

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

Jacquie Richardson, CU Boulder – Last updated 11/4/2020

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

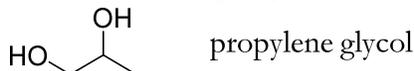


Alkyl halides Alcohols Thiols

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°.



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



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

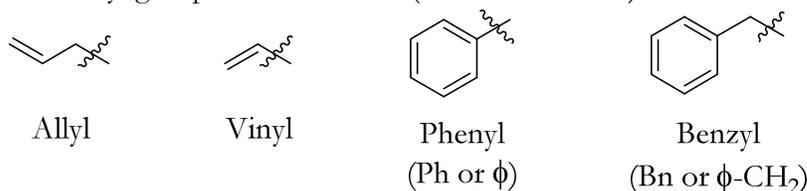
- Common: name of alkyl group + name of halide.



As a reminder, most alkyl groups have short abbreviations.

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

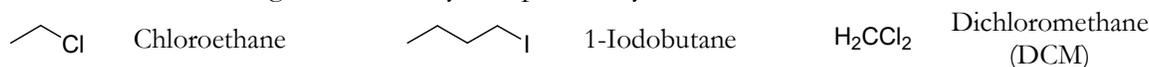
So ethyl chloride could be abbreviated as EtCl, and butyl iodide as BuI. There are also some non-alkyl groups that are useful (some from Ch. 4).



Some common names for alkyl halides with multiple halogens:

HX ₃	HCCl ₃	HCCl ₂	CCl ₄	H ₂ CCl ₂
Haloform	Chloroform	Bromoform	Carbon tetrachloride	Methylene chloride

- IUPAC: Halogen is treated the 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.



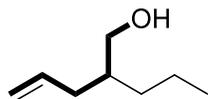
- Alcohols and Thiols

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- Common: name of alkyl group + “alcohol” (or “mercaptan” for thiols).
MeOH Methyl alcohol iPrOH Isopropyl alcohol
MeSH Methyl mercaptan EtSH Ethyl 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.

1. **Identify the principal functional group.** Alcohols have higher priority than thiols.
2. **Determine the parent chain.** Maximizing the number of principal FGs now takes priority over all other considerations.
 - a. Largest number of principal functional groups (2 alcohol groups are better than 1)
 - b. Largest number of alkenes
 - c. Longest chain
 - d. Most other substituents

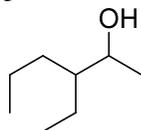


Parent chain is 5 carbons, not 7 (longest chain).

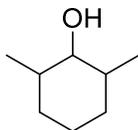
3. **Name each group coming off the parent chain.** This is the same as before.
4. **Number the carbons of the parent chain.** Start numbering at the end closest to the first principal FG, or (if both ends are equally close), then choose the end that gives the lower number at the first point of difference. If the locations of the principal FGs are the same no matter which end you count from, then you can start using the alkene rules to determine it.
5. **Name the compound as “location #”-“substituent”“parent”.** Change the end of the parent name as follows:

Types of FGs	Suffix change	Example
One OH	Drop e , add ol	Ethanol
Multiple OH	Keep e , add diol , triol , tetraol	Ethanediol
One SH	Keep e , add thiol	Ethanethiol
Multiple SH	Keep e , add dithiol , trithiol , tetrathiol	Ethanedithiol

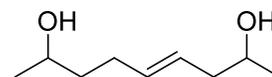
Note that for a chain with an alkene and an alcohol, this would change the end of the name to “enol” (e.g., ethenol). In many of these cases, you need one location number for alkene and one for alcohol. These are best placed in middle of parent chain name but you can also pull out the number for the alkene and put it before the parent.



3-Ethyl-2-hexanol



2,6-Dimethylcyclohexanol



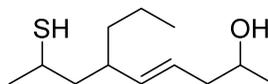
Non-4-ene-2,8-diol
(parent: nonenediol)

What if a molecule has both OH and SH groups? Since OH is the principal FG, SH just becomes a normal substituent, named as a “mercapto” group, and is numbered and alphabetized the same as any other group.

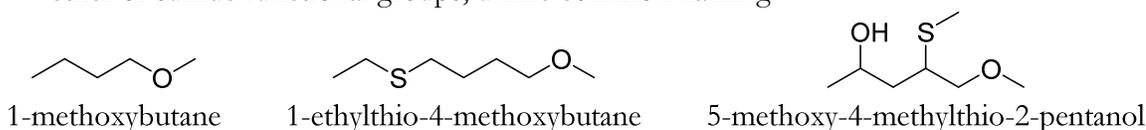
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8-mercapto-6-propylnon-4-en-2-ol
(parent: propylnonenol)



- 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.



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



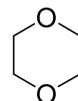
Furan



Tetrahydrofuran
(THF)



Thiophene



Dioxane



Oxirane
(ethylene oxide)

Degrees of Unsaturation

We already covered this in Ch. 2 for hydrocarbons, but now we're seeing heteroatoms. Remember that for saturated hydrocarbons, the formula is C_nH_{2n+2} , and each **pair of missing H atoms** from this formula is one **degree of unsaturation** (caused by either pi bonds or rings). To find the degree of unsaturation of a molecule that isn't a hydrocarbon, we need to convert it to an equivalent hydrocarbon. We'll use C_8H_8NOBr as an example.

- Replace halogens with hydrogens: C_8H_8NOBr becomes C_8H_9NO
- Omit oxygens and sulfurs: C_8H_9NO becomes C_8H_9N
- For each nitrogen, omit one nitrogen and one hydrogen: C_8H_9N becomes C_8H_8
- Find the degrees of unsaturation for the equivalent hydrocarbon: C_8H_8 has 5 deg. unsat.

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

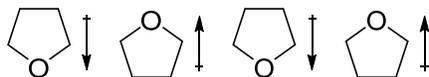


THF
BP = 66°C

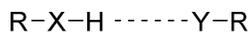
This is because THF molecules have a dipole that they can line up in alternating directions, to increase the electrostatic attraction between molecules.

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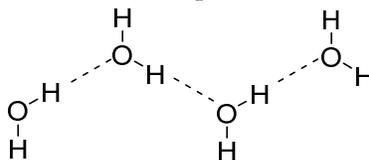
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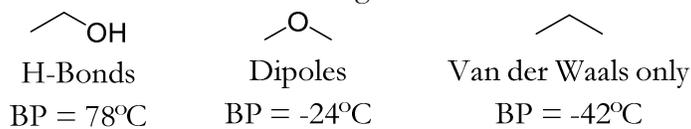
For alcohols, there's an even stronger factor that contributes to raising BP: hydrogen bonding. This is an intermolecular attraction of the form:



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:

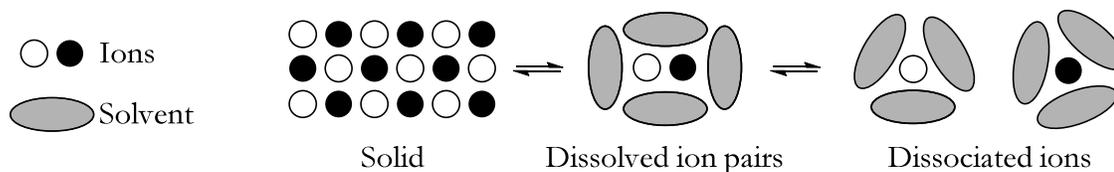
1. Protic vs. aprotic: Whether or not the solvent is an H-bond donor. Water, alcohols and carboxylic acids are protic; most others are aprotic.
2. Polar vs. nonpolar: whether a solvent has a high dielectric constant or not. This is a measure of how well the solvent shields charges from each other. A 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.

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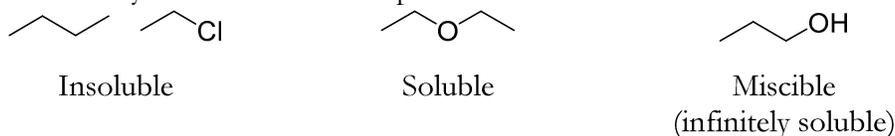
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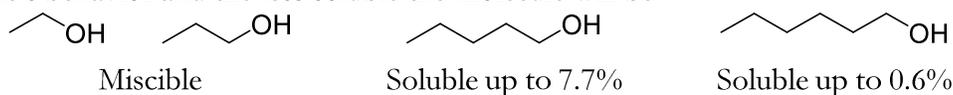
The cutoff between high and low dielectric constant is somewhat arbitrary, but it's officially set at 15. Some example values are given in the big table of solvents in Ch. 8. You do not have to memorize these or remember which solvents are polar for now. Note that solvent polarity is not the same thing 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.



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.



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.