Supplement

for

Organic Chemistry 51 and 52

Brooklyn College

of the

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Edited by Herman E. Zieger

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Foreword: Some 20-25 years ago Prof. Robert Tripp served as the editor for the previous edition of the Supplement for Organic Chemistry. He was assisted by several other colleagues some of whom have already retired. As time passed, certain nomenclature practices in the industrial world as well as in the academic world led to changes in nomenclature. It is endeavored here to update some of those changes.

The increasing use of instrumental methods of analysis combined with the impact of the microcomputer completely altered methods of organic structure determination. The diagnosis of functional groups in unknown materials by means of infrared- and nuclear magnetic resonance spectroscopy are mentioned to the beginning student in organic chemistry in the hope that some students will be encouraged to continue the study of these modern methods.

I wish to thank Prof. James Howell for having made several valuable suggestions for improving the present Supplement for Organic Chemistry 51 and 52. Any errors are my responsibility and corrections or suggestions from students would be gratefully received.

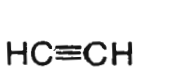
Nomenclature

I. Common or Trivial Names

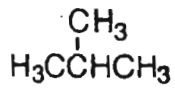
A number of simple, commonly used, organic compounds are most often referred to by their common or trivial names rather than by their systematic names (see IUPAC or Geneva names below). Most of these compounds were well known before a systematic nomenclature was devised, and it has been easier and less confusing to continue using the older common names while recognizing the existence of systematic names. A few of the compounds usually referred to by their common names are shown below with their IUPAC names in parentheses. For many of these simple compounds the trivial names have actually become the preferred IUPAC names. Learning the structures of these compounds and their common names is necessary for anyone studying organic chemistry. Additional common names will be encountered throughout this course. They should be learned as they are encountered.

ethylene (ethene)

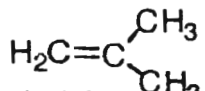
propylene (propene)



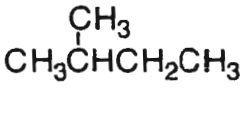
acetylene (ethyne)



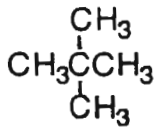
isobutane (2-methylpropane)



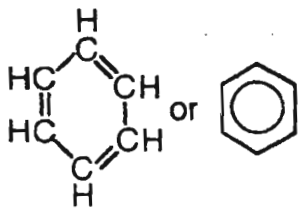
isobutylene (2-methylpropene)



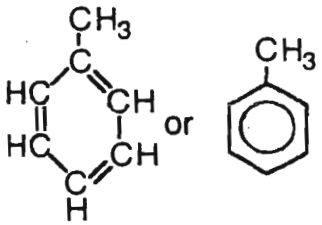
isopentane (2-methylbutane)



neopentane (2,2-dimethylpropane)



benzene

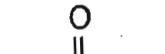


toluene

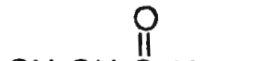
methyl alcohol (methanol)

ethyl alcohol (ethanol)

formaldehyde (methanal)



acetaldehyde (ethanal)



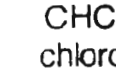
propionaldehyde (propanal)

acetone (propanone)

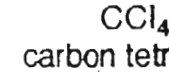
formic acid (methanoic acid)

acetic acid (ethanoic acid)

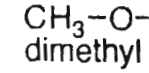
propionic acid (propanoic acid)



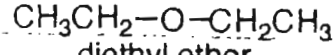
chloroform (trichloromethane)



carbon tetrachloride (tetrachloromethane)

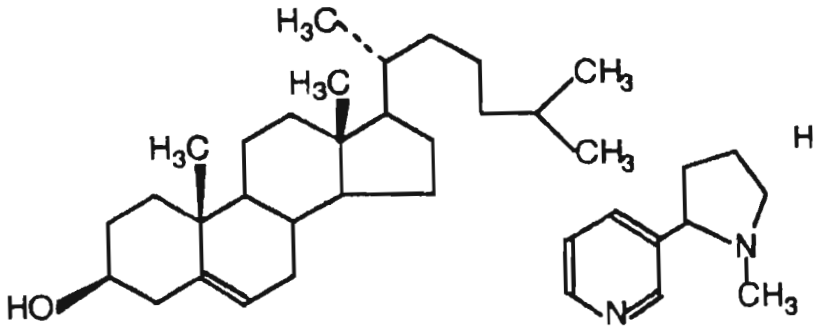


dimethyl ether (methoxymethane)

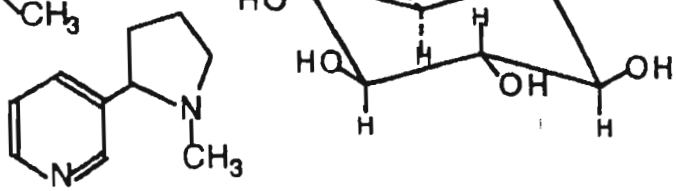


diethyl ether (ethoxyethane)

Common or trivial names are also used for very complex compounds, whose systematic names are almost as complex as the compounds themselves. Some examples are given below. The structures of these compounds need not be memorized.



cholesterol
(3 beta)-cholest-5-en-3-ol



nicotine
(S)-3-(1-methylpyrrolidinyl)pyridine

glucose

II. Systematic IUPAC Substitutive Nomenclature

The nomenclature system devised by the International Union of Pure and Applied Chemistry, sometimes called the IUC, IUPAC, or Geneva System, is the most widely accepted and widely used system. Once a few basic rules are known, a very large number of compounds can be systematically named.

A. The Unbranched Alkanes

The backbone of the IUPAC system is the series of unbranched alkanes starting with methane and proceeding by increments of $-CH_2-$ to longer chains.

CH_4	methane	$CH_3(CH_2)_6CH_3$	octane
CH_3CH_3	ethane	$CH_3(CH_2)_7CH_3$	nonane
$CH_3CH_2CH_3$	propane	$CH_3(CH_2)_8CH_3$	decane
$CH_3CH_2CH_2CH_3$	butane	$CH_3(CH_2)_9CH_3$	undecane
$CH_3(CH_2)_3CH_3$	pentane	$CH_3(CH_2)_{10}CH_3$	dodecane
$CH_3(CH_2)_4CH_3$	hexane		
$CH_3(CH_2)_5CH_3$	heptane	$CH_3(CH_2)_{20}CH_3$	eicosane ($C_{20}H_{42}$)

In the examples used below to illustrate the IUPAC nomenclature, alternative common names are given in parenthesis if their use is widespread.

B. The Naming of Alkanes (Saturated Hydrocarbons)

Branched-chain alkanes are named as derivatives of the unbranched alkanes.

Alkane Naming continued

RULE 1 To name any alkane:

(a) Name the longest continuous chain of carbon atoms.

(b) Number the carbon chain from one end to the other, beginning at the end nearest a substituent. (See below)

(c) Prefix the names of the substituents attached to this chain.

(d) Designate the position of each substituent with the number of the carbon atom to which it is attached.

This rule is the essence of the IUPAC system. It will be further elaborated and modified with some corollaries later to cover special cases. Additional rules will then be added for naming other classes of compounds.

Before proceeding we must know how to name the substituents or groups mentioned in the rule. Removal of a hydrogen atom from any alkane leaves a group of atoms with one position open for bonding. This group is called an alkyl group.

The normal (or n)[1] alkyl groups are those obtained by removal of a hydrogen atom from the extreme end of the chain of an unbranched alkane. Their names are obtained by replacing the *-ane* ending from the name of the alkane by *-yl*.

CH_3-	CH_3CH_2-	$CH_3CH_2CH_2$-	$CH_3CH_2CH_2CH_2$-	$CH_3CH_2CH_2CH_2CH_2$-
methyl	ethyl	propyl	butyl	pentyl[2]

Other common alkyl groups are derived from unbranched alkanes or branched alkanes by removal of a non terminal hydrogen. Special group names are derived by removal of a hydrogen from unsaturated or aromatic hydrocarbons. Memorize them. Although based originally on common names, these names have been incorporated into the IUPAC system and are the preferred names for these groups. See page 4.

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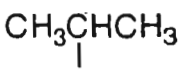
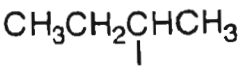
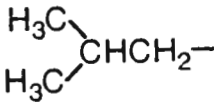
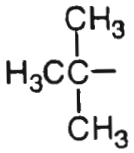
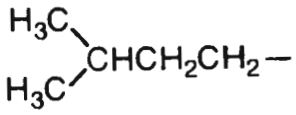
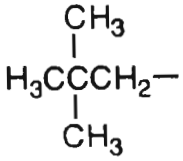
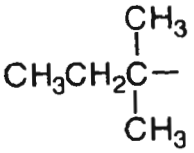
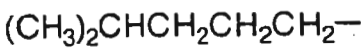
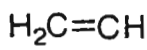
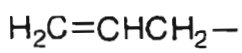
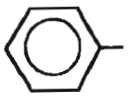
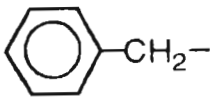
1 The prefix n- is no longer required nor desired but is still used occasionally to specify a normal alkyl group. Thus n-propyl and n-butyl mean exactly the same as propyl and butyl respectively.

2 The old names, amyl, isoamyl, and *tert*-amyl were formerly used instead of pentyl, isopentyl, and *tert*-pentyl, respectively. They are not correct IUPAC names, but are still used in new textbooks by authors who ignore the Nomenclature Commission.

	isopropyl[3]	derived from propane by removal of a hydrogen from the CH_2 carbon
	*sec*-butyl	derived from butane by removal of a secondary (2°) or methylene hydrogen
	isobutyl[3]	derived from isobutane by removal of a primary (1°) or methyl group hydrogen
	*tert*-butyl	derived from isobutane by removal of a tertiary (3°) or methinyl group hydrogen
	isopentyl[2,3]	derived from isopentane by removal of a hydrogen from the carbon atom which is farthest away from the methyl branch
	neopentyl	derived from neopentane
	tert-pentyl	derived from isopentane by removal of a tertiary (3°) hydrogen
	isohexyl[3]	
	vinyl	derived from ethene
	allyl	derived from propene
	phenyl	derived from benzene
	benzyl	derived from methylbenzene (toluene)

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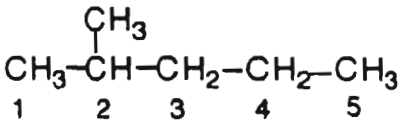
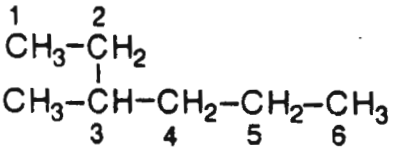
3 The isoalkyl groups all have a single methyl branch at the opposite end of the chain. The isoalkyl name is not approved by the IUPAC for groups larger than isohexyl.

Now we can return to the task of naming the branched alkanes.



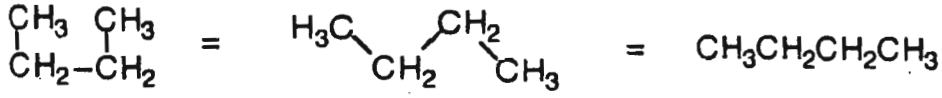
2-methylpentane
[not 4-methylpentane]



3-methylhexane
[not 4-methylhexane]
{not 2-ethylpentane]

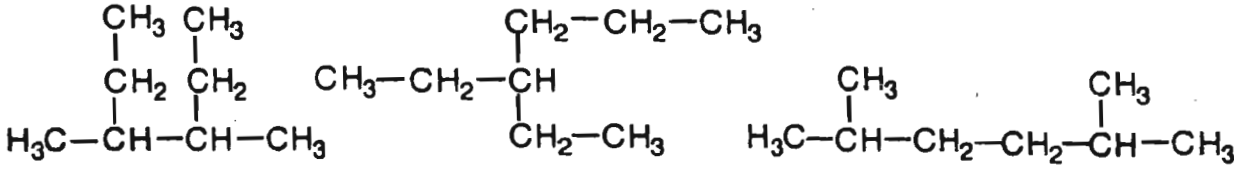
In each of these examples the longest chain is numbered from the end closest to the substituent, the methyl group, which is given a number (2- in the first example, 3- in the second) to designate its position on the chain. Note that numbering a chain from the end closest to the substituent gives the substituent the lowest possible number.

One problem that students often have is choosing the longest chain. The longest continuous chain of carbons does not depend on how the formula is written.



butane

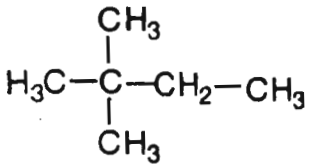
The longest straight chain is six in each of the following compounds.



The naming of alkanes with two or more substituents is explained in the following corollaries:

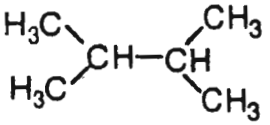
Corollary 1 If there are two or more identical groups attached to the same or to different carbon atoms, the multiplying prefixes, di-, tri-, tetra-, penta-, hexa-, etc. are used to show how many of that group are present.

Corollary 2 Each substituent must be given a number. If more than one group is attached to the same carbon atom, the number is repeated for each of them, even if the groups are identical.



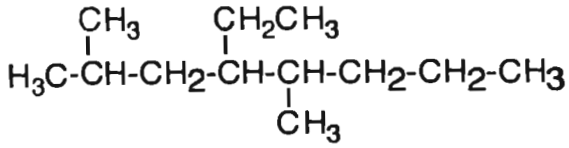
2,2-dimethylbutane

[not 2-dimethyl....]
[not 2,2-methyl....]
not 2-methyl-2-methyl...]

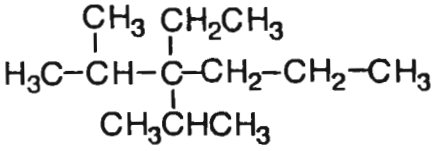


2,3-dimethylbutane
[not 2,3-methyl...]
[not 2-methyl-3-methyl...]

Corollary 3 If several different substituents are attached to the parent chain, they are named in alphabetical order. In applying alphabetical order, the multiplying prefixes (di-, tri-, etc.) and those prefixes ordinarily printed in italics (*sec-*. *tert-*, *quat-*,etc.) are ignored. Therefore ethyl- precedes dimethyl- (e before m) and both *sec*-butyl and *tert*-butyl precede ethyl (b before e). However, the structure defining prefixes, iso- and neo- (which are not printed in italics), are considered an integral part of the name. Thus isopropyl and neopentyl are alphabetized under i and n respectively.



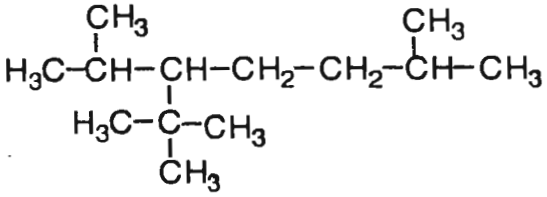
4-ethyl-2,5-dimethyloctane



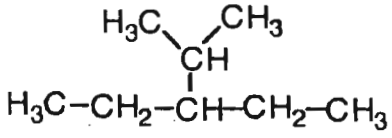
3-ethyl-3-isopropyl-2-methylhexane

With several substituents present, there may be more than one longest chain and there may seem to be more than one way to number the chain. Two corollaries deal with these cases.

Corollary 4 If two chains of equal length are found in a single compound, choose the chain with the greater number of substituents (ie, the most highly branched chain).

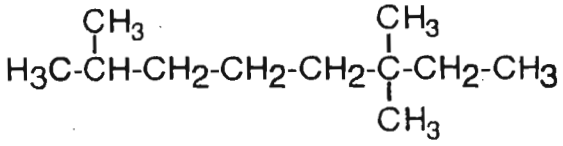


3-isopropyl-2,2,6-trimethylheptane
[not 3-*tert*-butyl-2,6-dimethylheptane]

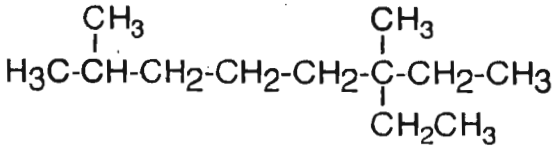


3-ethyl-2-methylpentane
[not 3-isopropylpentane]

Corollary 5 When comparing alternative numbering schemes to a chain which has two or more atoms or simple substituents one chooses that scheme which assigns the lowest number at the first point of difference. *When the atoms or groups of atoms are* functional groups then the fundamental chain rule dominates.



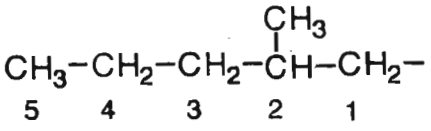
2,6,6,trimethyloctane
[not 3,3,7-trimethyloctane]



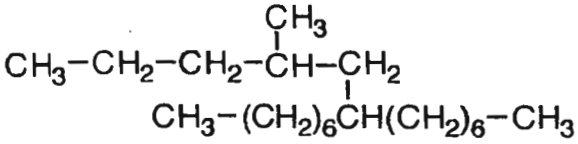
6-ethyl-2,6-dimethyloctane
[not 3-ethyl-3,7-dimethyloctane]

Corollary 6 If two substituents are found in equivalent positions, the lower number is given to the one coming first in alphabetical listing. 3-Ethyl-6-methyloctane is correct, not 6-ethyl-3-methyloctane.

Complex branched chain alkyl groups without special names are named as derivatives of the longest chain originating at the point of attachment to the parent chain. A new set of numbers is assigned to this chain starting at the point of attachment, and the substituents on this alkyl group are numbered accordingly. The name of the complex alkyl group is enclosed in parentheses to avoid ambiguity. For example



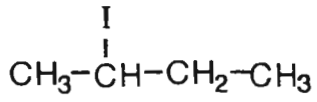
Group name is 2-methylpentyl



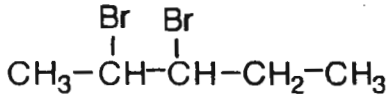
8-(2-methylpentyl)pentadecane

The halogens (fluoro-, chloro-, bromo-, iodo-), nitro groups (-NO_2), and alkoxy groups (methoxy, CH_3O-; ethoxy, CH_3CH_2O-; propoxy, $CH_3CH_2CH_2O$-; isopropoxy, $(CH_3)_2CHO$-) are named as substituents of the basic chain. These groups are always cited by prefixes in substitutive nomenclature and are listed alphabetically along with any alkyl groups which may be present.

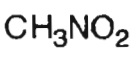
Ethers are derivatives of alcohols in which the hydrogen atom of the hydroxyl group has been replaced by carbon.Thus ethoxy ethane is diethyl ether. As a class of compounds, ethers rank below amines. See page 21 for the ranking of functional groups.



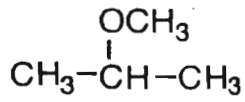
2-iodobutane



2,3-dibromopentane

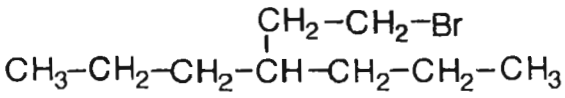


nitromethane



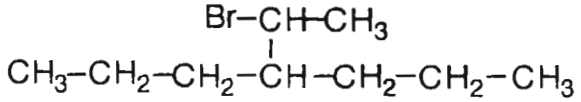
2-methoxypropane
isopropyl methyl ether

The introduction of a halogen atom or an oxygen atom increases the complexity of an alkyl group. For example one can have a chloromethyl group, $ClCH_2$-, or a bromoethyl group. Attachment to a hydrocarbon chain of either a 1-bromoethyl group or a 2-bromoethyl substituent results in isomeric bromoethylheptanes as is shown below.



4-(2-bromoethyl)heptane
not [1-bromo-3-propylhexane]

Compare with the isomeric



4-(1-bromoethyl)heptane

C. General Rules for Functional Groups.

The introduction of a functional group (a double or triple bond, an hydroxyl group, a carbonyl group, a carboxyl group, or an amino group) into an organic compound necessitates changes in the basic rules of nomenclature.

RULE 2 Select the longest continuous chain to contain the functional group.

RULE 3 Change the suffix of the name from the ane ending used for alkanes to one which identifies the type of functional group present. (A complete list of these suffixes is given in Table 1 on page 19). Insert a number in front of the stem name to show the position of the functional group if necessary. For example 2-pentanone or 3-pentanol.

RULE 4 If there are two or more of the same functional group present, select the longest carbon chain which incorporates the maximum number of these groups. Insert a multiplying prefix in front of the ending to indicate how many of the groups are present. For example glycerol is propan-1,2,3-triol. Adipic acid is hexan-1,6-dioic acid.

RULE 5 If there are two or more different functional groups present, use the suffix for the group having the highest priority. The fundamental chain must contain all of the functional groups. It is not necessarily the longest chain. (See Table 1, pg.19 for the complete order of precedence.) Name the other groups with prefixes. Only one suffix may be used in a name except when one of the groups is a double- or triple bond.

D. The Unsaturated Hydrocarbons: Alkenes and Alkynes.

When a double bond is present in a hydrocarbon, the longest continuous chain of carbon atoms containing the double bond is chosen as the basic chain. This basic chain is given the same name as the corresponding alkane except the suffix -ene is used. Thus, $CH_3CH_2CH_3$ is propane so $CH_3CH{=}CH_2$ is propene.

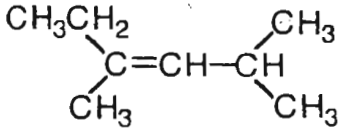
If the double bond can be in more than one position the basic chain is numbered from the end of the chain nearest the double bond and the position of the double bond is given by the number of the first doubly-bonded carbon encountered.

$H_2C{=}CHCH_2CH_3$

1-butene

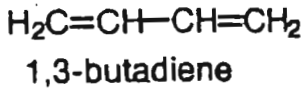
$H_3CCH{=}CHCH_2CH_3$

2-pentene
[not 3-pentene]

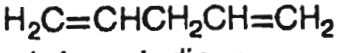


2,4-dimethyl-3-hexene

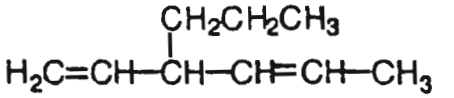
The parent chain is chosen to include the maximum possible number of double bonds if more than one is present. A number describes the position of each double bond, and a prefix (di, tri, etc., preceded by the letter a) inserted in front of the suffix -ene tells how many double bonds there are.



1,3-butadiene

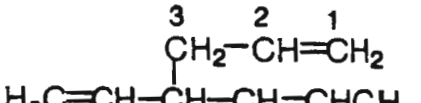


1,4-pentadiene



3-propyl-1,4-hexadiene

The longest chain is seven carbons, but the longest chain containing both double bonds is six carbons.

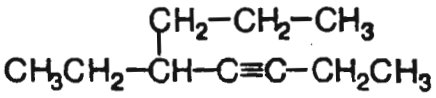


4-vinyl-1,5-heptadiene

(all three double bonds could not be included in the same chain)

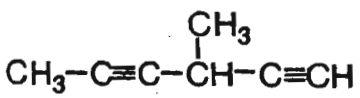
The suffix used for compounds containing triple bonds is -yne.

2-butyne



5-ethyl-3-octyne

[not 4-ethyl-5-octyne]

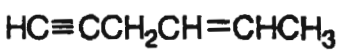


3-methyl-1,4-hexadiyne

A compound with both a double and a triple bond is named alkenyne (not alkynene). The double bond takes precedence in numbering over the triple when they occupy equivalent positions. Otherwise neither takes precedence over the other.

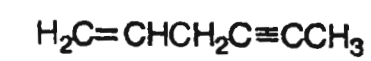
1-buten-3-yne

[not 3-buten-1-yne]



4-hexen-1-yne

[not 2-hexen-5-yne]



1-hexen-4-yne

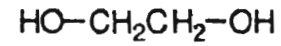
[not 5-hexen-2-yne]

E. Alcohols

If an hydroxyl group, and no other functional group, is present in a compound, the longest continuous chain of carbons to which the hydroxyl group is attached is chosen as the basic chain. The compound is then named as an alkanol, the suffix -ol indicating the compound is an alcohol.

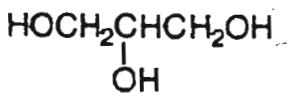
ethanol

(ethyl alcohol)



1,2-ethanediol

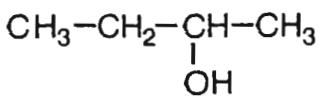
(ethylene glycol)



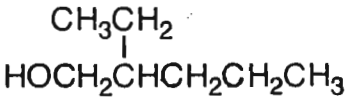
1,2,3-propanetriol

(glycerin)

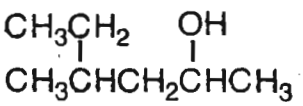
The position of the hydroxyl group is found by numbering the chain from the end nearest the hydroxyl group.



2-butanol
(sec-butyl alcohol)

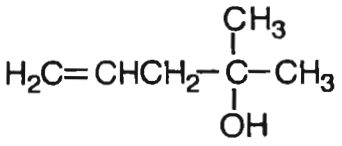


2-ethyl-1-pentanol
(the six carbon chain is longer but does not contain the functional group)

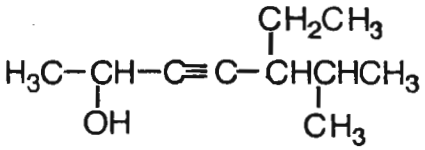


4-methyl-2-hexanol

If the alcohol also contains a double bond, the compound is named as an alkenol, and the alcohol function takes precedence over double and triple bonds in determining the direction of chain numbering.



2-methyl-4-penten-2-ol

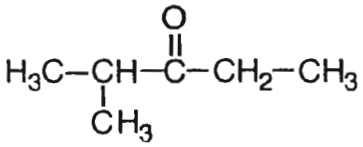


5-ethyl-6-methyl-3-heptyn-2-ol

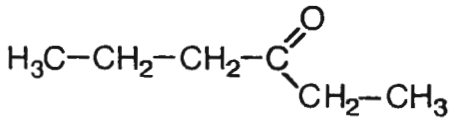
Note that the final -e is dropped from the ene ending when followed by another vowel. The prefix hydroxy- is used to designate the -OH group only when another group which takes precedence over -OH is also present such as carbaldehyde (-CHO), or carboxylic acid (COOH) groups.See page 21 for relative priorities of functional groups.

F. Ketones

The rules for naming alcohols also apply to ketones. The suffix used is -one.

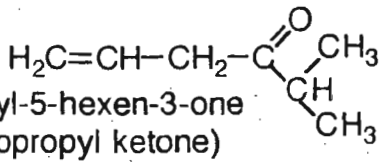


2-methyl-3-pentanone
(ethyl isopropyl ketone)

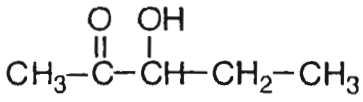


3-hexanone
(ethyl propyl ketone)

Other functional groups may be present in the same molecule as the keto group. For the groups studied to date, the order of preference is C=O > OH > C=C > C≡C



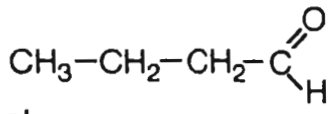
2-methyl-5-hexen-3-one
(allyl isopropyl ketone)



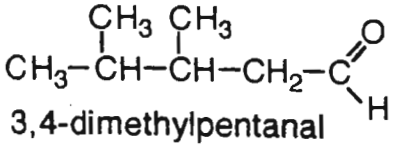
3-hydroxy-2-pentanone

G. Aldehydes

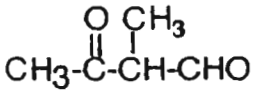
The IUPAC suffix used for aldehydes is -al. The carbonyl group of an aldehyde is necessarily at the end of the chain, so the carbonyl carbon atom is number one. Aldehydes take precedence over ketones except in cyclic ketones where the ring carbonyl carbon is given the number one. The prefix oxo is used for the carbonyl group of either an aldehyde or a ketone when a group of higher priority is present.

$CH_3CH_2CH_2CHO$ is 

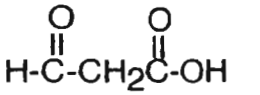
butanal



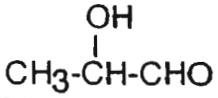
3,4-dimethylpentanal



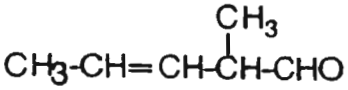
2-methyl-3-oxobutanal



3-oxopropanoic acid

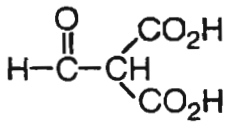


2-hydroxypropanal

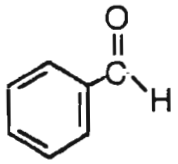


2-methyl-3-pentenal

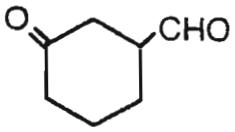
A systematic method for naming aldehydes in which the carbonyl group (-CHO) is attached to a cyclic alkyl or aryl group uses the name carbaldehyde or carboxaldehyde.The carbaldehyde group (CHO) is sometimes named as a formyl substituent.



2-formyl-1,3-propanedioic acid
(2-formylmalonic acid)



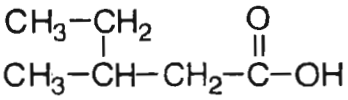
benzenecarbaldehyde
benzaldehyde



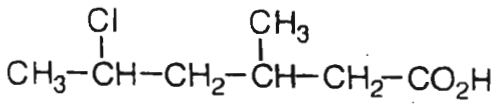
3-formylcyclo
hexanone

H. Carboxylic acids.

The carboxylic acid group ($-CO_2H$) usually appears at the end of a chain of carbon atoms in simple compounds. Vitamin C, however, is propane-1,2,3-tricarboxylic acid. Naming carboxylic acids, then, is much like naming aldehydes. The suffix *-oic acid* is added to the name of the longest continuous chain of carbons that includes the carbon of the carboxyl group after removal of the e from *ane*.

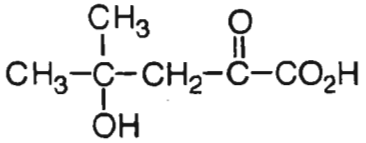


3-methylpentanoic acid

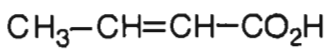


5-chloro-3-methylhexanoic acid

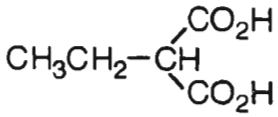
The carboxyl group takes precedence over all other groups discussed previously.



4-hydroxy-4-methyl-2-oxo-pentanoic acid



2-butenoic acid (crotonic acid)

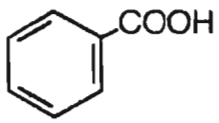


2-ethylpropanedioic acid (2-ethylmalonic acid)

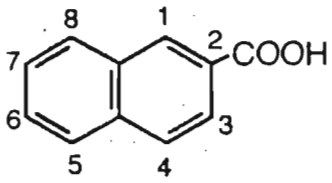
The simplest mono- and di-carboxylic acids are listed by their common names below.

Monocarboxylic acids		Di-Carboxylic acids	
formic acid	($HCOOH$)	oxalic acid	($HOOC\text{-}COOH$)
acetic acid	(CH_3COOH)	malonic acid	($HOOCCH_2COOH$)
propionic acid	(CH_3CH_2COOH)	succinic acid	($HOOCCH_2CH_2COOH$)
butyric acid	($CH_3CH_2CH_2COOH$)	glutaric acid	($HOOC(CH_2)_3COOH$)

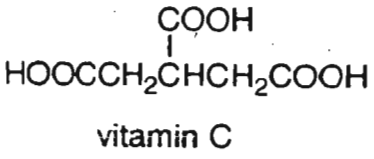
If a carboxylic acid group is substituted onto an aromatic ring, then the IUPAC name becomes benzoic acid. Similarly, the substitution of a carboxylic acid grouping onto a ring such as cyclopentane would result in the name cyclopentane carboxylic acid.



Benzoic acid



2-naphthoic acid



vitamin C

propane-1,2,3-tricarboxylic acid

I. Carboxylic Acid Derivatives.

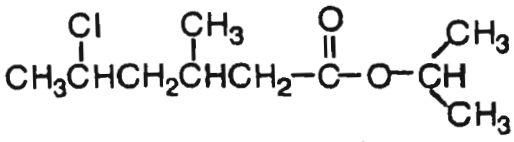
Carboxylic acid derivatives, including esters, amides, acid halides, and carboxylic acid salts are commonly encountered in organic chemistry. They may all be regarded as resulting from the replacement of the -OH group in the acid by another atom or group, and their names are closely related to those of the corresponding carboxylic acids.

In these functional groups the carbonyl carbon atom is regarded as occupying the first position. These groups have the order of precedence for nomenclature purposes:

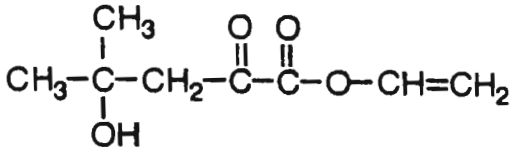
carboxylic acid > ester > acid halide > amide.

$RCOOH > RCOOR' > RCOX > RCONH_2$

1. Esters Esters are named by prefixing the name of the alkyl group R' to the name of the carboxylic acid to which it is attached and changing the -ic ending to -ate. For example, the ethyl ester of propanoic acid, CH_3CH_2-C=O(OCH_2CH_3) is called ethylpropanoate.

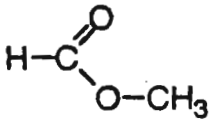


isopropyl 5-chloro-3-methylhexanoate

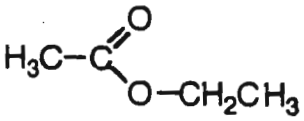


vinyl 4-hydroxy-4-methyl-2-oxopentanoate

Esters of methanoic acid (formic acid) and ethanoic acid (acetic acid) are commonly called formates and acetates.

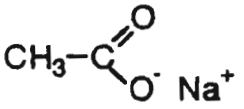


methyl methanoate
(methyl formate)

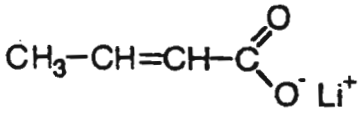


ethyl ethanoate
(ethyl acetate)

2. Carboxylic Acid Salts. The salts $R-CO_2^-$ M^+ are named like esters except that the name of the cation is used as the prefix.

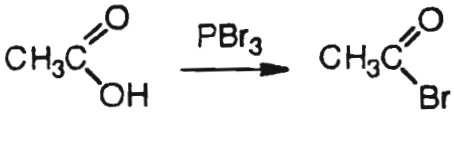


sodium ethanoate
(sodium acetate)



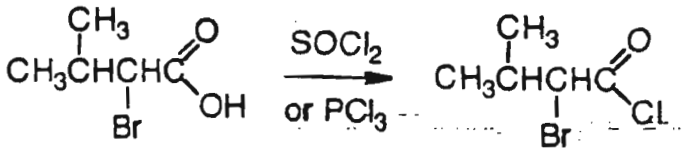
lithium 2-butenoate

3. Carboxylic Acid Halides. To name acid halides (RCOCl), the final -ic in the name of the acid is changed to -yl and the name of halide is suffixed.



acetic acid

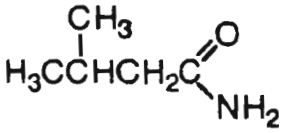
ethanoyl bromide
(acetyl bromide)



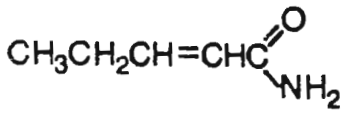
2-bromo-3-methyl-
butanoic acid

2- bromo-3-methyl-
butanoyl chloride

4. Amides. Amides of carboxylic acids ($RCONH_2$) are named by changing the -oic acid (-ic in the case of the common names like acetic and formic) to -amide.

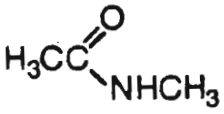


3-methylbutanamide

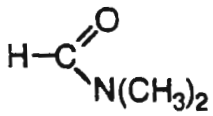


2-pentenamide

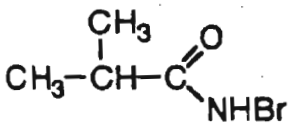
If one or both hydrogens on the nitrogen have been replaced, the resulting compounds are named as N-substituted amides.



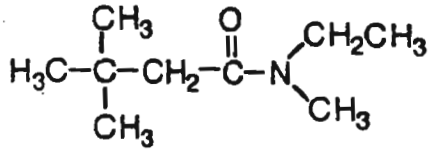
N-methylethanamid
(N-methylacetamide)



N,N-dimethylmethanamide
(N,N-dimethylformamide or DMF)

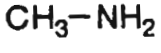


N-bromo-2-methylpropanamide

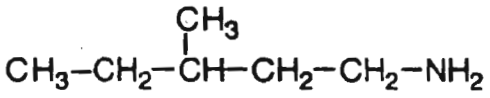


N-ethyl-N,3,3-trimethylbutanamide

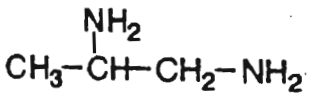
J. Amines. Amines are named as alkanamines, and the suffix is -amine. The prefix for the amine group is amino- and is used only when a functional group of higher priority is present. Amines rank below alcohols but higher than alkenes or alkynes. Amines are primary (RNH_2), secondary (R_2NH), or tertiary (R_3N) depending upon the replacement of one, two or three hydrogen atoms of the parent molecule, ammonia (NH_3).



methanamine
(methyl amine)

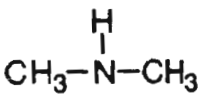


3-methyl-1-pentanamine

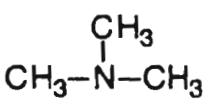


1,2-propanediamine
(propylenediamine)

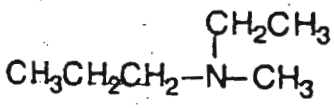
With secondary (2°) and tertiary (3°) amines, the longest chain attached to the nitrogen atom is selected as the parent chain. The other groups bonded to nitrogen are named with prefixes, preceded by the letter N to show that the groups are attached to nitrogen.



N-methylmethanamine
(dimethylamine)



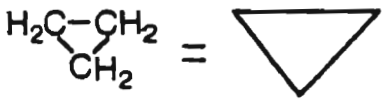
N,N-dimethylmethanamine
(trimethylamine)



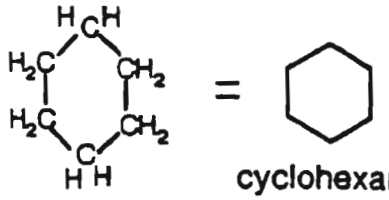
N-ethyl-N-methyl-1-propanamine

K. Alicyclic Compounds

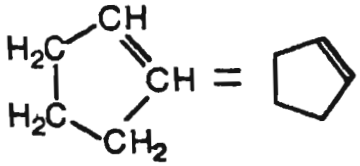
Monocyclic aliphatic (as opposed to aromatic) compounds are named by counting the number of carbons in the ring and prefixing cyclo- to the name that would be given to the corresponding open chain compound.



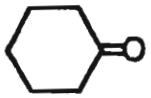
cyclopropane



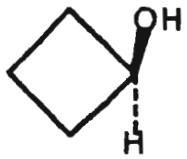
cyclohexane



cyclopentene

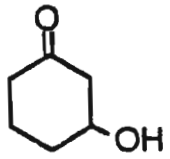


cyclohexanone

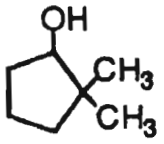


cyclobutanol

Since all positions are equivalent in an unsubstituted cycloalkane, no number is needed to show the position of a single substituent or functional group. If two or more groups of any kind are attached to the ring, the group of highest priority is assigned position 1, and the ring is numbered from there in the direction that gives the lowest numbers to the other substituent (s). Several examples are given below.

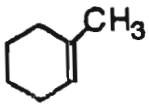


3-hydroxycyclohexanone

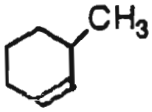


2,2-dimethylcyclopentanol

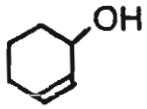
1,3-cyclohexadiene



1-methylcyclohexene

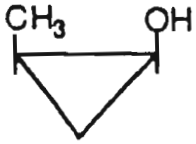


3-methylcyclohexene

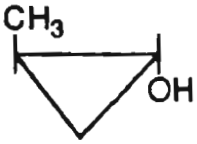


2-cyclohexenol
(or 2-cyclohexen-1-ol)

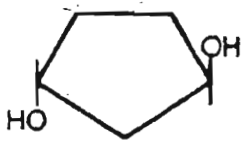
When two substituents are attached to different carbon atoms, the prefixes cis- & trans- are used to show whether they lie on the same side or on the opposite side of the ring.



cis-2-methylcyclopropanol

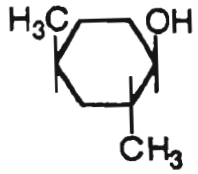


trans-2-methylcyclopropanol

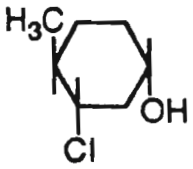


trans-1,3-cyclopentanediol

When there are three or more groups attached to a ring, the prefixes cis- and trans- refer to the relationship of the designated substituent to the group at carbon-1.

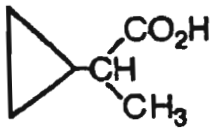


2-trans-4-cis-2.4-dimethylcyclohexanol

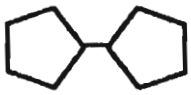


cis-3-chloro-trans-4-methylcyclohexanol

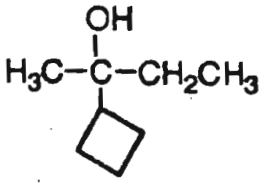
In some structures the cycloalkyl group is a substituent to an acyclic chain or to another ring.



2-cyclopropylpropanoic acid

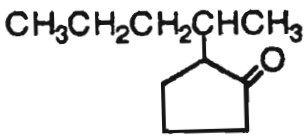


cyclopentylcyclopentane

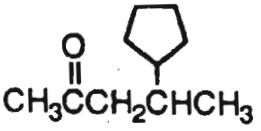


2-cyclobutyl-2-butanol

When a ring and a chain are both present, the name is based on whichever is attached to the functional group of highest priority.

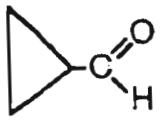


2-(1-methylbutyl)cyclopentanone

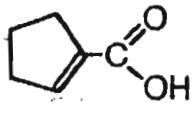


4-cyclopentyl-2-pentanone

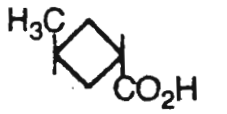
To name an aldehyde or a carboxylic acid in which the functional group is attached directly to a ring, the suffix carboxaldehyde or carboxylic acid is appended to the name of the cycloalkane.



cyclopropanecarboxaldehyde



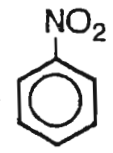
2-cyclopentenecarboxylic acid



trans-3-methylcyclo-butane carboxylic acid

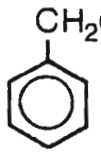
L. Aromatic Compounds.

Those benzenes which are substituted only with groups normally named as substituents, e.g., alkyl, alkoxy, halo, and nitro groups, are named as derivatives of benzene.



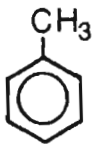
Nitrobenzene

Chlorobenzene

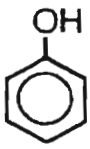


Ethylbenzene

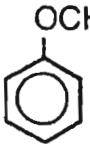
A number of important benzenes have common names which have served as base names for a "common" systematic nomenclature of aromatic compounds. These compounds also have IUPAC names based on rules we have already discussed. Some of these compounds with their systematic- and common names (in parentheses), are shown below. **Both systematic and common names should be memorized.**



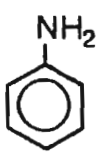
Methylbenzene (Toluene)



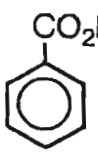
Benzenol (Phenol)



Methoxybenzene (Anisole)



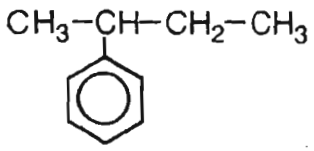
Benzeneamine (Aniline)



Benzenecarboxylic acid (Benzoic acid)

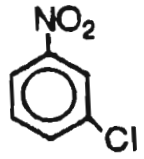
The past literature used only the common names. The current literature uses a mixture of systematic and common names but the IUPAC nomenclature committee tries to move in the direction of increased simplicity while the Chemical Abstracts (CA) service gives first consideration to the requirements of computer assisted indexing. Consequently, CA has created its own nomenclature without regard for IUPAC rules.

At times an aromatic compound will be named using the aromatic ring as a substituent. For example, the compound below could be named 2-phenyl butane

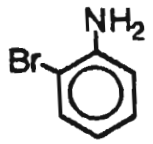


as well as sec-butylbenzene (see pg. 4 for the names of substituents). The choice of a name when more than one name is acceptable depends on which portion of the molecule you wish to emphasize.

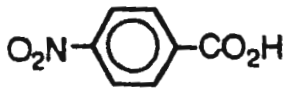
Disubstituted benzenes must be numbered to indicate the positions of the two substituents. One substituent is assigned the number one (1), which is usually understood and not written, and the second substituent is numbered accordingly. The terms ortho, (o-), meta (m-), and para (p-) are often used in naming disubstituted benzenes and refer to substituents positioned 1,2-, 1,3-, and 1,4- respectively.



3-Chloronitrobenzene
(*m*-Chloronitrobenzene)

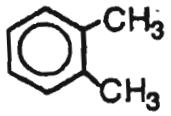


2-Bromobenzenamine
(2-Bromoaniline or
o -Bromoaniline)

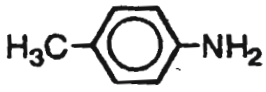


4-Nitrobenzenecarboxylic acid
(4-Nitrobenzoic acid or
p -Nitrobenzoic acid)

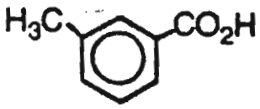
Some disubstituted benzenes also have common names. The dimethylbenzenes are called xylenes, the methylbenzenamines are called toluidines (to-lu'-i-den), and the methylbenzenecarboxylic acids are called toluic acids.



1,2-Dimethylbenzene
(*o* -Xylene)

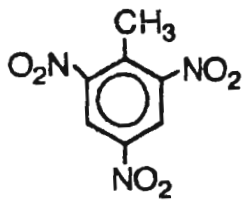


4-Methylbenzenamine
(*p* -Toluidine)

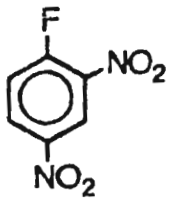


3-Methylbenzenecarboxylic acid
(*m* -Toluic acid)

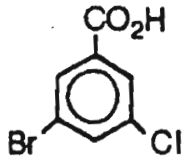
The multisubstituted benzenes are numbered to indicate the positions of the substituents. Again one substituent is assigned the number one (1) and the other substitutents are numbered accordingly.



2,4,6-Trinitrotoluene
(TNT)



2,4-dinitrofluorobenzene



3-Bromo-5-chlorobenzene
carboxylic acid
(3-bromo-5-chlorobenzoic acid)

Table 1 IUPAC Nomenclature

Class of Compound	Structure	Substitutive Name If Prefix	Substitutive Name If Suffix	Functional Class Name	Structural Formula / Substitutive Name	Functional Class Name
Alkane	R-H		-ane		$(CH_3)_2CHCH_2CH_3$ 2-methylbutane	
Alkene	$R_2C=CR_2$		-ene		$H_2C=CHCH_2CH_2CH_2CH_3$ 1-hexene	
Alkyne	RC≡CR		-yne		$H_3CC\equiv CCH(CH_3)_2$ 4-methyl-2-pentyne	
Alicyclic		cyclo-			3,6-dimethylcyclohexene	
Alkyl Halide	R-F	fluoro-		alkyl fluoride	$CH_3CH_2CH_2CH_2F$ 1-fluorobutane	butyl fluoride
	R-Cl	chloro-		alkyl chloride	$(CH_3)_2CHCH_2Cl$ 1-chloro-2-methylpropane	isobutyl chloride
	R-Br	bromo-		alkyl bromide	$CH_3CH_2CHBrCH_3$ 2-bromobutane	sec-butyl bromide
	R-I	iodo-		alkyl iodide	$(CH_3)_3CI$ 2-iodo-2-methylpropane	tert-butyl iodide
Alcohol	R-OH	hydroxy	-ol	alkyl alcohol	$(CH_3)_2CHCH_2CH_2OH$ 3-methyl-1-butanol	isopentyl alcohol
Ether	R-O-R	alkoxy-		dialkyl ether	$CH_3OCH(CH_3)_2$ 2-methoxypropane	isopropyl methyl ether
Aldehyde	$RC(=O)H$	oxo formyl	-al		$CH_3CH_2CH_2CH_2CHO$ pentanal	
Ketone	$R-C(=O)-R$	oxo	-one	dialkyl ketone	$CH_3C(=O)CH_2CH_2CH_2CH_2CH_3$ 2-heptanone	methyl pentyl ketone
Carboxylic acid	$RC(=O)OH$	carboxy-	-oic acid		$CH_3CH_2CH_2CH_2C(=O)OH$ pentanoic acid	
amine primary	RNH_2	amino-	-amine	alkyl amine	$CH_3CH_2CH_2CH_2NH_2$ 1-butanamine	butyl amine
amine secondary	R_2NH	alkyl amino-	-amine	dialkyl amine	$CH_3NHCH_2CH_2CH_3$ N-methyl-1-propanamine	methyl-propyl-amine
amine tertiary	R_3N	dialkyl amino	-amine	trialkyl amine	$(CH_3)_2NCH_2CH_2CH_3$ N,N-dimethyl-1-propanamine	dimethyl propyl amine

III. **Other Systematic Nomenclature**

In addition to the IUPAC substitutive nomenclature described in Part II above, other systems of nomenclature have evolved over the years and are used to some extent.

The systems of functional class names is the most comprehensive of these. The name of the class of compounds (i.e., alcohol, ether, ketone, chloride, amine, etc) is preceded by the name of the alkyl group.The use of this system is illustrated in Table 1.

IV General References on Nomenclature.

James G. Traynham, *Organic Nomenclature: A Programmed Introduction*, Fifth Edition, Prentice Hall, 1997

A Guide to IUPAC Nomenclature of Organic Compounds, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, Oxford, 1993. Prepared by R. Panico, W.H.Powell and K.C.Richter

Nomenclature of Organic Chemistry Sections A,B,C,D,E,F, and H. 4th Edition (1982, c1979, Pergamon Press, Oxford, New York, edited by J. Rigaudy and S.P. Klesney

International Union of Pure and Applied Chemistry
1957 Report of The Commission on The Nomenclature of Organic Chemistry
(now known as the 1957 IUPAC Rules
Definitive Rules for Nomenclature of Organic Chemistry
Journal of the American Chemical Society, 1960, **8 2**, pages 5545-5584

Nomenclature of Reaction Intermediates

The rules for naming neutral and charged organic species follow the same rules learned for more stable classes of compounds. A parent hydride name such as alkane, alkene or alkyne is modified by a suffix that signifies the particular type of functionality. Systematic suffixes for some reaction intermediates are given in the Table below.

Parent Hydride	Formal Operation	Intermediate	Suffix	examples
R—H	loss of H·	R·	-yl	·CH_3 methyl radical
R_2CH_2	loss of 2 H·	R_2C:	-ylidene	CH_3CH: ethylidene
R—H	loss of H^+	$R:^-$	-ide	$CH_3:^-$ methide anion
R—H	loss of $H:^-$	R^+	-ylium	CH_3^+ methanylium
R—H	plus H^+	RH_2^+	-ium	CH_5^+ methanium

Substitutive Name Prefixes and Suffixes for Some Important Functional Groups

[Arranged in Descending Order of Preference for Citation as Suffixes]

Class	Formula of Group[a]	Prefix[b]	Suffix[c]
Radicals	RR'CH·		-yl
Anions	RR'R"C: $^-$		-ide
Cations	RR'R"C $^+$		-ylium
Carboxylic acids	—COOH	carboxyl	-carboxylic acid
sulfonic acids	—SO_3H	sulfo	-sulfonic acid
Esters	—COOR	R-oxycarbonyl	R...-carboxylate
"	—(C)OOR[a]	-----	R...oate
Acid Halides	—COX	halocarbonyl	carbonyl halide
"	—(C)O—X[a]		-oyl (or-yl) halide
Amides	—CO—NH_2	aminocarbonyl or carbamoyl	-carboxamide
"	—(C)O—NH_2[a]	-----	amide
Nitriles	—C:::N:	cyano	-carbonitrile
"	—(C):::N:	-----	-nitrile
Aldehydes	—CHO	formyl	-carbaldehyde[e]
"	—(C)HO	oxo	-al
Ketones	(C)::O	oxo	-one
Alcohols	—OH	hydroxy	-ol
Phenols	—OH	hydroxy	-ol
Thiols	—SH	sulfanyl	-thiol
Amines	—NH_2	amino or azanyl	-amine
Ethers	—OR	R-oxy	----
Sulfides	—SR	R-sulfamyl	-

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a = C in parentheses is included in the stem of the parent chain and not in the prefix or suffix.
b = Functional group is treated as a substituent
c = Functional group is part of a parent compound; suffix is added to name of corresponding hydrocarbon.
d = R is alkyl or aryl, etc: when R is part of a prefix, the name of the R group is written as part of the prefix name without a hyphen except with locants. e = *Chemical Abstracts* uses carboxaldehyde.

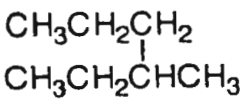
Order of Precedence: carboxylic acid, ester, acid halide, amide, aldehyde, ketone, alcohol, amine, alkene, alkyne

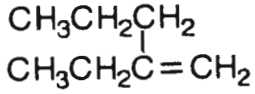
V. Problems

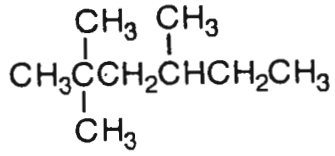
1. Draw structures for each of the following compounds. If a name is not consistent with IUPAC rules, suggest a better name. If a name is incorrect give the correct name.

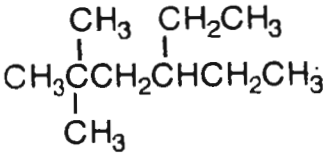
a. 3-isopropyl-2,3-dimethylheptane
b. (Z)-3-bromo-2-hexene
c. 4-ethyl-2-hexyne
d. 6-chloro-3-hexen-2-ol
e. 4-cyclopropyl-2-pentanone
f. 3-ethyl-4-methyl-3-pentenal (E- or Z-?)
g. N-Methyl-2-buten-1-amine
h. 3-bromo-2-methyl-4-oxobutanoic acid
i. cyclopentanecarboxylic acid
j. tert-butyl-2-ethyl-3-pentenoate (E- or Z- ?)
k. 4-nitrophenylbenzenecarboxylate
l. potassium-3-bromopropanoate
m. phenylethanoyl chloride (phenylacetylCl)
n. N-ethyl-6-chloro-4-phenylhexanamide
o. 5-methyl-2-cyclohexen-1-ol
p. 4-methylbenzenol (p-methylphenol)
q. 3,5-dinitrobenzoic acid
r. 2,3-diethylbutane.

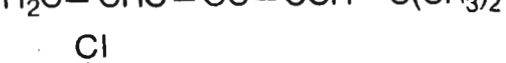
2. For each of the following compounds supply the IUPAC substitutive name and, where possible, another name.

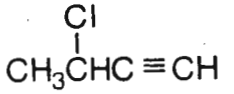
a. 

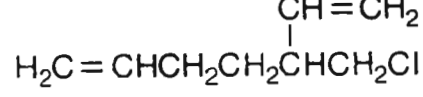
b. 

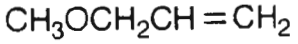
c. 

d. 

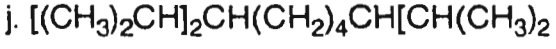
e. 

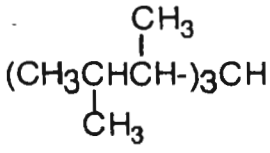
f. 

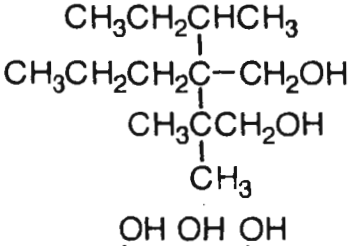
g. 

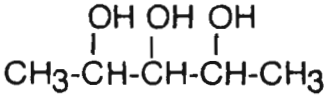
h. 

i. 

j. 

k. 

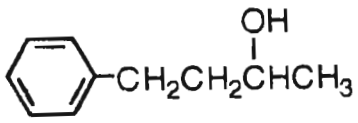
l. 

m. 

n.

o.

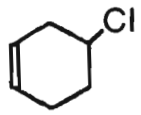
Q. 2 continued. Give IUPAC names and another name if possible.

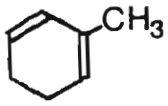
p. 

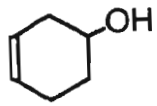
q. $HOCH_2CH_2CH_2CH_2CH_2CH_2CHCH_2CH_2CO_2H$ (CO_2H on the CH)

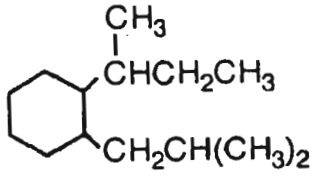
r. $(CH_3)_3CCH_2CHCH_2CH_2CH_2CH_3$ (CH_2OH on the CH)

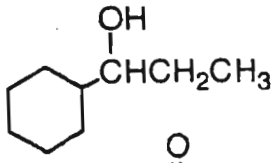
3. For each of the following compounds give the IUPAC substitutive name and, where possible, another name.

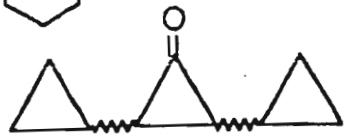
a. 

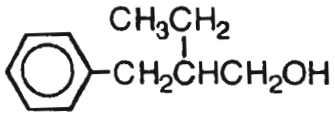
b. 

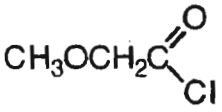
c. 

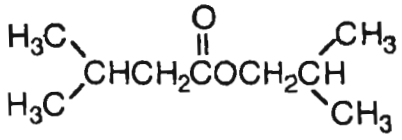
d 

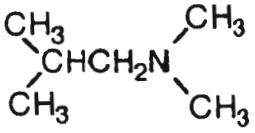
e 

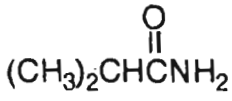
f 

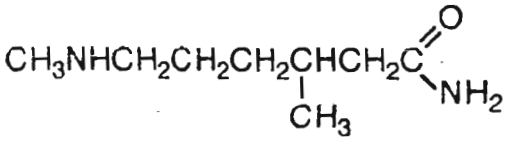
g. 

h 

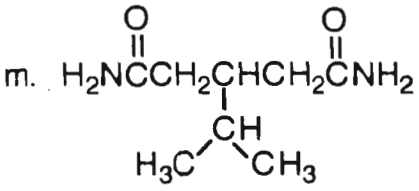
i 

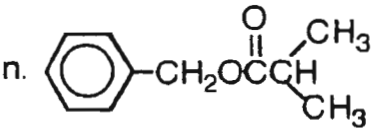
j 

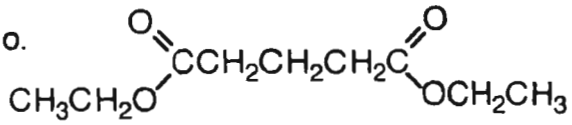
k 

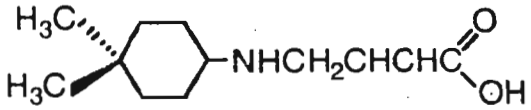
l. 

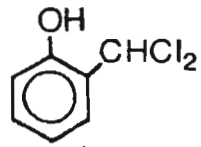
3. continued....give IUPAC substitutive name and where possible another name.

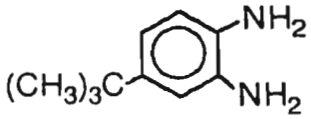
m. 

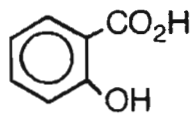
n. 

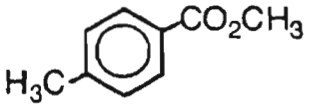
o. 

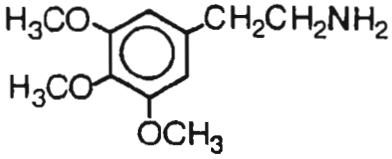
p. 

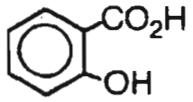
q. 

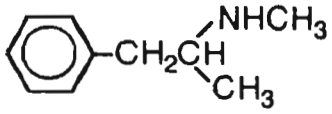
r. 

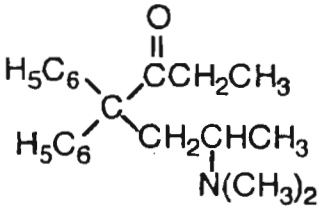
s. 

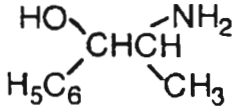
t 

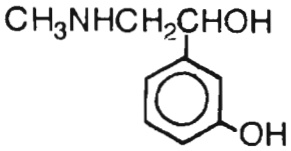
u. 

v. 

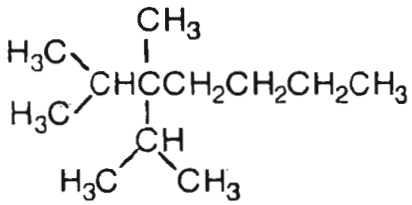
w. 

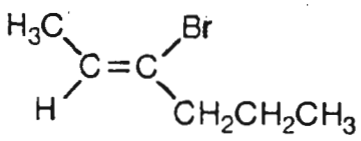
x. 

y. 

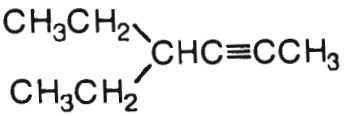
z. 

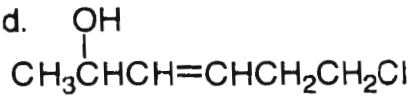
Answers to Nomenclature Problems on page 22.

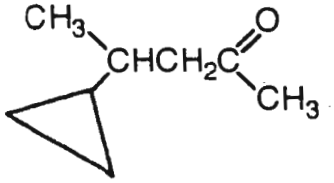
1. a 

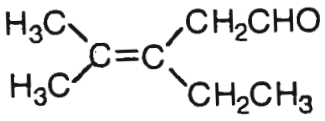
b. 

Answers To Nomenclature Problems on pages 22-24 continued

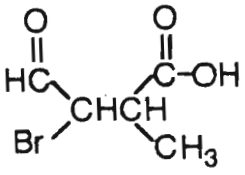
c. 

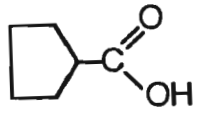
d. 

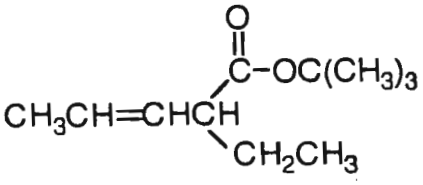
e. 

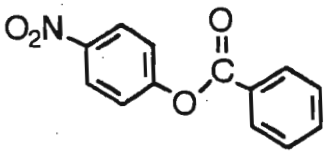
f. 

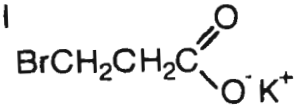
g. $CH_3CH{=}CHCH_2NHCH_3$

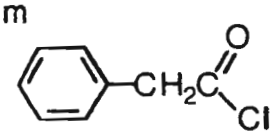
h. 

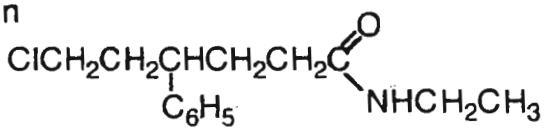
i. 

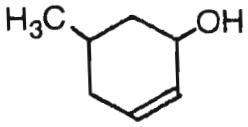
j. 

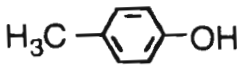
k. 

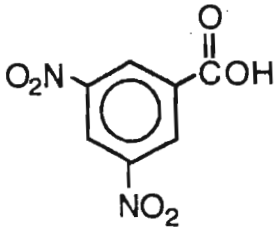
l 

m 

n 

o 

p 

q 

2 a. 3-methylhexane

b. 2-ethyl-1-pentene

c. 2,2,4-trimethylhexane

d. 4-ethyl-2,2-dimethylhexane

e.8-methyl-1,7-nonadiene-3,5-diyne

f. 3-chloro-1-butyne

g. 3-(chloromethyl)-1,6-heptadiene

h. 3-methoxypropene

i. 3,3-di-tert-butyl-2,2,4,4-tetramethylpentane also (tetra-tert-butylmethane)

j. 3,8-diisopropyl-2,9- dimethyldecane

k. 4-(1,2-dimethylpropyl)- 2,3,5,6-tetramethyl heptane

l. 2-sec-butyl-3,3-dimethyl-2-propyl-1,4-butanediol

m. 2,3,4-pentanetriol

m. 2,3,4-pentanetriol

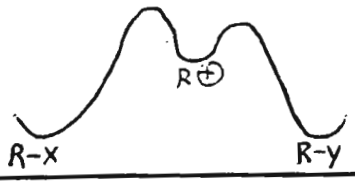
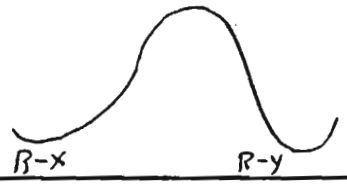
Answers to Nomenclature problems continued.

2. n. 2-(dimethylamino)ethanol
   o. 2-hexylpropanedial
   p. 4-phenyl-2-butanol
   q. 2-(6-hydroxyhexyl)pentanedioic acid
   r. 2-neopentyl-1-hexanol
3. a. 4-chlorocyclohexene
   b. 2-methyl-1,3-cyclohexadiene
   c. 3-cyclohexen-1-ol
   d. 1-sec-butyl-2-isobutylcyclohexane
   e. 1-cyclohexyl-1-propanol
   f. 2,3-dicyclopropylcyclopropanone
   g. 2-benzyl-1-butanol
   h. methoxyethanoyl chloride (ie. methoxyacetyl chloride)
   i. isobutyl-3-methylbutanoate (isobutylisovalerate)
   j. N,N,2-trimethyl-1-propanamine (isobutyldimethylamine)
   k. 2-methylpropanamide (isobutyramide)
   l. 3-methyl-6-(methylamino)hexanamide
   m. 3-isopropylpentanediamide
   n. benzyl-2-methylpropanoate (benzylisobutyrate)
   o. diethylpentanedioate (diethylglutarate)
   p. 4-(4,4-dimethylcyclohexylamino)3-hydroxy-2-methylbutanoic acid
   q. 2-(dichloromethyl)benzenol (o-dichloromethylphenol)
   r. 4-tert-butyl-1,2-benzenediamine
   s. 2-nitrobenzenecarboxylic acid (o-nitrobenzoic acid)
   t. methyl-4-methylbenzene carboxylate (methyl-p-toluate)
   u. 2-(3,4,5-trimethoxyphenyl)ethanamine (mescaline)
   v. 2-hydroxybenzene carboxylic acid (o-hydroxybenzoic acid; salicyclic acid)
   w. N-methyl-1-phenyl-2-propanamine (methamphetamine)
   x. 6-(dimethylamino-4.4- diphenyl-3-heptanone (methadone)
   y. 2-amino-1-phenyl-1-propanol (norephedrine)
   z. 1-(3-hydroxyphenyl)-2-methylaminoethanol (phenylephrine)

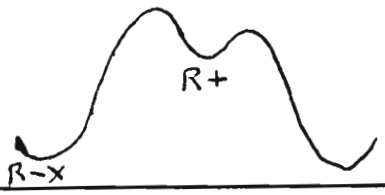
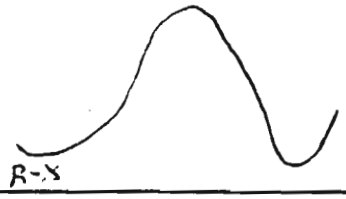
The second name given in parentheses is not the IUPAC name but a common name likely to be encountered for this compound.

Comparison of S_n1 and S_n2 Reactions

$$R\text{-}X + :Y^- \longrightarrow R\text{-}Y + :X^-$$

		S_N1	S_N2
Mechanism		unimolecular ionization; intermediate cation; two-step-reaction	Bimolecular reaction; backside attack; one-step reaction
Kinetic Order		First order $v = k_1[R\text{-}X]$	Second order $v = k_2[R\text{-}X][Y^-]$
Reaction Profile			
Occurrence of molecular rearrangements		Rearrangement will occur by 1,2-shift if a more stable carbocation will result	no rearrangements
Stereochemistry		Mostly racemization	Inversion of configuration
Effects of structure of the alkyl group on reactivity	Steric Effects	Size of groups has little effect on the rate of reaction	Large groups decrease rate through steric inhibition of backside attack. Reactivity: 1° > 2° > 3°
	Electronic Effects	Neutralization or delocalization of charge on the intermediate by induction or resonance. Rate increases allyl > 3° > 2° > 1°	Only small effects on rate; allyl halides and alpha halo ketones are special cases of compounds that react rapidly by this mechanism.
Effect of the leaving group		As the basicity of the leaving group decreases, rates of both S_N1 and S_N2 reactions are increased	
Effect of the strength of the nucleophile		Little or no effect	Stronger nucleophile increases rate
Solvent effects		Rate enhancement by polar solvents	Slight decrease in rate by polar solvent for negative nucleophiles.

Comparison of E1 and E2 Reactions

	E1	E2
Mechanism	Unimolecular ionization; intermediate catioin forms two-step reaction; competitive with S_N1	Bimolecular, one-step, concerted reaction; competitive with S_N2
Kinetic Order	First Order $v = k_1$[alkyl halide]	Second Order $v = k_2$[alkyl halide] [base]
Reaction Profile		
Occurrence of Molecular Rearrangements	Rearrangement will occur by 1,2-shift if a more stable carbocation will result as in S_N1	No rearrangements
Stereochemistry	Non-stereospecific	anti elimination occurs via a planar transition state
Isotope Effects	No isotope effect	large deuterium isotope effect
Effect of Structure of the substrate	Stabilization of intermediate carbocation by delocalization of positive charge increases rate of reactivity 3° > 2° > 1°	Reactivity: 3° > 2 ° > 1° opposite of S_N2
Effect of leaving group	As basicity of leaving group decreases, rates of both E1 and E2 reactions as well as S_N1 and S_N2 increase	
Effect of solvent	Proceeds best in non-basic, polar solvent	Proceeds best with strong base in non-polar, aprotic solvents
Structure of product	The predominant product is the most highly substituted alkene (Saytzeff)	Predominant product is the Saytzeff alkene; the proportion of less highly substituted alkene increases with increasing electron withdrawal by the leaving group and by increasing bulk of the base (Hofmann orientation)

Supplemental Notes on Electrophilic Substitution

ortho-para Directors		meta Directors: Deactivating	
Strongly activating	Weakly Activating	$-NO_2$	$-NH_3^+$
$-O^-$ -OH	-R	$-SO_2OH$	$-NR_3^+$
$-NH_2$, -NHR , NR_2	-Ar , -CH=CHR	$-SO_2OR$	$-PR_3^+$
Moderately activating	Weakly Deactivating	$-CO_2H$	$-SR_2^+$
-OR, -OAr	$-CH_2X$, $-CHX_2$	-COX	$-IAr^+$
-OCOR , -OCOAr	-F , -Cl , -Br , -I	-CHO	$-CX_3$
-NH-COR , -NH-COAr	-CH=CCH-X	-COR	
	X is any electron withdrawing (—I) group	$-C\equiv N$	

Note that *o- / p*-directors structurally fall into three groups:

1) those with at least one pair of unshared electrons on the atom directly attached to the aromatic ring. Such groups release electrons through resonance (+R effect) and always orient *o / p* despite their inductive effects (actually all such groups except $-O^-$ have electron-withdrawing inductive effects.

2) alkyl groups, all of which have electron-releasing inductive effects (+ I), and most of which also exhibit hyperconjugation which is a +R effect.

3) aryl groups and vinyl groups, which have pi electrons conjugated with the aromatic ring undergoing substitution and which can be released by resonance (+ R).

The meta-directors fall into two groups:

1) those in which the atom connected to the aromatic ring is itself doubly (or triply) bonded to some more electronegative atom.

2) those in which a formal positive charge is located on the atom connected to the aromatic ring (or an induced positive charge in the case of substituents such as $-CX_3$).

General Availability of *para*, but not *ortho*, isomers from the *ortho-para* mixture:

Because steric effects most *o / p* -orienting reactions produce much larger amounts of *para* than *ortho* isomers. Furthermore, it is easier to isolate pure *para* isomer from *o/p*mixtures because of its higher m.pt. and consequently lower solubility. Therefore reactions should be considered synthetically useful only for the production of *para* isomers in laboratory syntheses. Important exceptions include the nitration of toluene and the nitration and sulfonation of phenol which give substantial amounts of both *o-* and *p-* isomers. Other exceptions to the general rule will be cited from time to time.

Competition between substituents for control of orientation in disubstituted benzenes:

1) In competition between two substituents, the *o* / *p* directors always prevail over *meta* directors for control over orientation.
2) Strongly activating substituents prevail over all others.
3) Moderately activating substituents prevail over weakly activating and deactivating substituents.
4) In other competitive situations mixtures are formed the exact compositions of which are difficult to predict. Note in particular that the weakly activating substituents do not necessarily prevail over the weakly deactivating substituents.
5) Steric effects may require modifications of these general rules.

D-(+)-Glucose

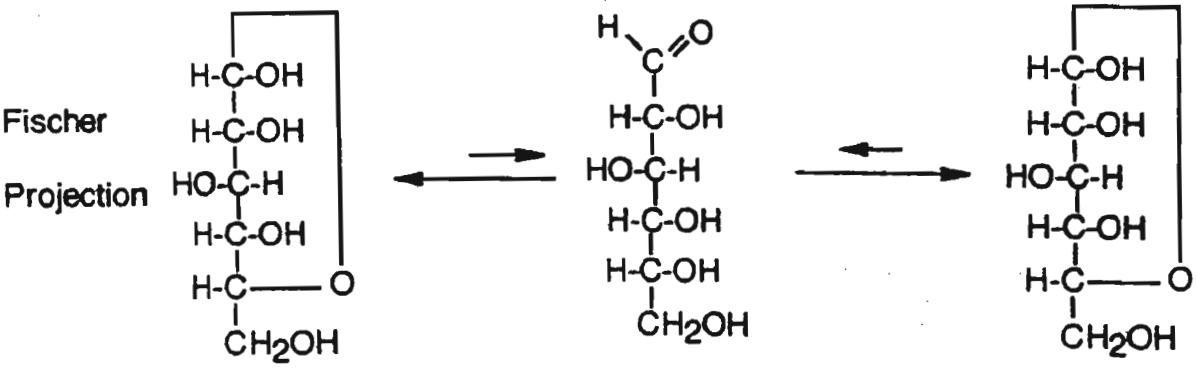
equilibrium mixture
[alpha]$_D$ = + 52.7°

precipitation with ethanol

crystallization from hot water

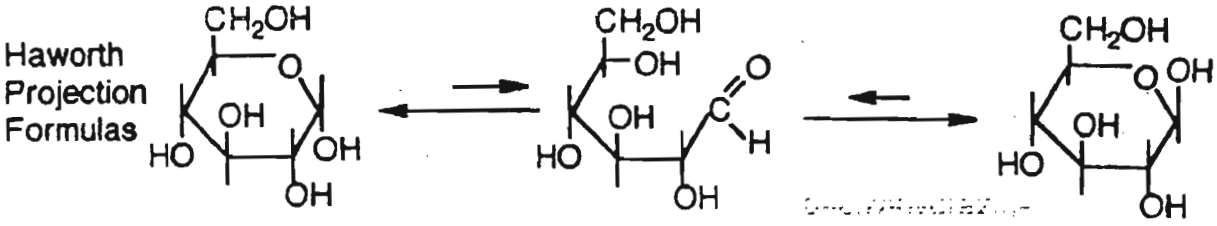
α-D-(+) glucose	open chain form	β-D-(+)glucose
(α-D-(+)-glucopyranose)	(never isolated)	(β-D-(+)-glucopyranose)
m.p. = 146°		m.p. = 150°
$[\alpha]_D$ = + 112°		$[\alpha]_D$ = 19°

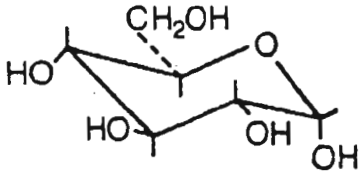
Fischer Projection



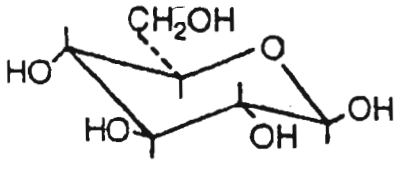
36.2% of the equilibrium mixture | 0.02 % of the mixture | 63.8 %

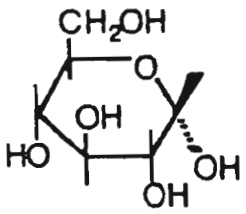
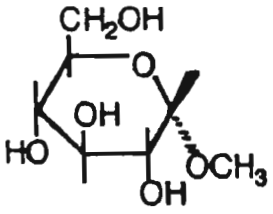
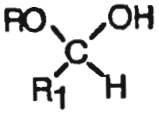
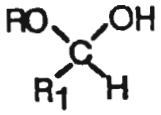
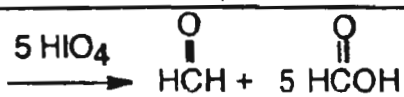
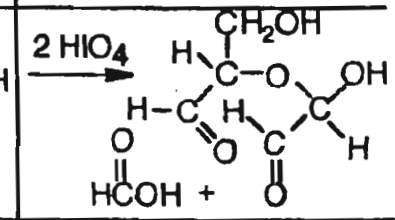
Haworth Projection Formulas





Conformations

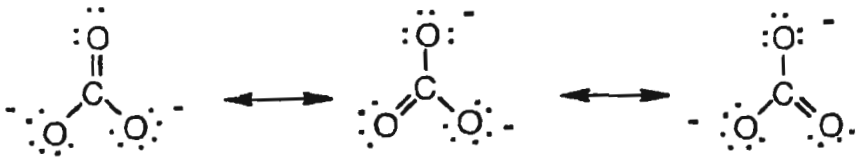


Chemical Class Nomenclature	Glycose α-D-glucopyranose (or β)	Glycoside methyl-α-D-glucopyranoside
Structural Formula		
Functional Group	Hemiacetal: 	Acetal: 
Anomerism stereoisomerism about C-1	Two anomers a and b	Two anomers a and b
Interconversion of anomers	In solution either anomer undergoes mutarotation to give the equilibrium mixture	No interconversion
Equilibrium with open chain aldehyde	Trace of aldehyde in equilibrium mixture	No equilibrium with any open-chain form.
Interconversion of glycose and glycoside	Reaction of either anomer with ROH and dry HCl gives mixture of a- & b-glucosides	Hydrolyzed by aqueous acid under very mild conditions to give a mixture of a- & b-glucose
Mild Oxidation	Reducing sugar is oxidized by Br_2/H_2O, Ag^+, Cu^{++}	Non reducing sugar is not oxidized
Periodic Acid Oxidation		
Reaction with phenylhydrazine	1 $C_6H_5NHNH_2$ → phenyl-hydrazone 3 $C_6H_5NHNH_2$ → phenyl-osazone + $C_6H_5NH_2$ + NH_3	no reaction with phenyl-hydrazine except in the presence of acid which hydrolyzes glucoside to glucose, which then reacts with phenylhydrazine.

Conjugation and Resonance

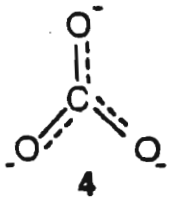
The question often arises " How accurately do our electron dot and dash line structures represent real molecules?" The answer sometimes is "...not so well." In an effort to deal with the problem of the inadequacy of our symbols for molecules, resonance theory was born. What resonance theory says is: (i) Whenever a molecule can be represented by two or more structures that differ only in the arrangement of electrons and have the same spatial arrangement of atoms, there resonance exists. (ii) The molecule is said to be a hybrid of all the different electronic structures and cannot be satisfactorily represented by any one of the structures alone. (iii) If the different structures are approximately or exactly equal in energy, then resonance is important. The contribution of each structure to the hybrid, or real molecule, depends on the energy content or relative stability of that structure; more stable structures make larger contributions than high energy, less stable structures. (iv) The resonance hybrid, ie the real molecule, is more stable than any of the contributing structures.

Previously we have learned that carbonate ion (CO_3^{2-}) has three Lewis style electron dot-dash structures (**1**,**2** and **3**) for the 24 electrons. These structures show one

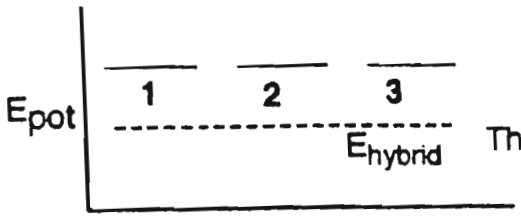


1 **2** **3**

oxygen atom to be held by a double bond and two by two single covalent bonds. In compounds that have carbon to oxygen single bonds, the bond lengths are 1.36 Å on the average and compounds with carbon oxygen double bonds have bond lengths of 1.23 Å. What should we expect for carbonate ion, one short carbon to oxygen double bond (C=O) and two longer single carbon to oxygen bonds (C—O)? *In reality all three* atoms have the same bond distance of 1.31 Å. We get around the failure of structure **1** to portray carbonate ion accurately by drawing two additional hypothetical structures **2** and **3** connecting them with a double headed arrow which means a resonance structure. None of these resonance structures or resonance contributors will be a correct representation for the molecule. The actual molecule or real ion will be a hybrid of these structures. What might a hybrid look like? Structure **4** below is a possibility.



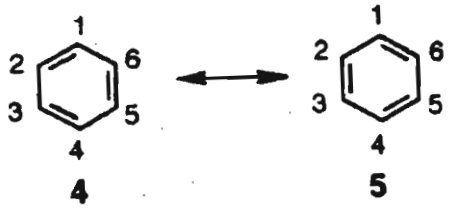
4



Three equal energy structures

The hybrid is lower in energy than 1 to 3

Benzene was drawn by Kekule as 1,3,5-cyclohexatriene. When someone suggested that this would mean that benzene should be a distorted hexagon and have alternate short carbon-carbon double bonds of 1.34 Å bond lengths and long single bonds of 1.54 Å , Kekule said well there is an equilibrium between 1,3,5-cyclohexatriene and its 2,4,6-cyclohexatriene isomer. We now know that this idea of an equilibrium is wrong and that the orbitals are not localized but combined in a closed loop so that the electrons move continuously in a single molecular orbital derived from p type atomic orbitals of carbon. That benzenes are planar with all six carbon to carbon bonds of equal length has been shown by an x-ray crystal structure determination on



4 5

All six carbon to carbon bonds have the same length ~ 1.39 Å.

hexamethylbenzene[1].

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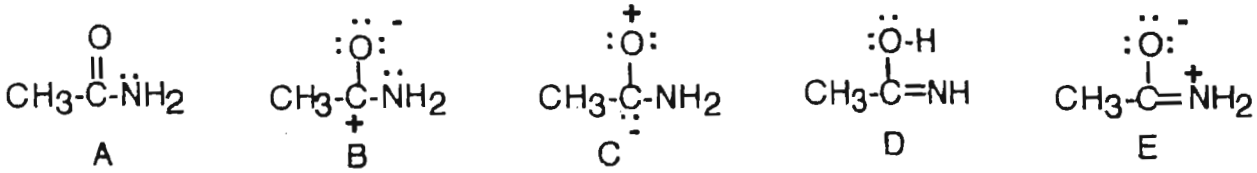
1. Lonsdale, Kathleen, Nature (1928), **122**, 810; Proc. Roy. Soc. London A (1929), **123**, 494-515 non vide.

Resonance Problems

1. Write the significant contributing structures to represent each of the following resonance hybrids: (a) methyl nitrite (CH_3ONO); (b) methyl formate ($HCOOCH_3$) ; boron tribromide (BBr_3).

2. Arrange the resonance contributors depicted in problem 1 above in order of decreasing stability. Explain the reasons for this order.

3. Acetamide is a resonance hybrid, usually represented by A below. Which of the structures B - E can be considered contributing structures of the acetamide hybrid?



A B C D E

Arrange the contributing structures in order of decreasing stability and explain the reasons for this order.

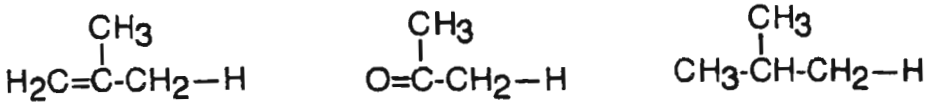
4. Account for the fact that addition of hydrogen chloride to vinyl chloride ($H_2C=CHCl$) gives 1,1,-dichloroethane and not 1,2-dichloroethane.

5. Account for the fact that the formation of a bromohydrin from an alkene and aqueous bromine follows the Markovnikov rule in which the electrophilic bromine atom ends up on the less substituted carbon and the nucleophilic OH group on the more highly substituted carbon.

6. Account for the fact that guanidine ($H_2N\text{-}C(=NH)\text{-}NH_2$) is a very strong base.

[Hint: Which nitrogen atom accepts an H^+?]

7. Which of the compounds below is the most acidic? Which is the least acidic? Why? [Hint: Other factors in addition to resonance must be considered]



A B C

8. Draw one of the hyperconjugation structures for each of the following carbocations:

A $(CH_3)_3C^+$ B $(CH_3CH_2)_3C^+$

How many additional hyperconjugation structures exist for each? On the basis of resonance stabilization, which of the two carbonium ions is predicted to be the more stable? In fact, B is more stable than A. What factors in addition to resonance must be considered?

Spectrometric Determination of Functional Groups[1]

It is possible to determine which functional group (s) an unknown has by means of infrared spectroscopy. When supplemented with proton-nmr and carbon-thirteen nmr analyses, functional group diagnosis can be done with much greater confidence than by means of the simple chemical tests described on pages 35-37. See Pg. 38 &

[1] Spectrometric Identification of Organic Compounds, Silverstein, R.M.; Webster, F.X., 6th Ed.,Wiley, 1998.

Some Tests Used In Qualitative Organic Analysis A Simplified Scheme of Analysis

(1) H_2SO_4	Solubility in conc. sulfuric acid [+ = soluble; — insoluble]
(2) Beilstein	A hot loop of copper wire is dipped into the compound. The loop is then heated in the edge of a non-luminous flame. [+ = green or blue-green color; — = no green or blue green color]
(3) Na fusion	A mixture of sodium and the compound is heated. The mixture is decomposed with water, filtered and the filtrate after acidification with nitric acid, boiling to expel HCN and H_2S, is treated with HNO_3 (aq). + = white or yellow precipitate; — no precipitate
(4) Br_2	A 2 or 3% solution of bromine in CCl_4 is added dropwise to a solution of the compound in carbon tetrachloride. [+ = decolorization with no evolution of HBr gas; — = no decolorization or slower decolorization with concomitant evolution of HBr].
(5) Baeyer	The compound is treated with a dilute, neutral, aqueous $KMnO_4$ solution at room temperature. [+ = bleaching of the purple permanganate color and the appearance of a brown precipitate of manganese dioxide; — = no, or very slight change in the purple color of potassium permanganate within 5 minutes].
(6) CrO_3	A mixture of the compound and a solution of chromium trioxide in aqueous sulfuric acid is left for a short time at room temperature. [+ = an opaque blue-green suspension within 2- 10 seconds; — = orange color of the reagent is unchanged during this time.]
(7) $Cu(NH_3)_2^+$ $Ag(NH_3)_2^+$	The compound is added to any one of the following solutions: (a) aqueous solution of the diammine copper ion or of the diammine silver ion; (b) a 5 % solution of $AgNO_3$ in 95% ethanol; (c) an alkaline solution of potassium and mercuric iodides. [+ = formation of an immediate precipitate (chocolate colored with Cu^+, white or grey-white with Hg^{++}); — = no precipitate even after 6 minutes at +50°].

tests continued on the next page

(8) NaI The compound is mixed with a solution of sodium iodide in dry acetone. If no precipitate appears within 3-4 minutes at room temperature, the mixture is heated at 50° up to 6 minutes. [++ = precipitate within 3-4 minutes at room temperature; + = precipitate only when heated at 50°; — = no precipitate even after 6 minutes of mixing and heating.

(9) $AgNO_3$ The compound is added to a 2 % solution of silver nitrate in ethanol. If no precipitate is observed within 5 minutes, the solution is heated to boiling for several minutes. [++ = a precipitate that is insoluble in dilute nitric acid at room temperature; + = precipitate only on heating.]

(10) Na (H_2) A small amount of sodium is added to a liquid organic compound. If the sodium dissolves , the solution is then mixed with ether. [+ = sodium dissolves accompanied with the evolution of a gas, and a precipitate is formed when ether is added; — = only a slight or no evolution of gas and little, or no, precipitate is formed the addition of ether.]

(11) Lucas The compound is dissolved in a solution of zinc chloride in conc. hydrochloric acid at room temperature. [++ = an immediate turbidity, emulsion or separation of an insoluble layer; + = the solution becomes cloudy in 2-5 minutes; — = the solution remains clear for at least five minutes.]

(12) CHI_3 iodoform test A solution of the compound and potassium iodide in methanol is treated with aqueous sodium hypochlorite. If no precipitate forms within 5 min., 5 mL of water is added. [+ = yellow precipitate; — = no precipitate.]

(13) HIO_4 The compound is dissolved in an aqueous or aqueous-dioxane solution containing paraperiodic acid ($H_5IO_6 = HIO_4.2H_2O$) and a little nitric acid. One or two drops of 5 % aqueous silver nitrate solution is added. [+ = a white precipitate of $AgIO_3$ appears immediately; — = no immediate white precipitate or a brown precipitate which redissolves on shaking.

(14) $NaHCO_3$ The compound alone or dissolved in methanol is mixed with 5 % aqueous sodium bicarbonate. [+ = evolution of a gas; — = no gas evolved.]

(15) DNP A solution of the compound in ethanol is mixed with a solution of 2,4-dinitro-phenylhydrazine in ethanol-water containing a strong acid (sulfuric). The solution is left at room temperature for 15 minutes. [+ = yellow, orange-red or red precipitate (or occasionally an oil); — = a clear yellow solution.

(16) Tollens The compound is added to an aqueous solution of diammine silver ion, $Ag(NH_3)_2^+$ [+ = a silver mirror forms or a black precipitate of metallic silver; — no Ag.]

Limited Interpretations of the Results of some tests used in qualitative organic analysis

(1) H_2SO_4 Saturated hydrocarbons, alkyl halides, simple aromatic hydrocarbons and their halogen derivatives are insoluble; methane is an exception. Alkenes most acetylenes (but not acetylene itself) are soluble. Most organic compounds that contain oxygen, nitrogen and sulfur are soluble in this reagent.

(2) Beilstein A negative test, if conducted with a blank and a control, suggests the absence of Cl, Br, or I in the compound. A positive test should be confirmed by means of sodium fusion followed by a silver nitrate test.

(3) Na fusion Chlorine, bromine and iodine , but not fluorine, can be detected. Modifications of subsequent tests permits distinguishing between Cl, Br and I. Sulfur and nitrogen can also be detected after Na fusion as S^{-2} or CN^-.

(4) Br_2 Alkenes and alkynes decolorize carbon tetrachloride solutions of bromine unless the unsaturated linkage is deactivated by the presence of electron withdrawing groups such as carbonyl or phenyl groups on the ethylenic carbons.Cyclopropanes are said to decolorizedilute bromine solutions.

(5) Baeyer Alkenes and alkynes, but not cyclopropanes, give positive reactions. This is a better test for unsaturation than the bromine test but aldehydes and formic acid and its esters also reduce permanganate. Pure alcohols do not reduce the reagent, although some impurities in some alcohols may do so resulting in the partial bleaching of the test reagent.

(6) CrO_3 Positive tests are given by primary and secondary alcohols and aldehydes but not tertiary alcohols.

(7) $Cu(NH_3)_2^+$ gives a cuprous acetylide salt, $RC{:::}C^-Cu^+$ with terminal alkynes.

$Ag(NH_3)_2^+$ also yields a water insoluble salt with terminal- but not internal alkyne.

$HgCl_2$ + KI + KOH ---> $(RC{:::}C)_2Hg$. This is a white or grey-white precipitate.

Pasto, D.J.; Johnson, C.R., Organic Structure Determination, Prentice Hall, 1969, p339

(8) NaI This test measures the ability of an alkyl chloride or bromide to participate in an Sn2 reaction. ++ reactions are given by primary bromides, allyl halides, α–haloketones, α–haloesters, α–haloamides, and α–halonitriles.

(9) $AgNO_3$ This test measures the ability of an alkyl halide to form a carbocation. Fast formation of AgX precipitate(++) are given by allyl-, benzyl- and tertiary alkyl halides, all classes of alkyl iodides, and α–haloethers. + reactions are given by 1° and 2° chlorides and tertiary bromides on warming.

Organic Structure Determination

During the past thirty to forty years most chemists determined the chemical composition of the products of their reactions with the aid of instrumental methods of analysis. Some of the instruments now routinely available are spectroscopic in nature and involve the passage of light energy through a sample.

Ultraviolet spectroscopy was the first spectrometric analytical tool to be developed in the 1930s and played a primary role in the detection of conjugated dienes, aromatic systems and alpha-beta unsaturated carbonyl compounds.

Infrared spectrometers were the next tool which became available in the 1950s in both industrial and academic research laboratories. With the aid of a good infrared spectrum(IR) one could positively distinguish an aldehyde from a ketone or identify any functional group such as an alcohol, an ether, or a carboxylic acid, etc.

When nuclear magnetic resonance spectroscopy(NMR) became available at first for protons in the late 1950s and then later for carbon thirteen in the 1960s, a new tool increased the research chemist's ability to carry out organic structure determinations.

With improved computer based analytical techniques in mass spectroscopy and in x-ray crystal structure analyses since 1981, chemists were able to determine exact structural details varying from precise molecular weight determinations to exact bond distances and bond angles in the various conformations available to molecules.

Characteristic Infrared Absorptions

Carbonyl Compound	**C=O** stretching signal cm^{-1}	
Aldehydes	1690-1740 strong	aliphatics are 1740-1720
Ketones	1680-1750 strong	acetone is 1715; acetophenone is 1685
Esters	1735-1750 strong	aliphatics are 1735-1750
Carboxylic acids	1680-1760 stronger	aliphatic dimers 1720-1706
amides	1630-1690 strong	primary amides ~1650 in KBr
Hydroxylic Compounds	**O—H** stretching signal	
Alcohols, phenols	3610-3640 sharp	dilute solutions of monomers
Alcohols, phenols	3200-3600 broad	hydrogen bonded
Carboxylic acids	2500-3000 very broad	strongly hydrogen bonded

By means of IR data in Tables of different classes of compounds such as is shown in the Table above, an analyst can diagnose the presence or absence of a functional group in an unknown compound. If the compound also gives a proton NMR signal in the delta = 10.0 ppm region, an aldehyde is present. Further confirmation of the carbonyl group's presence will appear in the C-13 NMR's spectrum near δ = 200 ppm.