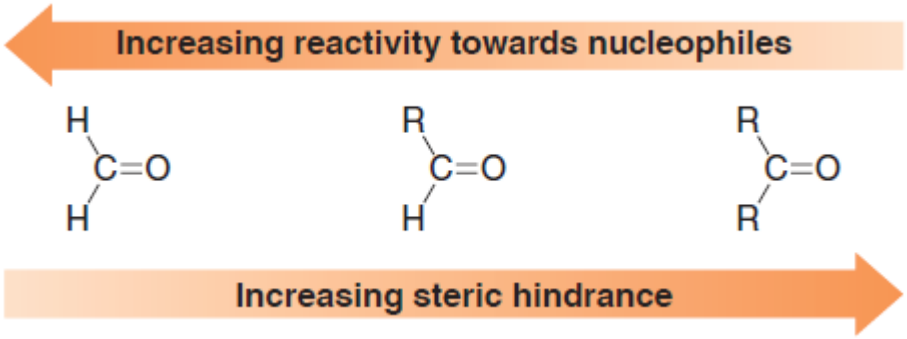


(*R*)-Carvone



- The carbonyl group is sp^2 hybridized and trigonal planar, making it relatively uncrowded.
- The electronegative oxygen atom polarizes the carbonyl group, making the carbonyl carbon electrophilic.

As a result, **aldehydes and ketones react with nucleophiles.** The relative reactivity of the carbonyl group is determined by the number of R groups bonded to it. **As the number of R groups around the carbonyl carbon increases, the reactivity of the carbonyl compound decreases,** resulting in the following order of reactivity:



Nomenclature

Naming Aldehydes in the IUPAC System:

In IUPAC nomenclature, aldehydes are identified by a suffix added to the parent name of the longest chain. Two different suffixes are used, depending on whether the CHO group is bonded to a chain or a ring.

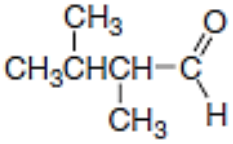
To name an aldehyde using the IUPAC system:

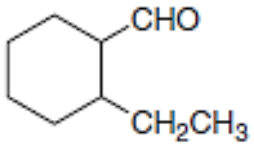
1. If the CHO is bonded to a chain of carbons, find the longest chain containing the CHO group, and change the ***-e*** ending of the parent alkane to the suffix ***-al.*** If the CHO group is bonded to a ring, name the ring and add the suffix ***-carbaldehyde.***

2. Number the chain or ring to put the CHO group at C1, but omit this number from the name. Apply all of the other usual rules of nomenclature.

Sample Problem

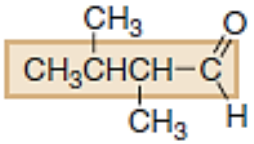
Give the IUPAC name for each compound.

a. 

b. 

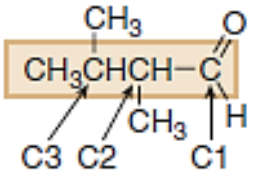
Solution

a. [1] Find and name the longest chain containing the CHO:



butane ⟶ butanal
(4 C's)

[2] Number and name substituents:



Answer: 2,3-dimethylbutanal

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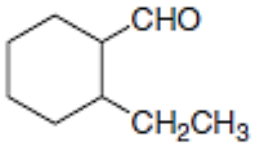
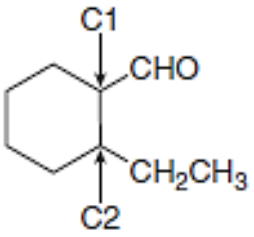
b. [1] Find and name the ring bonded to the CHO group:



cyclohexane + carbaldehyde
(6 C's)

[2] Number and name substituents:

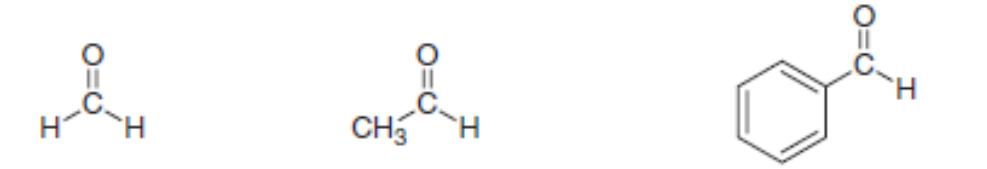


Answer:
2-ethylcyclohexanecarbaldehyde

Common Names for Aldehydes

- A common name for an aldehyde is formed by taking the common parent name and adding the suffix *-aldehyde.*

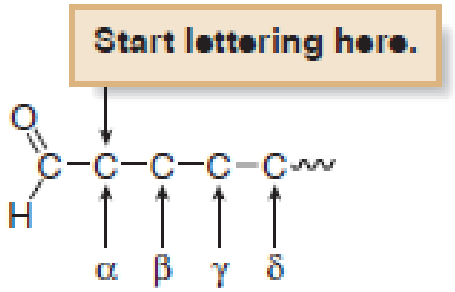
The common names **formaldehyde, acetaldehyde,** and **benzaldehyde** are virtually always used instead of their IUPAC names.



formaldehyde (methanal) | acetaldehyde (ethanal) | benzaldehyde (benzenecarbaldehyde)

(IUPAC names are in parentheses.)

Greek letters are used to designate the location of substituents in common names. **The carbon adjacent to the CHO group is the ` carbon,** and so forth down the chain.



Naming Ketones in the IUPAC System

- In the IUPAC system all ketones are identified by the suffix *-one*.

To name an acyclic ketone using IUPAC rules:

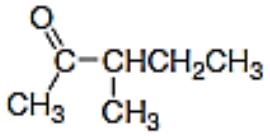
1. Find the longest chain containing the carbonyl group, and change the ***-e*** ending of the parent alkane to the suffi x ***-one.***

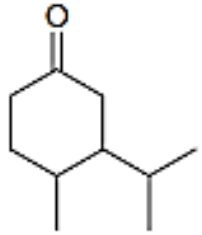
2. Number the carbon chain to give the carbonyl carbon the lower number. Apply all of the other usual rules of nomenclature.

With cyclic ketones, numbering always begins at the carbonyl carbon, but the “1” is usually omitted from the name. The ring is then numbered clockwise or counter clockwise to give the first substituent the lower number.

Sample Problem

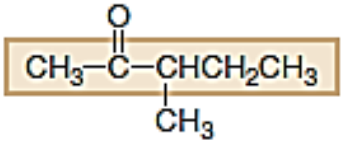
Give the IUPAC name for each ketone.

a. 

b. 

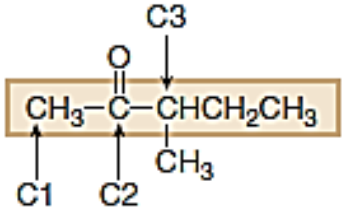
Solution

a. [1] Find and name the longest chain containing the carbonyl group:



pentane ⟶ pentan*one*
(5 C's)

[2] Number and name substituents:



Answer: 3-methyl-2-pentanone

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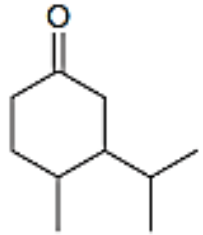
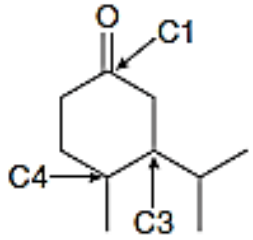
b. [1] Name the ring:



cyclohexane ⟶ cyclohexan*one*
(6 C's)

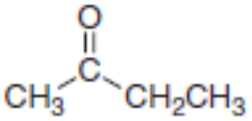
[2] Number and name substituents:



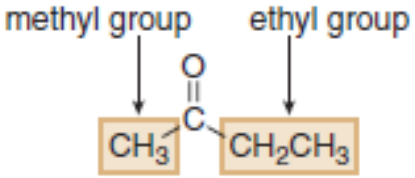
Answer:
3-isopropyl-4-methylcyclohexanone

Common Names for Ketones

Most common names for ketones are formed by **naming both alkyl groups** on the carbonyl carbon, **arranging them alphabetically,** and adding the word ***ketone.*** Using this method, the common name for 2-butanone becomes ethyl methyl ketone.

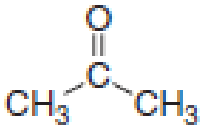


IUPAC name: **2-butanone**

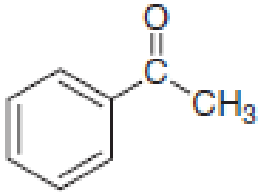


Common name: **ethyl methyl ketone**

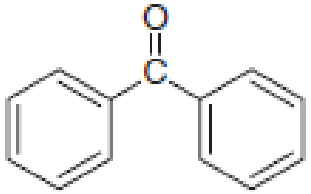
Three widely used common names for some simple ketones do not follow this convention:



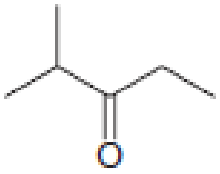
acetone



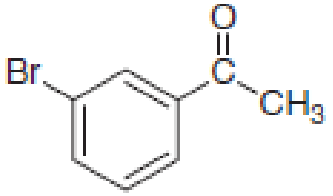
acetophenone



benzophenone



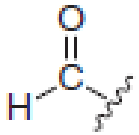
IUPAC name: 2-methyl-3-pentanone
Common name: ethyl isopropyl ketone



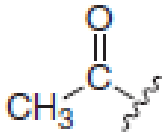
m-bromoacetophenone
or
3-bromoacetophenone

Additional Nomenclature Facts

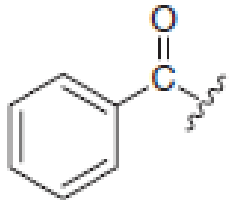
Sometimes acyl groups (RCO –) must be named as substituents. To name an acyl group, take either the IUPAC or common parent name and add the suffix ***-yl*** or ***-oyl.*** The three most common acyl groups are drawn below.



formyl group

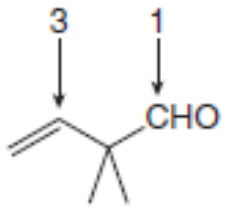


acetyl group

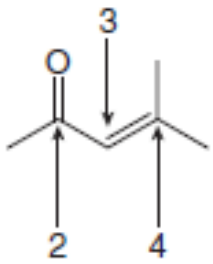


benzoyl group

Compounds containing both a C – C double bond and an aldehyde are named as **enals,** and compounds that contain both a C – C double bond and a ketone are named as **enones.** The chain is numbered to give the carbonyl group the lower number.



2,2-dimethyl-3-butenal

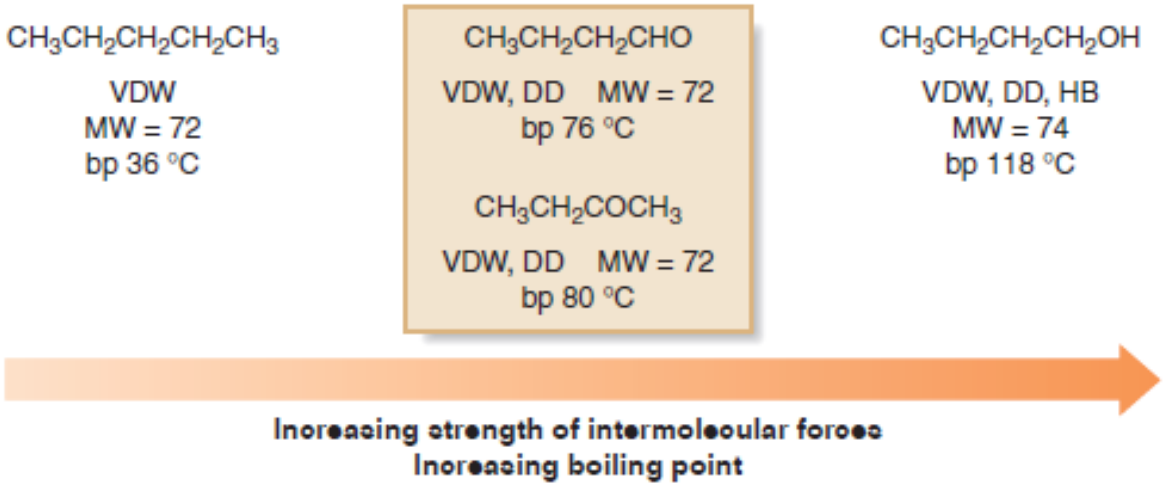


4-methyl-3-penten-2-one

Physical Properties of Aldehydes and Ketones

Aldehydes and ketones exhibit dipole–dipole interactions because of their polar carbonyl group. Because they have no O – H bond, two molecules of RCHO or RCOR are incapable of intermolecular hydrogen bonding, making them less polar than alcohols and carboxylic acids.

Property	Observation
Boiling point and melting point	• For compounds of comparable molecular weight, bp's and mp's follow the usual trend: The stronger the intermolecular forces, the higher the bp or mp.
Solubility	• RCHO and RCOR are soluble in organic solvents regardless of size. • RCHO and RCOR having ≤ 5 C's are H_2O soluble because they can hydrogen bond with H_2O (Section 3.4C). • RCHO and RCOR having > 5 C's are H_2O insoluble because the nonpolar alkyl portion is too large to dissolve in the polar H_2O solvent.



Key: VDW = van der Waals, DD = dipole–dipole, HB = hydrogen bonding, MW = molecular weight