Special Topics of IUPAC Nomenclature of Organic Compounds

Nature makes complex compounds regardless of how difficult they are to name. The IUPAC "blue book" describing how to name organic compounds contains over 500 pages. Our short descriptions barely scratch the surface of nomenclature, and very few chemists have a deep understanding of the complexity of the nomenclature conventions.
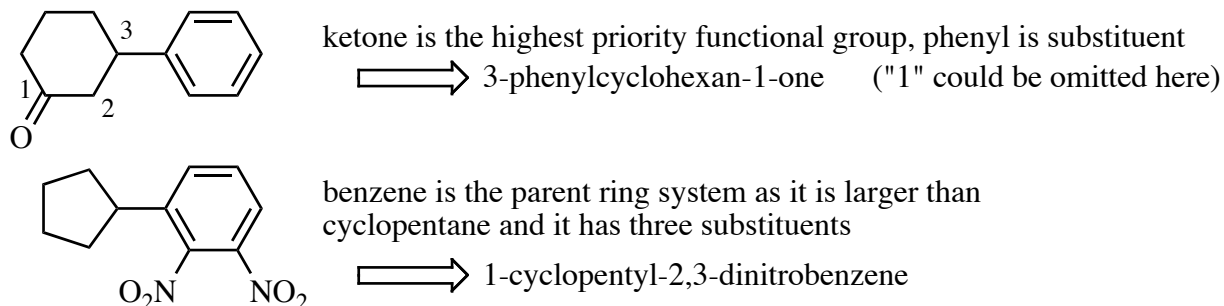
The purpose of this addendum to the IUPAC Nomenclature summary is to describe three areas of naming compounds beyond the basics. They are: 1. Nomenclature of Bicyclic Compounds; 2. Replacement Nomenclature of Heteroatoms; and 3. Stereochemical Designations (R and S, E and Z, the Cahn-Ingold-Prelog system).

SPECIAL TOPIC 1. Nomenclature of Bicyclic Compounds
"Bicyclic" compounds are those that contain two rings. There are four possible arrangements of two rings that depend on how many atoms are shared by the two rings. The first arrangement in which the rings do not share any atoms does not use any special nomenclature, but the other types require a method to designate how the rings are put together. Once the ring system is named, then functional groups and substituents follow the standard rules described in the Summary document.

Type 1. Two rings with no common atoms
These follow the standard rules of choosing one parent ring system and describing the other ring as a substituent.

ketone is the highest priority functional group, phenyl is substituent

⟹ 3-phenylcyclohexan-1-one   ("1" could be omitted here)

benzene is the parent ring system as it is larger than cyclopentane and it has three substituents

⟹ 1-cyclopentyl-2,3-dinitrobenzene

Type 2. Two rings with one common atom—spiro ring system
The ring system in spiro compounds is indicated by the word "spiro" (instead of "cyclo"), followed by brackets indicating how many atoms are contained in each path around the rings, ending with the alkane name describing how many carbons are in the ring systems including the spiro carbon. (If any atoms are not carbons, see Special Topic 2.) Numbering follows the smaller path first, passing through the sprio carbon and around the second ring.
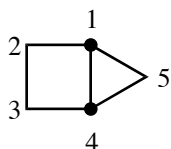
spiro[3.4]octane

spiro[4.5]decane
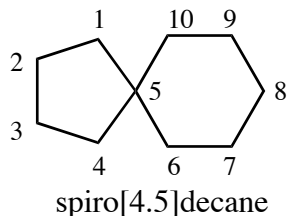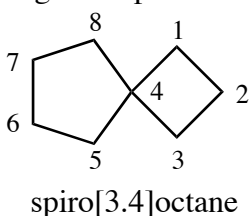
Substituents and functional groups are indicated in the usual ways. Spiro ring systems are always numbered smaller before larger, and numbered in such a way as to give the highest priority functional group the lower position number.

spiro[3.4]oct-5-ene

7,7-dimethylspiro[4.5]decan-2-one
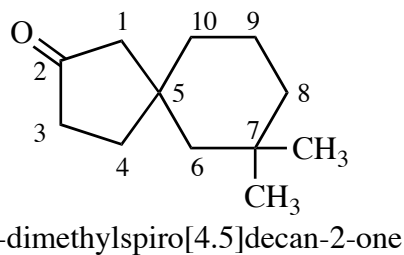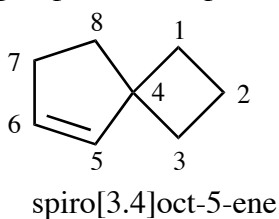
Special Topics of IUPAC Nomenclature, continued

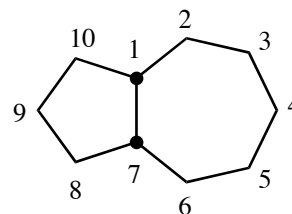Type 3. Two rings with two common atom—fused ring system

Two rings that share two common atoms are called fused rings. This ring system and the next type called bridged rings share the same designation of ring system. Each of the two common atoms is called a bridgehead atom, and there are three paths between the two bridgehead atoms. In contrast with naming the spiro rings, the *longer* path is counted first, then the shorter, then the shortest. In fused rings, the shortest path is always a zero, meaning zero atoms between the two bridgehead atoms. Numbering starts at a bridgehead, continues around the largest ring, through the other bridgehead and around the shorter ring. (In these structures, bridgeheads are marked with a dark circle for clarity.)

bicyclo[2.1.0]pentane
(path of 2 atoms and a
path of 1 atom)
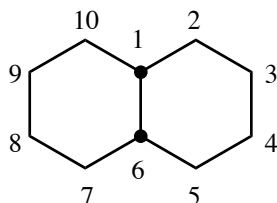
bicyclo[4.4.0]decane
(path of 4 atoms in
each direction)

bicyclo[5.3.0]decane
(path of 5 atoms and
path of 3 atoms)

Substituents and functional groups are indicated in the usual ways. Fused rings systems are always numbered larger before smaller, and numbered in such a way as to give the highest priority functional group the lower position number.

Type 4. Two rings with more than two common atom—bridged ring system

Two rings that share more than two common atoms are called bridged rings. Bridged rings share the same designation of ring system as Type 3 in which there are three paths between the two bridgehead atoms. The longer path is counted first, then the medium, then the shortest. Numbering starts at a bridgehead, continues around the largest ring, through the other bridgehead and around the medium path, ending with the shortest path numbered from the original bridgehead atom. (In these structures, bridgeheads are marked with a dark circle for clarity.)
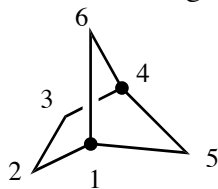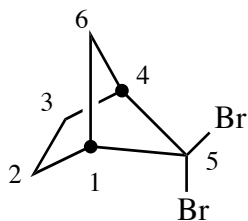
bicyclo[2.1.1]hexane
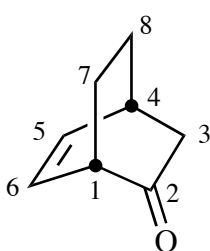(paths of 2 atoms, 1
atom, and 1 atom)
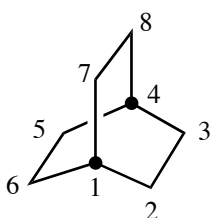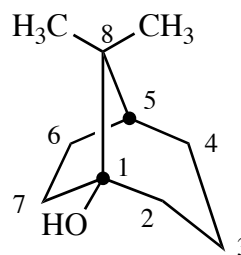
bicyclo[2.2.2]octane
(three paths of 2 atoms)
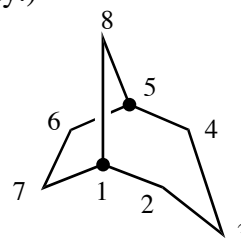
bicyclo[3.2.1]octane
(paths of 3 atoms, 2 atoms,
and 1 atom)

5,5-dibromo-
bicyclo[2.1.1]hexane

bicyclo[2.2.2]oct-5-en-2-one

8,8-dimethyl-
bicyclo[3.2.1]octan-1-ol

2

Special Topics of IUPAC Nomenclature, continued
SPECIAL TOPIC 2. Replacement Nomenclature of Heteroatoms
The term "heteroatom" applies to any atom other than carbon or hydrogen. It is common for heteroatoms to appear in locations that are inconvenient to name following basic rules, so a simple system called "replacement nomenclature" has been devised. The fundamental principle is to name a compound as if it contained only carbons in the skeleton, plus any functional groups or substituents, and then indicate which carbons are "replaced" by heteroatoms. The prefixes used to indicate these substitions are listed here *in decreasing priority and listed in this order in the name:*

Element	Prefix
O	oxa
S	thia
N	aza
P	phospha
Si	sila
B	bora

Example

nonan-1-ol

2-thia-8-aza-4-sila-6-boranonan-1-ol

In the above example, note that the (imaginary) compound no longer has nine carbons, even though the name still includes "nonan". The heteroatoms have replaced carbons, but the compound is named as if it still had those carbons.

Where the replacement system is particularly useful is in polycyclic compounds. Shown below are three examples of commercially available and synthetically useful reagents that use this system.

parent hydrocarbon	reagent	abbreviation
bicyclo[2.2.2]octane	1,4-DiAzaBiCyclo[2.2.2]Octane (upper case added to explain abbreviation)	DABCO
bicyclo[5.4.0]undec-7-ene	1,8-DiazaBicyclo[5.4.0]Undec-7-ene (upper case added to explain abbreviation)	DBU
bicyclo[3.1.1]nonane	9-BoraBicyclo[3.1.1]Nonane (upper case added to explain abbreviation)	9-BBN

3

SPECIAL TOPIC 3. Designation of Stereochemistry; Cahn-Ingold-Prelog system

Is this alkene cis or trans?

F   I

Cl   Br
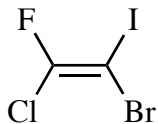
How can we distinguish this structure from its mirror image?

F

I ,,,,,,,   Cl

Br
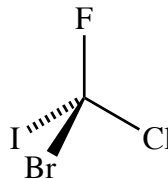
Compounds that exhibit stereoisomerism, whether geometric isomers around double bonds, substituent groups on rings, or molecules with asymmetric tetrahedral atoms (which are almost always carbons), require a system to designate relative and absolute orientation of the groups. The terms cis/trans, D/L in carbohydrates and amino acids, and d/l for optically active compounds, are limited and cannot be used generally, although each still is used in appropriate situations. For example, cis/trans still is used to indicate relative positions of substituents around a ring.

A system developed by chemists Cahn, Ingold, and Prelog, uses a series of steps to determine group priorities, and a definition of position based on the relative arrangement of the groups. In alkenes, the system is relatively simple:

high   high

low   low
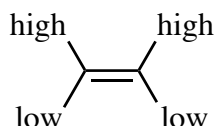
this arrangement is defined
as Z = zusammen, together,
from both high priority groups
on the same side of the C=C

high   low

low   high
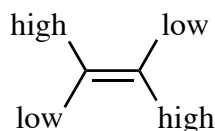
this arrangement is defined as
E = entgegen, opposite, from
the two high priority groups
on opposite sides of the C=C

As with alkenes, the orientation around an asymmetric carbon can be only one of two choices. In three dimensions, clockwise and counterclockwise are the only two directions that are definite, and even that description requires a fixed reference point. To designate configuration, the lowest (fourth) priority group is always placed farthest away from the viewer (indicated by a dashed line), and the group priorities will follow 1 to 2 to 3 in either a clockwise or a counterclockwise direction.

1
4
3   2
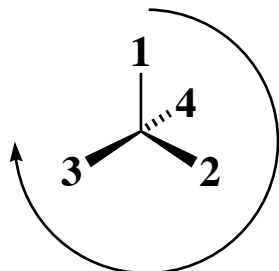
1 to 2 to 3 is clockwise,
defined as the R = *rectus*
configuration

1
4
2   3
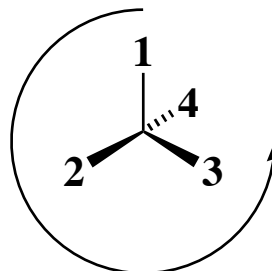
1 to 2 to 3 is
counterclockwise, defined as
the S = *sinister* configuration

The only step remaining is to determine the priority of groups, for which there is a carefully defined set of rules.

Rule 1. Consider the first atom of the group, the point of attachment. Atoms with higher atomic number receive higher priority. Heavier isotopes have higher priority than lighter isotopes.

I > Br > Cl > F   O > N > C > H $^{14}C > ^{13}C > ^{12}C$
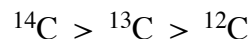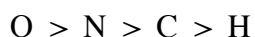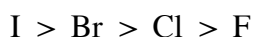
Special topics of IUPAC Nomenclature, continued

Rule 2. If the first atoms of two or more groups are the same, go out to the next atoms to break the tie. One high priority atom takes priority over any number of lower-priority atoms.
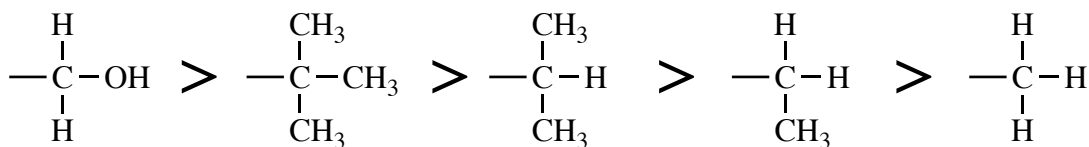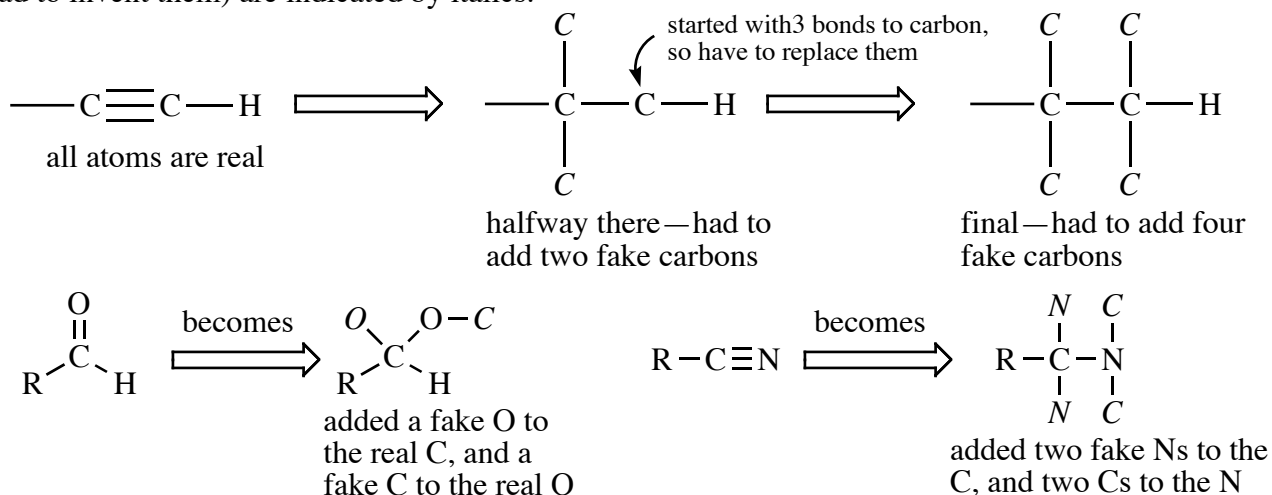

Rule 3. Treat multiple bonds as if they were all single bonds; one will be to the real atom, the others will be to imaginary atoms.

This is the hardest rule to put into practice. This example of an alkyne shows stepwise how to accomplish this. In the pictures, imaginary atoms (ones that did not start out in the structure, we had to invent them) are indicated by italics.

started with 3 bonds to carbon, so have to replace them

all atoms are real

halfway there—had to add two fake carbons

final—had to add four fake carbons

becomes

added a fake O to the real C, and a fake C to the real O

becomes

added two fake Ns to the C, and two Cs to the N

Examples applying the Cahn-Ingold-Prelog sytem

comparing F and Cl

comparing I and Br

E

E

Z

Often, the hard part of applying the R/S system to asymmetric carbons is orienting the molecule so that the fourth priority group is farthest away. Sometimes it is easier to put the fourth priority group toward you, then take the opposite of what the direction of 1 to 2 to 3 says.

top view

flip Br up so F goes back

R

R

Putting the F (4th priority) pointing up toward you, the groups 1 to 2 to 3 appear counterclockwise, but we have to take the opposite, so instead of S, it is R.