

Loudon Chapter 8 Review: Alkyl Halides, Alcohols, etc.

Jacque Richardson, CU Boulder – Last updated 9/12/2016

In this chapter, we look at a lot of non-hydrocarbon functional groups.

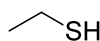


Alkyl halides

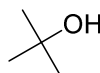
Alcohols

Thiols

These first three – alkyl halides, alcohols, and thiols – are all functional groups with only one bond to the rest of the molecule. They can all be categorized by the substitution of the carbon where they're attached - 1°, 2°, or 3°.

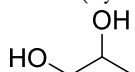


1° thiol



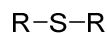
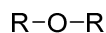
3° alcohol

Compounds with two or more OH (hydroxyl) groups on adjacent carbons are glycols.



propylene glycol

Compounds with 2 R groups on either side of an O are ethers, while compounds with 2 R groups on either side of an S are sulfides.



Ether

Sulfide

Nomenclature

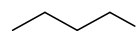
Most of this chapter involves looking at how to name all of these compounds, using both common (old, nonsystematic) naming, and IUPAC (substitutive) naming. You should be able to interpret both types of name when you see them, but if you're asked to name a structure yourself then IUPAC is the most flexible and widely applicable system.

- Alkyl Halides

- Common: name of alkyl group + name of halide.



Ethyl chloride

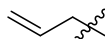


Butyl iodide

As a side note: The book doesn't cover this yet, but most alkyl groups have short abbreviations.

Methyl	Me	Isopropyl	iPr
Ethyl	Et	Isobutyl	iBu
Propyl	Pr or nPr	<i>sec</i> -Butyl	sBu
Butyl	Bu or nBu	<i>tert</i> -Butyl	tBu

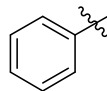
So ethyl chloride could be abbreviated as EtCl, and butyl iodide as BuI. There are also some non-alkyl groups that are useful (some from Ch. 4).



Allyl

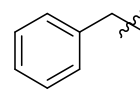


Vinyl



Phenyl

(Ph or ϕ)



Benzyl

(Bn or ϕ -CH₂)

Some common names for alkyl halides with multiple halogens:



Haloform



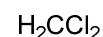
Chloroform



Bromoform



Carbon
tetrachloride

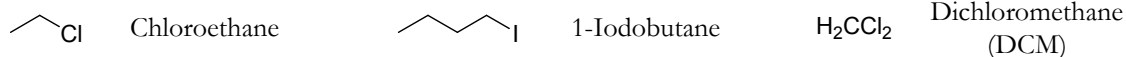


Methylene
chloride

Loudon Chapter 8 Review: Alkyl Halides, Alcohols, etc.

Jacque Richardson, CU Boulder – Last updated 9/12/2016

- IUPAC: Halogen is treated that same as any other substituent, only it drops “ine” from its name and adds “o”. Like in other IUPAC cases, you can drop the substituent numbering if there’s only one possibility for location.



- Alcohols and Thiols

- Common: name of alkyl group + “alcohol” (or “mercaptan” for thiols).

MeOH Methyl alcohol
MeSH Methyl mercaptan
iPrOH Isopropyl alcohol
iPrSH Isopropyl mercaptan

- IUPAC: This is the first time we’ve seen naming for groups that can be considered “principal” functional groups, which change the end of the name. The book has a complete list of principal functional groups in Appendix I. We’ll slowly expand this list as we cover new functional groups in future chapters, but for now all we need to know is that alcohol groups have higher priority than thiol groups. Steps for naming any compound with a principal functional group:
 1. Identify principal group (alcohol > thiol)
 2. Identify parent chain, based on:
 - a. Largest number of principal functional groups (2 alcohol groups are better than 1)
 - b. Most alkenes/alkynes
 - c. Longest chain
 - d. Most other substituents
 3. Number the parent chain, starting at the end that gives:
 - a. Lowest numbers for principal functional groups at first point of difference
 - b. Lowest numbers for alkenes/alkynes at first point of difference
 - c. Lowest numbers for other substituents at first point of difference
 - d. Lowest number for first-cited substituent, listed alphabetically
 4. Put name together
 - a. Cite principal group by suffix and location number. For alcohols, drop terminal “e” and add “ol”. For thiols, keep terminal “e” and add “thiol”. Note that for a chain with an alkene and an alcohol, this would change the end of the name to “enol” (e.g., ethenol). In many of these cases, you need one location number for alkene and one for alcohol. These are best placed in middle of parent chain name (e.g., but-3-en-1-ol). For compounds with multiple copies of principal group, name as “diol”, “triol”, tetraol”, or “dithiol”, “trithiol”, “tetrathiol”.
 - b. All other functional groups are named as substituents.
 - c. If there is no principal functional group, name as a regular substituted hydrocarbon.
 - d. List names & locations of other substituents, in alphabetical order.

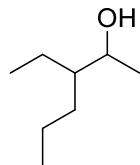
Let’s work through some examples:

MeOH Methanol

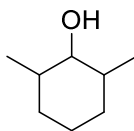
Loudon Chapter 8 Review: Alkyl Halides, Alcohols, etc.

Jacque Richardson, CU Boulder – Last updated 9/12/2016

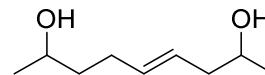
MeSH Methanethiol
iPrOH 1-Methylethanol
iPrSH 1-Methylethanethiol



3-Ethyl-2-hexanol



2,6-Dimethylcyclohexanol



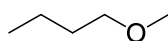
Non-4-en-2,8-diol

• Ethers and Sulfides

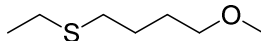
- Common: alphabetically list 2 alkyl groups on either side of oxygen/sulfur, plus “ether” or “sulfide”. If the two alkyl groups are the same, list as di-alkyl.

MeOMe or Me₂O Dimethyl ether
EtOEt or Et₂O Diethyl ether (or just “ether”)
iPrOMe Isopropyl methyl ether
MeSMe or Me₂S Dimethyl sulfide (DMS)

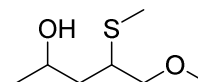
- IUPAC: Ethers and sulfides cannot be principal functional groups. Instead, choose one side of the ether/sulfide to be the parent chain, based on rules above. Treat alkoxy groups (RO-) and alkylthio groups (RS-) as substituents of the parent chain, just like any other substituent. This allows you to handle molecules with multiple ether or sulfide functional groups, unlike common naming.



1-methoxybutane



1-ethylthio-4-methoxybutane



5-methoxy-4-methylthio-2-pentanol

Some cyclic ethers have specific, nonsystematic names that you should know.



Furan



Tetrahydrofuran
(THF)



Thiophene



Dioxane



Oxirane
(ethylene oxide)

Structure & Physical Properties

Compounds in this chapter are more polar and have a higher dipole moment than hydrocarbons. This means they usually have a higher boiling point, compared to the same structure without heteroatoms (anything other than C & H).

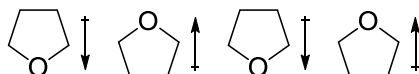


Cyclopentane
BP = 49°C



THF
BP = 66°C

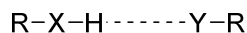
This is because THF molecules have a dipole that they can line up in alternating directions, to increase the electrostatic attraction between molecules.



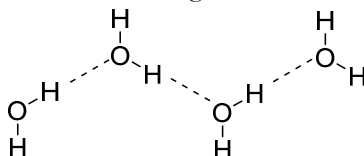
For alcohols, there's an even stronger factor that contributes to raising BP: hydrogen bonding. This is an intermolecular attraction of the form:

Loudon Chapter 8 Review: Alkyl Halides, Alcohols, etc.

Jacque Richardson, CU Boulder – Last updated 9/12/2016

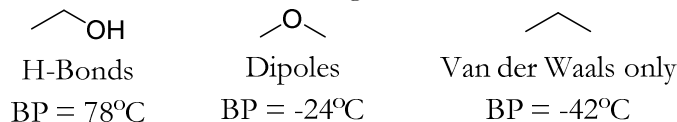


X & Y are usually N, O or F, or some combination of these atoms. S can H-bond a little too, but it's much weaker. In this example, X is the H-bond donor and Y is the H-bond acceptor, which must have a lone pair. H can only have a total of one bond, so by forming a slight, partial bond to Y, it weakens its attachment to X. You can think of H-bonds as acid-base (proton transfer) reactions that stop partway through the mechanism. Water is both a donor and acceptor, so all of its molecules can link together. The same is true for alcohols.



Ethers are H-bond acceptors but not donors, so they can't H-bond to other ether molecules. However, if you mix ether and water, these two molecules can H-bond to each other.

Hydrogen are the strongest intermolecular force and raise BP by a lot. Here are some sample BPs for compounds with similar molecular weights:



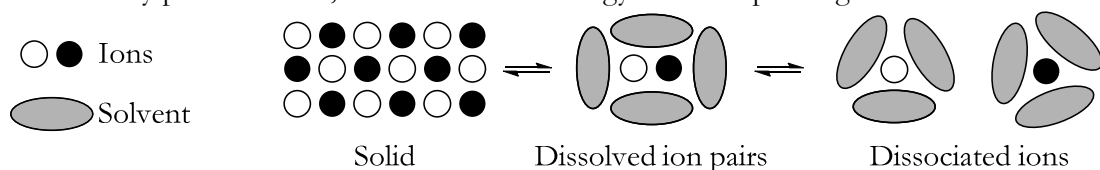
Solvents

Most organic reactions are done in solution, which involves using some type of liquid solvent to dissolve all the reagents. Sometimes the solvent itself is also a reagent. Solvents can have a very strong influence on the outcome and rate of a reaction. There are three major ways to classify them:

1. Protic vs. aprotic: Whether or not the solvent is an H-bond donor. Water, alcohols and carboxylic acids are protic; most others are aprotic.
2. Polar vs. nonpolar: whether a solvent has a high dielectric constant or not. This is a measure of how well the solvent shields charges from each other. A solvent with low dielectric constant does little to shield charges, so they feel each other's full force based on electrostatic potential. A solvent with high dielectric constant blocks the charges so that opposite charges can remain separated from each other without such a high energy cost.



When an ionic compound is being put into solution, there are several different levels of "dissolved". Solvents can be dissolved as a pair, or individually. The latter option is more stabilized by polar solvents, since there's less energy cost to separating the ions.



Loudon Chapter 8 Review: Alkyl Halides, Alcohols, etc.

Jacque Richardson, CU Boulder – Last updated 9/12/2016

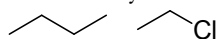
The cutoff between high and low dielectric constant is somewhat arbitrary, but it's officially set at 15. Some example values are given in the big table of solvents in Ch. 8.

You do not have to memorize these or remember which solvents are polar for now.

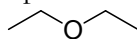
Note that solvent polarity is not the same thing as molecule polarity! It is possible to have polar molecules that act as nonpolar solvents (e.g. acetic acid is a polar molecule, but a nonpolar solvent since its dielectric constant is 6.1).

3. Donor vs. nondonor: Whether a molecule has a lone pair it can donate. Ether, THF and methanol are all donors, for example.

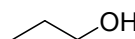
The best way to choose a solvent for a reaction is “like dissolves like” – choose a solvent with similar properties to the compound you're trying to dissolve. For example, in water, alkanes and alkyl halides are insoluble because they're neither donors nor protic. Ethers are somewhat soluble because they're donors but not protic, and alcohols are very soluble or miscible because they're both donors and protic.



Insoluble

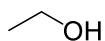


Soluble

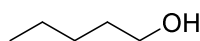
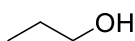


Miscible
(infinitely soluble)

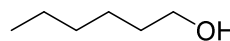
This doesn't mean that having a single OH group will make a molecule miscible though. The smaller a percent of the molecule the OH makes up, the less influence it will have on the molecule's behavior and the less soluble the molecule will be.



Miscible



Soluble up to 7.7%



Soluble up to 0.6%

Moderately-polar solvents like THF, acetone and DCM are good choices when you need to dissolve both a polar compound and a nonpolar compound at the same time, like H₂O and hydrocarbons.