

Constitutional Isomers

Dr. Sapna Gupta

Constitutional Isomers

- Compounds that have same molecular formula but different structure.
- E.g. C_4H_{10} : two isomers: butane and 2-methyl propane.
- Think of constitutional isomers as having a given number of colored lego blocks that you can make whatever you want.
- The table below shows the number of isomers possible for the given formula of an alkane.

Molecular Formula	Possible Number of Constitutional Isomers
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{30}H_{62}$	4,111,846,763
$C_{40}H_{82}$	62,481,801,147,341

Constitutional Isomers –General Info

1. The first step is to see whether the molecular formula is that of alkane, alkene (2H less than alkane) or alkyne (4H less than alkane).
2. Use the C_nH_{2n+2} formula to check point number 1. I use the C_nH_{2n} and then see if I have more or less Hs – it's an easier calculation. E.g. C_4H_{10} , C_nH_{2n} would give me 8 H for 4 C; and I have 2 more Hs – so I have an alkane formula.
3. If there is a halide (Cl, Br etc.) – treat it as a H.
4. An oxygen can just fit in between two atoms, so don't use it in the C_nH_{2n} formula.
5. If there is a N then you are writing amines. At this point, you will be writing only saturated amines (no double bonds).

Constitutional Isomers –General Info – contd...

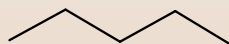
1. Write the isomers systematically. If you move too many atoms then its hard to keep track of all the isomers.
2. Move carbons first or move functional group first, depending on what is easier.
3. Be careful of writing duplicates.
4. Carbons or functional groups going up and down are the same, unless you are writing cyclic isomers, then the direction matter.
5. Try to write isomers in line structures. Don't write hydrogens. It will take too much time and you might forget a hydrogen here or there. If your functional group is correct then your hydrogens will also be correct.
6. It is a good idea to count the carbons and hydrogens for the first structure you write for every different functional group. It helps in keeping track of atoms.
7. Number your carbons and locations of substituents/functional group, if necessary, to make sure you are not repeating an isomer.

Constitutional Isomers –General Info – contd...

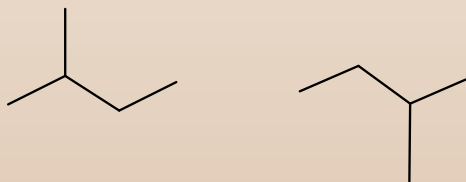
1. These are only tips for functional groups and constitutional isomers – but they are good guide, as you will see in the examples that follow.
2. The following functional groups have the same molecular formula:
 - Alkanes are just alkanes
 - Alkenes and cycloalkanes
 - Alkynes and cycloalkenes
 - Alcohols and ethers
 - Aldehyde and ketones
 - Carboxylic acids and esters
 - 1^o, 2^o and 3^o amines

Constitutional Isomers of Alkanes

- Write constitutional isomers for C_5H_{12}
- Make sure that the molecular formula follows the C_nH_{2n+2} number of hydrogens.
- Start with the straight chain (that counts as one isomer!)

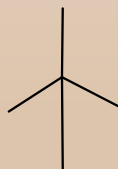


- Move one carbon – avoid identical isomers! The following two are the same.



- Move a second carbon.

- Total of 3 isomers only.



Constitutional Isomers of Alkenes

- Write constitutional isomers for C_5H_{10}
- Make sure that the molecular formula follows the C_nH_{2n} number of hydrogens.
- Start with the straight chain. The following two are the same.



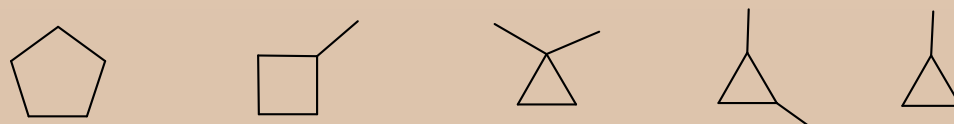
- Move the double bond. The following two are the same.



- Move a carbon using the above isomers. The first two are the same.



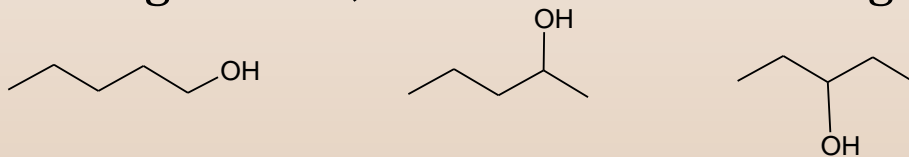
- Now write the cycloalkanes. Start with the largest ring possible.



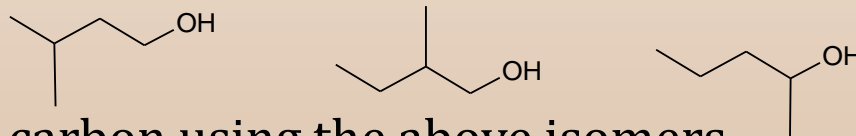
- Total of 11 isomers!

Constitutional Isomers of Oxygen

- Write constitutional isomers for $C_5H_{12}O$
- The molecular formula follows the C_nH_{2n+2} number of hydrogens, indicating all single bonds. Don't count the oxygen.
- Write one functional group first. I will start with alcohols.
- Start with the straight chain, and move the alcohol group.



- Move one carbon. The last one here is the same as the 2nd one above.



- Move the second carbon using the above isomers.



- Now write the ethers. First the straight chains, then move carbons.



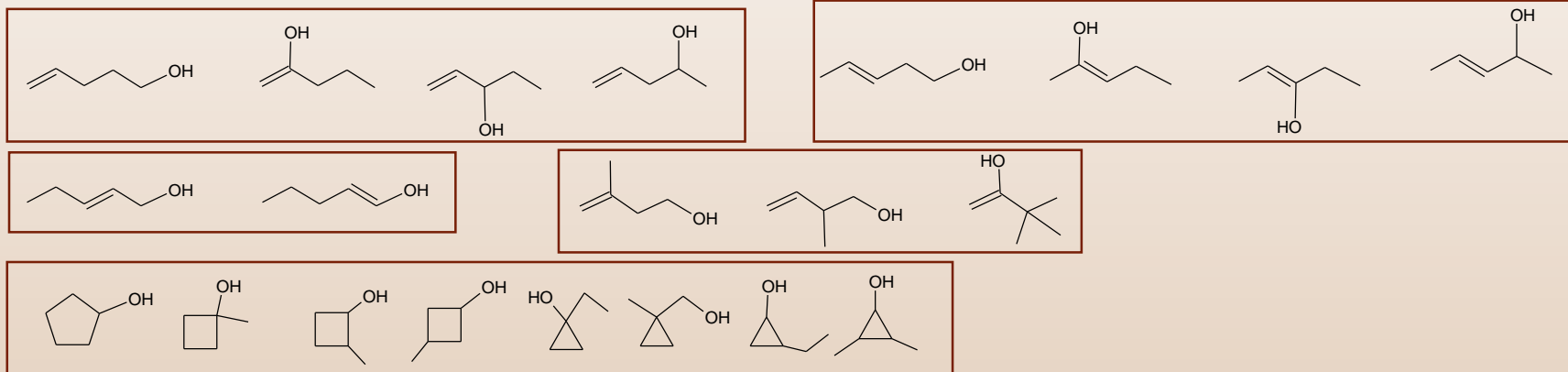
- Total of 11 isomers!

Constitutional Isomers of Oxygen

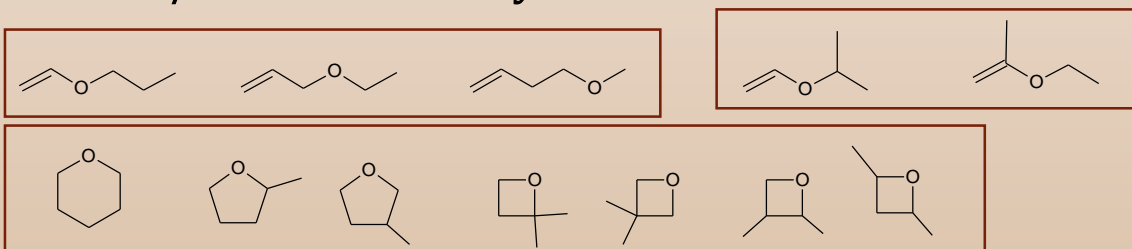
- Write constitutional isomers for $C_5H_{10}O$
- The molecular formula follows the C_nH_{2n} number of hydrogens indicating that there is ONE double bond somewhere. Don't count the oxygen in the formula.
- Write one functional group at a time. The next slide has all the isomers grouped together in functional groups.
 - Alcohols/Alkenes and Cyclic Alcohols
 - Ethers/Alkenes and Cyclic Ethers
 - Aldehydes/Ketones
 - There are total 40!!!

All isomers of $C_5H_{10}O$

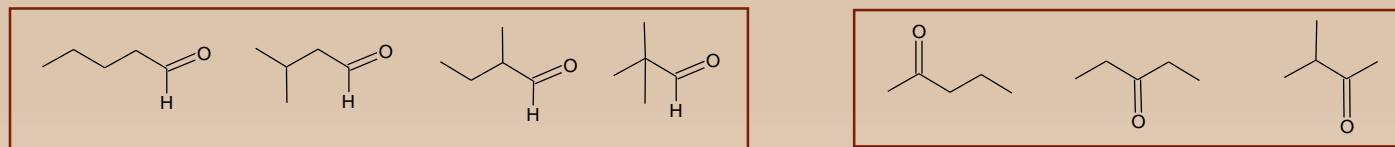
• Alcohols/Alkenes and Cyclic Alcohols



• Ethers/Alkenes and Cyclic Ethers

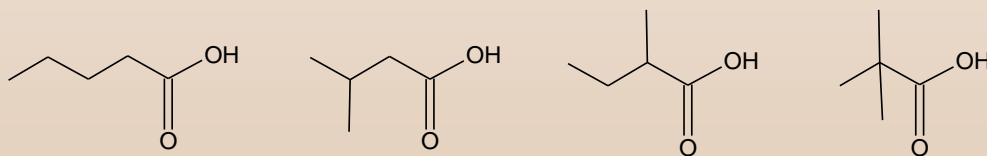


• Aldehydes/Ketones

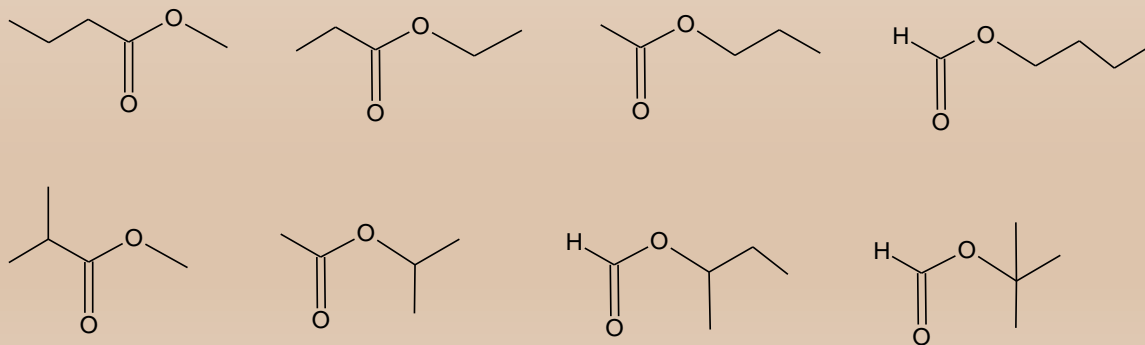


Constitutional Isomers of Acids

- Write the constitutional isomers of $C_5H_{10}O_2$.
- The two oxygens and one double bond indicates acids and esters.
- More isomers are possible - alcohols+aldehydes; alcohols+ketones etc.
- Here we will focus on just acids and esters.
- Acids



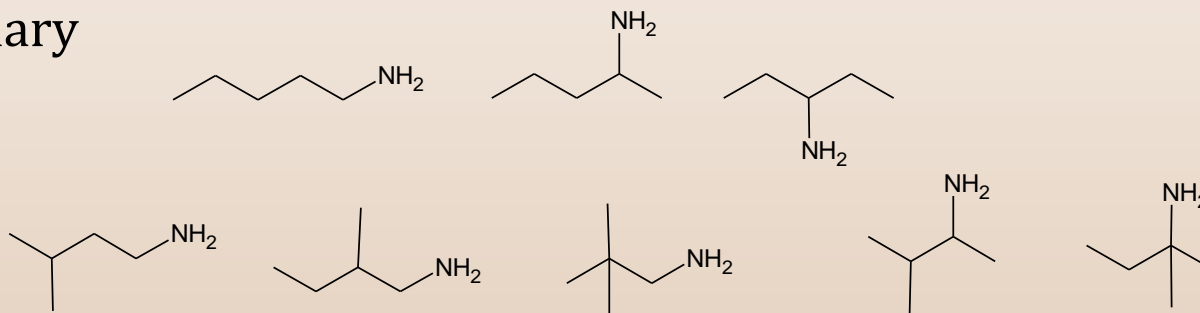
- Esters



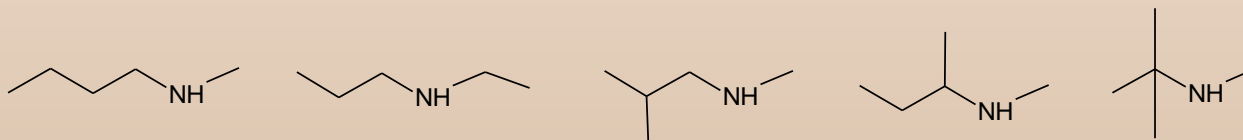
Constitutional Isomers of Amines

- Write all constitutional isomers of $C_5H_{13}N$.
- Amines can be primary, secondary and tertiary.

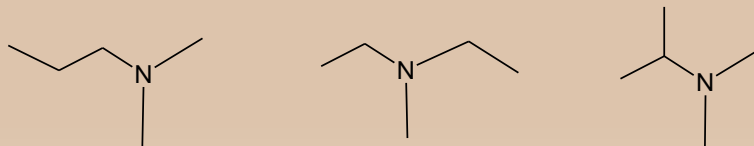
- Primary



- Secondary



- Tertiary



Concepts

- Know your functional groups.
- As the number of carbons and hydrogens increase the number of isomers will also increase. It can be overwhelming! I have chosen 5 carbons to give a good idea of the number of isomers possible.
- There is no formula that tells you how many isomers you will have. You just have to write them all.
- For the above two reasons, you are generally asked for either a specific number of isomers or specific functional group of isomers.