

Organic Structures

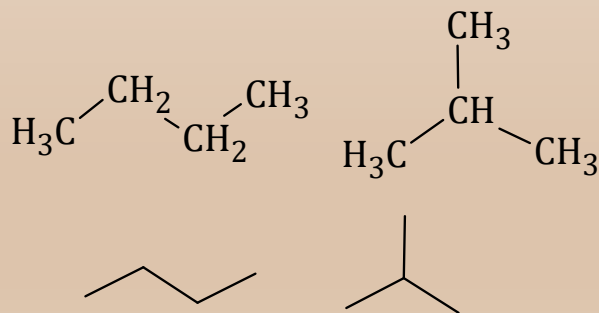
3 – Constitutional Isomers

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Constitutional Isomers - Introduction

Constitutional isomers are compounds that have same molecular formula but different structure.

- For example, C_4H_{10} can have two isomers: butane and 2-methyl propane, shown below in both carbon chain and line structure.
- Think of constitutional isomers as having a given number of colored lego blocks that you can make whatever you want.
- The table shows the number of isomers possible for the given formula of an alkane.



Molecular Formula	Number of Isomers Possible
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
$C_{15}H_{32}$	4,374

Constitutional Isomers – General Info

Writing and recognizing constitutional isomers is an integral part of learning about organic structures. You will generally be given a molecular formula and be asked to write a certain number or certain functional groups of constitutional isomers.

Below is the guideline on how to get started with the formula given.

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). Use the C_nH_{2n+2} formula to check for this. The quick way is to use C_nH_{2n} and see if there are increase, – it's an easier calculation. increase, C_4H_{10} , C_nH_{2n} would give 8 H for 4 C; and since there are 2 more Hs it is an alkane formula.
2. If there is a halide (Cl, Br etc.), it should be treated as a H.
3. An oxygen can just fit in between two atoms, so don't use it in the C_nH_{2n} formula as it does not change the number of H.
5. If there is a increase, then you are writing amines. At this point, you will be writing only saturated amines (no double bonds).

As mentioned in the previous slide, as the number of carbons increase, the number of isomers also increase, and it becomes important to be organized in your writing.

Constitutional Isomers – General Info – contd...

Let us see how to draw and recognize constitutional isomers.

1. Write the isomers systematically. If you move too many atoms, then it's hard to keep track of all the isomers.
2. Move carbons first or move functional group first, depending on what is easier but be careful of writing duplicates.
3. Carbons or functional groups going up and down are the same, unless you are writing cyclic isomers, then the direction matters.
4. 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.
5. 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.
6. If necessary, number your carbons and locations of substituents/functional group to help you make sure you are not repeating an isomer.

Constitutional Isomers –General Info – contd...

The tips I have given in the slide before are only tips for functional groups and constitutional isomers – but they are good guide, as you will see in the examples that follow.

Although one can write any number of constitutional isomers for a formula, it is nice to note that some different functional groups can have the same molecular formula. 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

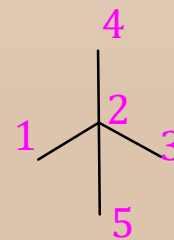
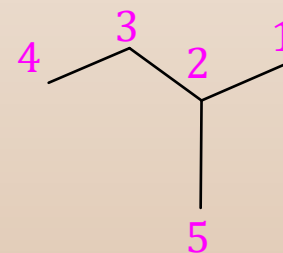
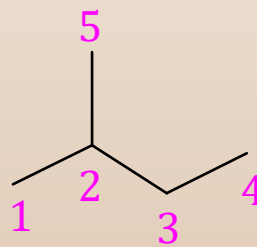
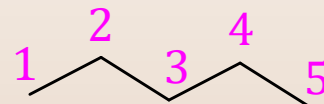
1^o, 2^o and 3^o amines

Solved Example: Constitutional Isomers of Alkanes

Write constitutional isomers for C_5H_{12}

ANSWER

- Make sure that the molecular formula follows the C_nH_{2n+2} number of hydrogens ($2 \times 5 + 2 = 12$)
- Start with the straight chain (that counts as one isomer!)
- Move one carbon – avoid identical isomers! The following two are the same. Numbering the carbon chain helps to see that there is a branching on second carbon.
- Move a second carbon.
- Total of 3 isomers only.



Solved Example: Constitutional Isomers of Alkenes

Write constitutional isomers for C_5H_{10}

ANSWER

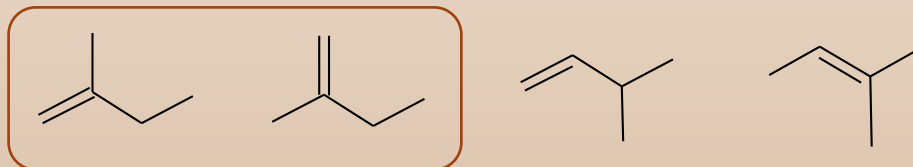
- Make sure that the molecular formula follows the C_nH_{2n} number of hydrogens.
- Start with the straight chain. The following two are the same.



- 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 10 isomers!

Constitutional Isomers of Oxygen

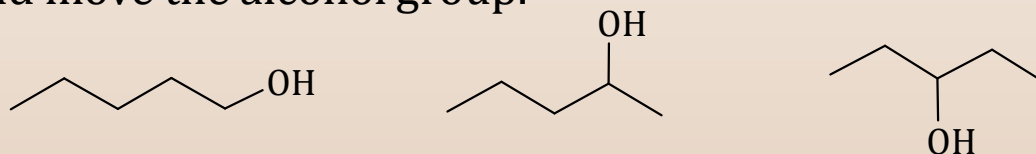
- Write constitutional isomers for $C_5H_{12}O$
- The molecular formula follows the C_nH_{2n+2} number of hydrogens indicating that there are only single bonds as total H are 12. Don't count the oxygen in the formula.
- Write one functional group at a time. The next slide has all the isomers grouped together in functional groups.
 - Alcohols and Ethers

Solved Example: Constitutional Isomers of Saturated Oxygen

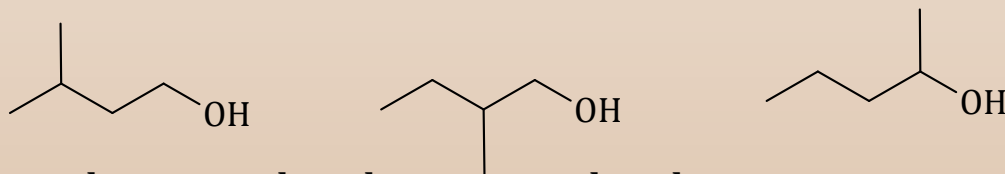
Write constitutional isomers for $C_5H_{12}O$

ANSWER

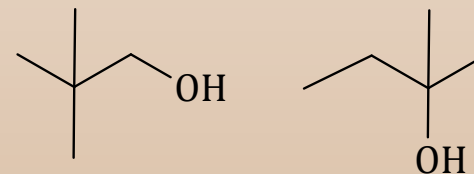
- The molecular formula follows the C_nH_{2n+2} number of hydrogens, indicating all single bonds. Don't count the oxygen.
- Write one functional group first. I will start with alcohols. Start with the straight chain, and move the alcohol group.



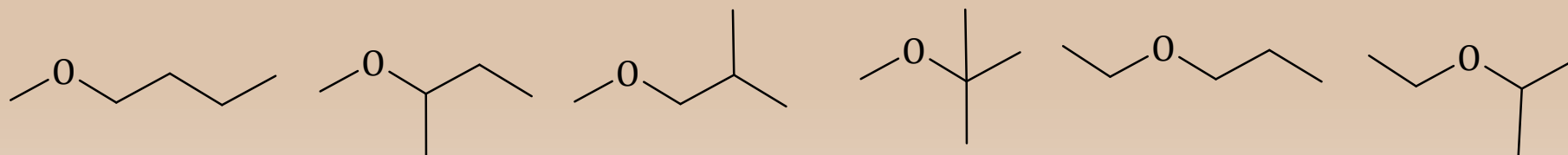
- Move one carbon. The last one here is the same as the 2nd one above.



- Move the second carbon using the above isomers.



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



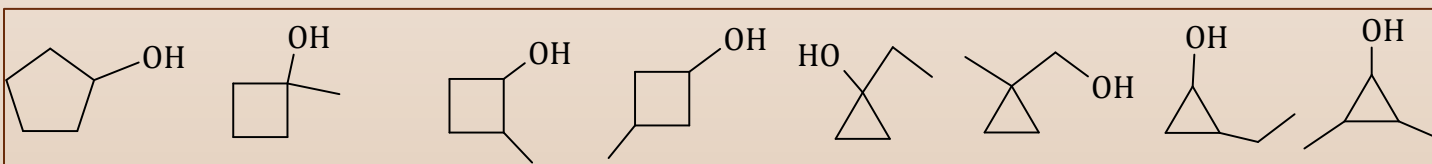
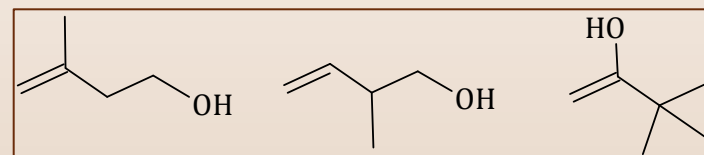
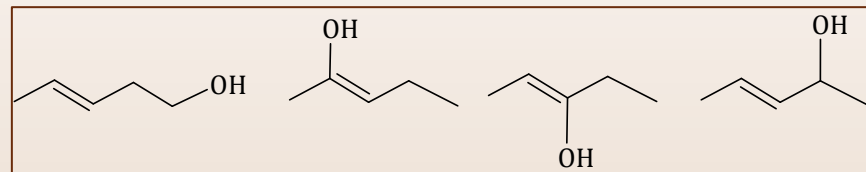
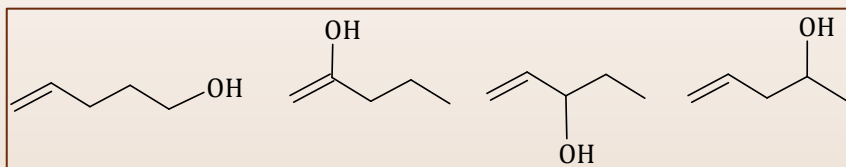
- Total of 14 isomers!

Constitutional Isomers of Oxygen

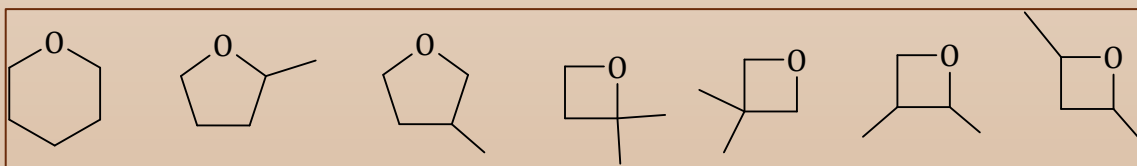
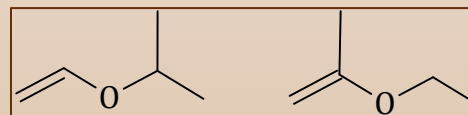
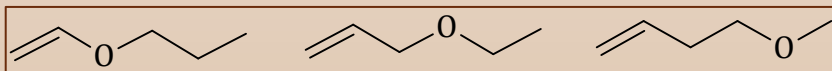
- Write constitutional isomers for $C_5H_{10}O$
- The molecular formula follows the C_nH_{2n} number of hydrogens indicating that there is ONE double bond somewhere. Don't count the oxygen in the formula.
- Write one functional group at a time. The next slide has all the isomers grouped together in functional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

All isomers of C₅H₁₀O

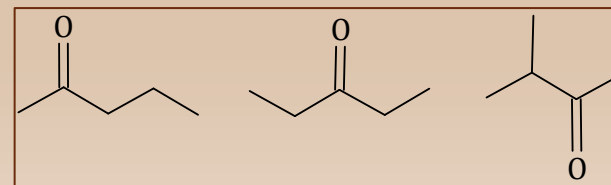
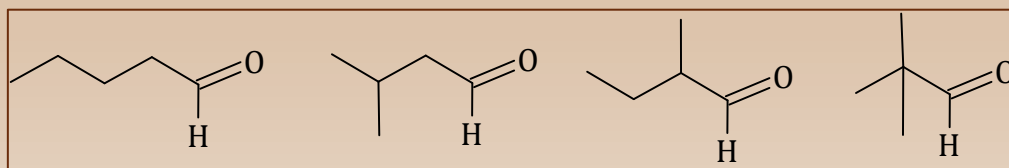
• Alcohols/Alkenes and Cyclic Alcohols



Ethers/Alkenes and Cyclic Ethers



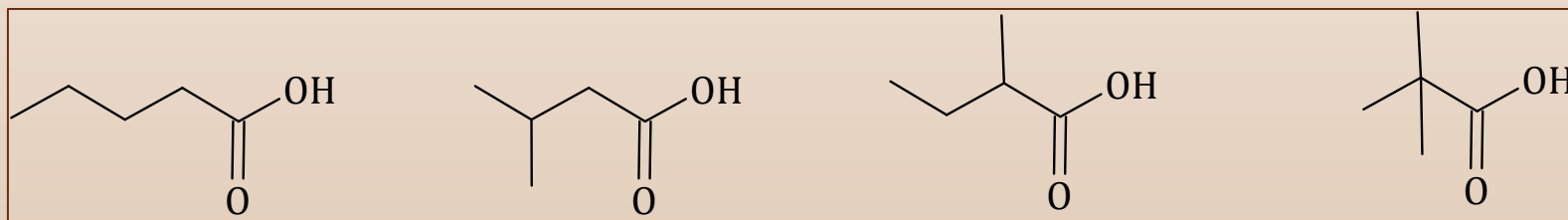
Aldehydes/Ketones



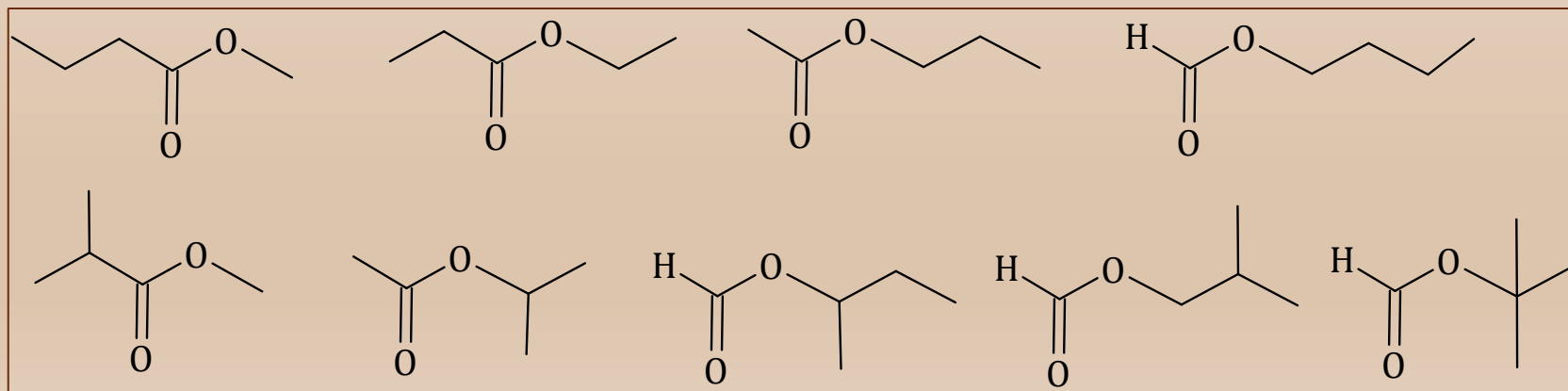
Constitutional Isomers of Acids

- 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



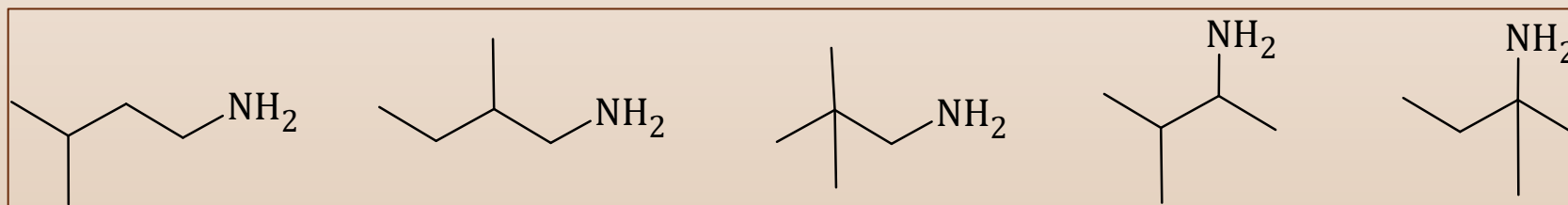
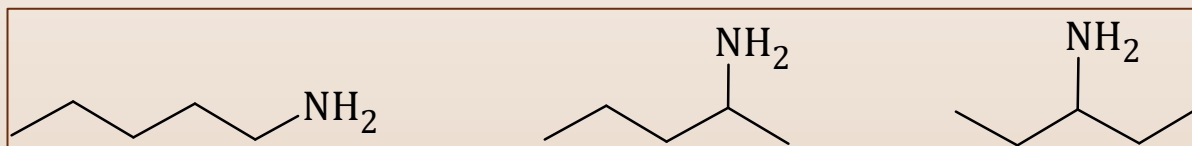
Esters



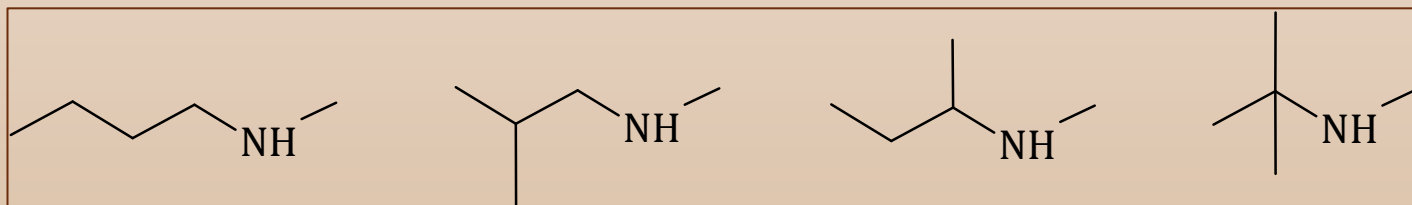
Constitutional Isomers of Amines

- Write all constitutional isomers of $C_5H_{13}N$.
- Amines can be primary (one C on N), secondary (2 C on N) and tertiary (3 C on N).

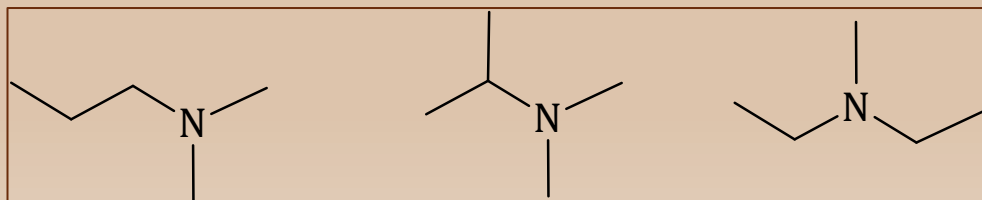
Primary



Secondary



Tertiary



Key Concepts

The more you know your functional groups the better you will be at constitutional isomers.

- 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.