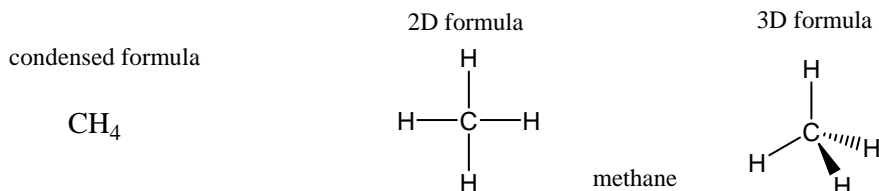
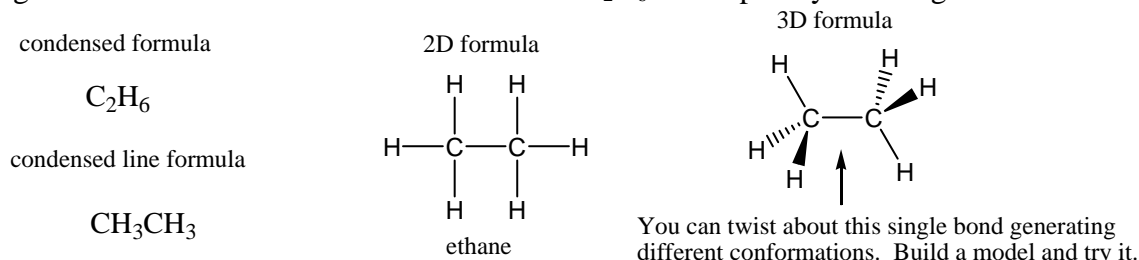


## Structural Isomers – Just how many structures can you make from a simple formula?

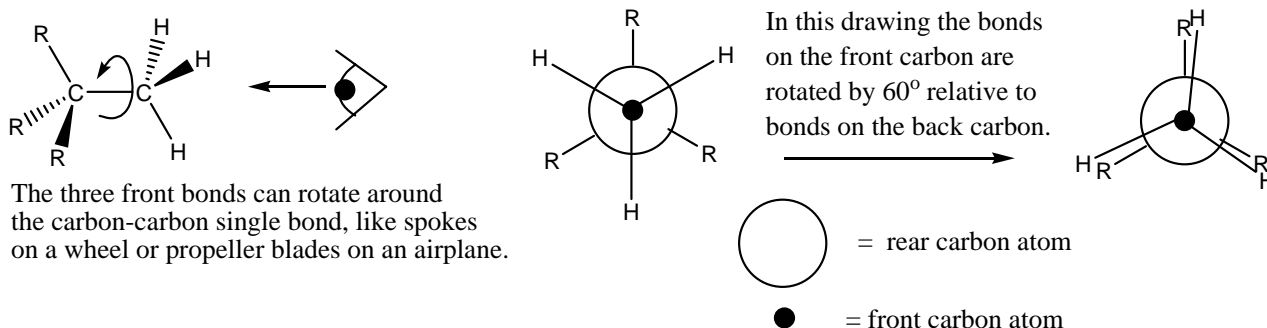
### 1. methane: $\text{CH}_4$



### 2. ethane: $\text{C}_2\text{H}_6$



The carbon-carbon single bond allows rotation of one group of three C-H sigma bonds past the other group of three C-H sigma bonds. Using a molecular model of ethane, fix one carbon with one hand and spin the other carbon with your other hand. The different arrangements of the atoms as they rotate past one another are called conformations. Conformations are the result of differences in a structure from rotation about single bonds. We will study conformations more in a later topic.



A straight-on view shows the three bonds as lines connecting to the front carbon atom, written as a small dot. The rear carbon is usually drawn as a large circle and the three bonds to that carbon are also drawn as lines, but only down to the circle. Rotation of the front bonds is easily seen in two different structures. These are called Newman projections and we will see more of them later.

### 3. propane: $\text{C}_3\text{H}_8$

Once again, there is only one possible arrangement of the bonding atoms. The third carbon has to be attached to either of the other two carbons forming a three carbon chain with eight additional bonding sites, each bonded to a hydrogen atom. Propane is a saturated molecule.  $\text{C}_3\text{H}_8$  is completely unambiguous.

## Lecture 6

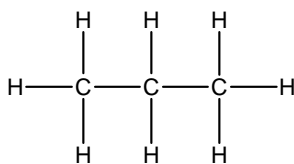
condensed formula



condensed line formula

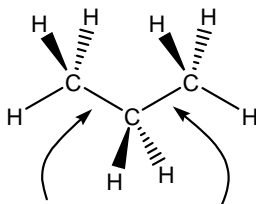


2D formula

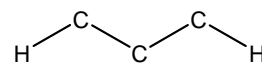


propane

3D formula

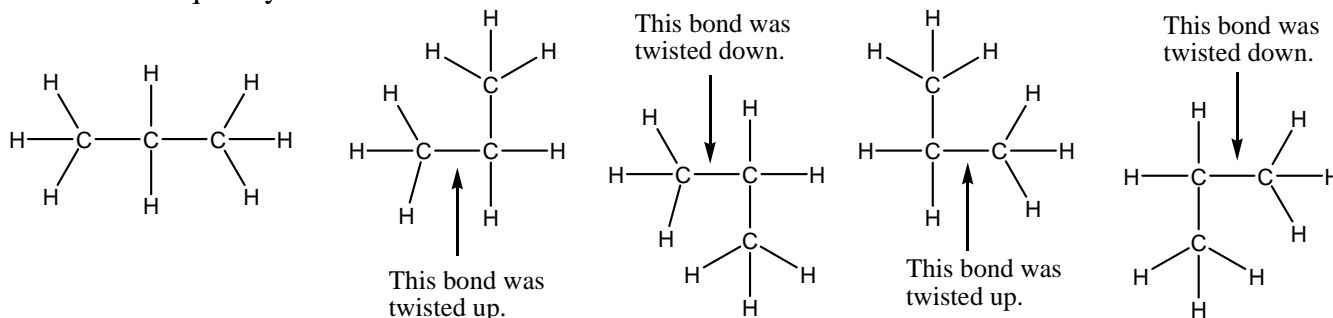


You can twist about either single bond generating different conformations. Build a model and try it.



Because the backbone of the carbon skeleton (plus the two hydrogen atoms at the end positions) go up and down, this shape is sometimes referred to as a zig-zag shape. It can also be called a wedge and dash formula.

Because single bonds allow rotation, there are a number of ways that propane can be drawn using slightly different representations. If you have models, now is a time to use them. Keep them handy. You'll want to use them frequently.



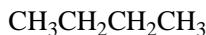
The point you should get from this example is that three sequentially attached  $sp^3$  carbon atoms can be drawn in a variety of ways, but are still the same structure. With additional carbon atoms (4, 5, 6...) the possibilities increase, but the feature to focus on when deciding if two structures are identical or different is the length of the carbon chain and the length and positions of its branches. Whether you have 3, 4, 5, or more carbon atoms zig-zagged in any manner possible, you can always redraw it in a simpler straight chain form. The straight chain representation is easier for you to work with, so choose it as your method of drawing a 2D structure (even if it is changing its shape thousands of times per second). Drawing your structures with a straight chain, as much as possible, will give you the best chance of not overlooking a structure. We will use this approach in our subsequent examples.

4. butane and 2-methylpropane (isobutane):  $C_4H_{10}$ 

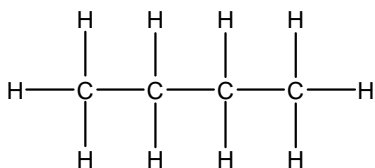
We finally encounter an example where there is more than one possible carbon skeleton. First draw the longest possible carbon chain, which would be...four carbons (you guessed it!). There are ten additional bonding sites that are all saturated with hydrogen atoms.  $C_4H_{10}$  is ambiguous.

condensed formula  
(ambiguous)

condensed line formula

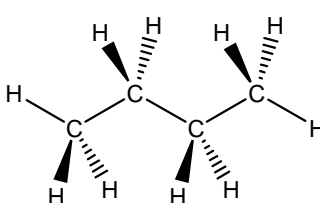


2D formula



butane

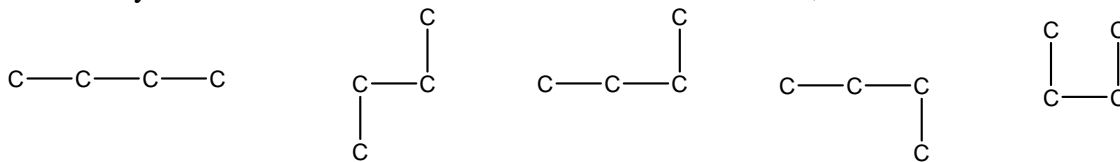
3D formula



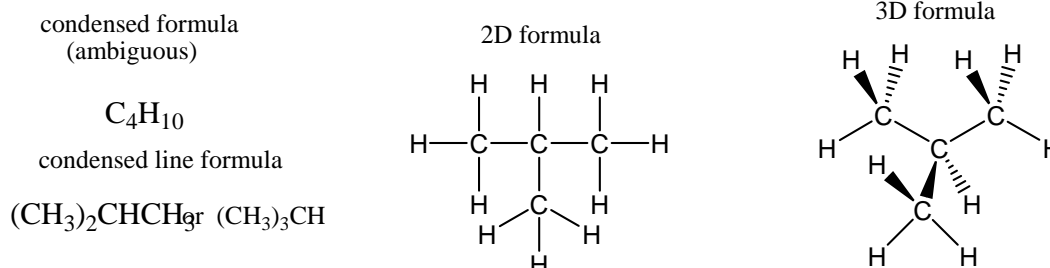
Rotation is possible about any of the carbon-carbon single bonds, generating different conformations. Build a model and try it.

## Lecture 6

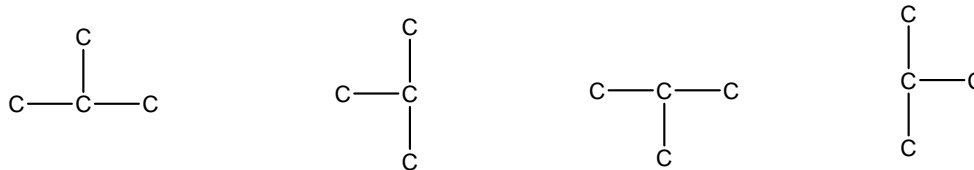
A four carbon chain can be drawn and rotated in a variety of ways, but there is no change effected in the skeletal connectivity of the atoms. No matter how the bonds are twisted, it's still a four carbon chain.



Let's now shorten our chain by one carbon atom so that the longest chain is three carbon atoms. Can we attach our remaining carbon atom in such a way so as to not make a four carbon chain. By attaching the fourth carbon atom to the middle carbon of our three carbon chain, the longest chain is only three carbon atoms in any direction, and we have a one carbon atom branch in the middle. This is a different carbon skeleton, and it has a different name: 2-methylpropane.



There are a lot of ways to write this as a 2D carbon skeleton on a piece of paper.



These are all representations of the same structure, but different from our first four carbon structure. These two molecules have exactly the same formula  $C_4H_{10}$  but they are not at all the same in their physical properties. The melting points, boiling points, densities and heats of formation are given below to emphasize this. Their spectra and chemistry would not be expected to be just alike either (and it's not). This should not be surprising. Think about how you would interact with the world if one of your arms was attached where your belly button is.

|  | melting<br>point | boiling<br>point | density | heat of<br>formation |
|--|------------------|------------------|---------|----------------------|
| butane, $CH_3CH_2CH_2CH_3$                       | -138             | -1               | 0.579   | -30.4                |
| 2-methylpropane, $CH_3CH(CH_3)_2$<br>(isobutane) | -159             | -12              | 0.549   | -32.4                |

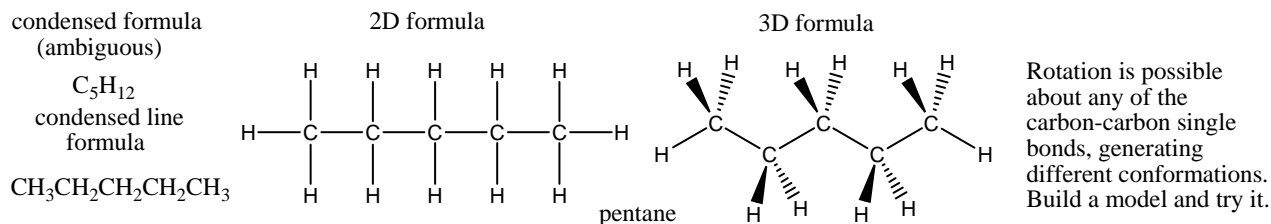
We refer to these two different compounds, having identical molecular formulas, as isomers (equal units). Isomers can be different in the connectivity of the atoms; that is their skeletons are different. Or, isomers can have the same connectivity of atoms, but differ in their orientation in space (stereoisomers). To try and visualize this, think of your left hand and your right hand. Both hands have the same types of fingers, but pointing in different directions in space, with important consequences for how you interact with the world.

In this example, since both four carbon alkanes have different skeletal connections, we call them structural or skeletal or constitutional isomers. We will encounter other types of isomers as we progress on our journey through organic chemistry.

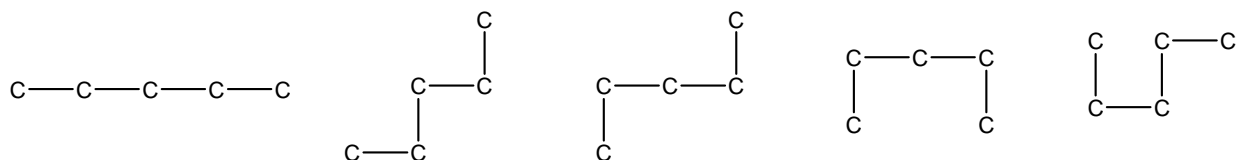
## Lecture 6

5. pentane isomers:  $C_5H_{12}$ 

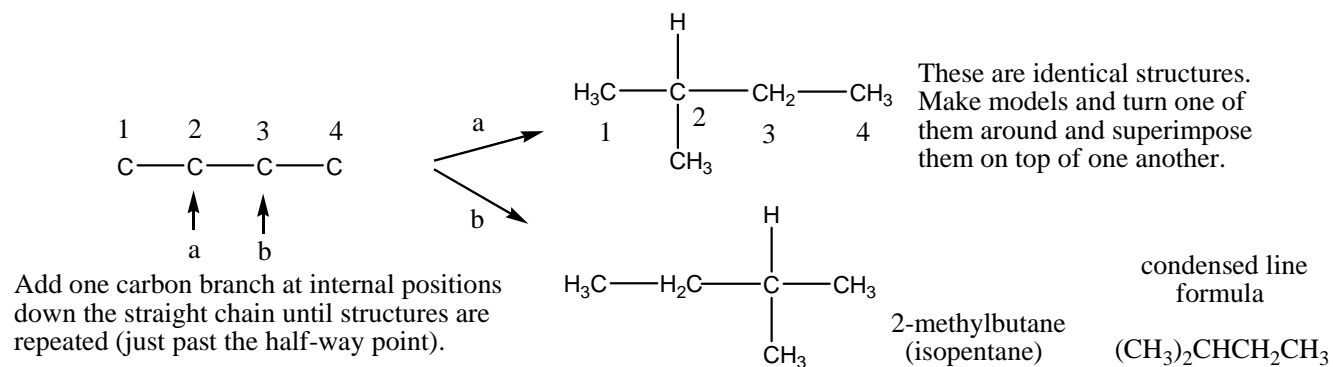
As before, we will begin with a five carbon straight chain isomer. There are 12 additional bonding sites, all filled with a hydrogen atom.  $C_5H_{12}$  is saturated and it is ambiguous.



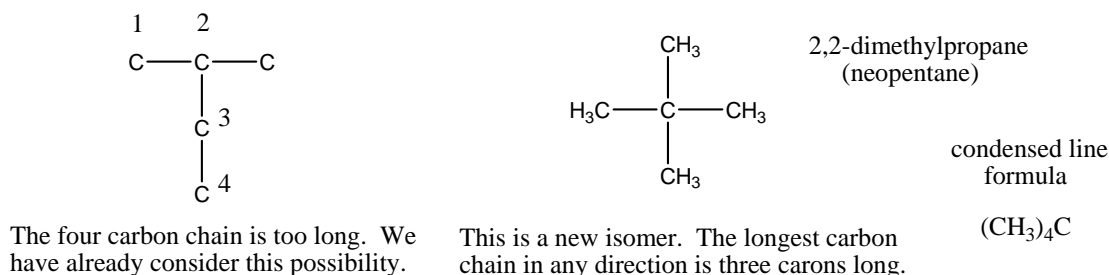
Each C-C single bond can be rotated so, again, there are a variety of ways to represent these five carbons, some of which are shown.



We can shorten this chain by one carbon atom (the longest chain is now four carbon atoms) and attach the one extra carbon atom at a nonterminal position to create a second isomer. There is only one additional isomer resulting from this operation.



Shortening the four carbon chain by an additional carbon atom, leaves us with a longest chain of three carbon atoms. Two carbon atoms remain to be added on. We have to avoid the terminal carbons because any additions to these increases the chain length to four carbons. We only have a single internal carbon position and two carbons to add on. If we add the two carbon atoms together, as a single branch, we have a four carbon chain, which we just did above. However, if we add on each of our two extra carbon atoms as one carbon branches to the internal carbon, then our longest chain is only three carbon atoms and this is yet another isomer.



## Lecture 6

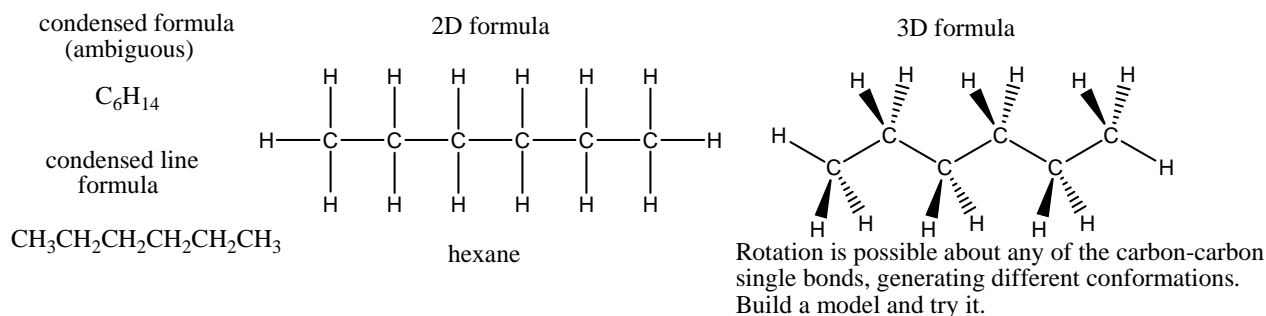
We cannot shorten our carbon chain to two carbon atoms because as soon as we add on our next carbon atom we are back up to a three carbon chain, and we just did that. So there are three different skeletal or structural or constitutional isomers for our saturated formula of  $C_5H_{12}$ .

Drawing all possible isomers of the five examples, thus far, has not proven particularly difficult.

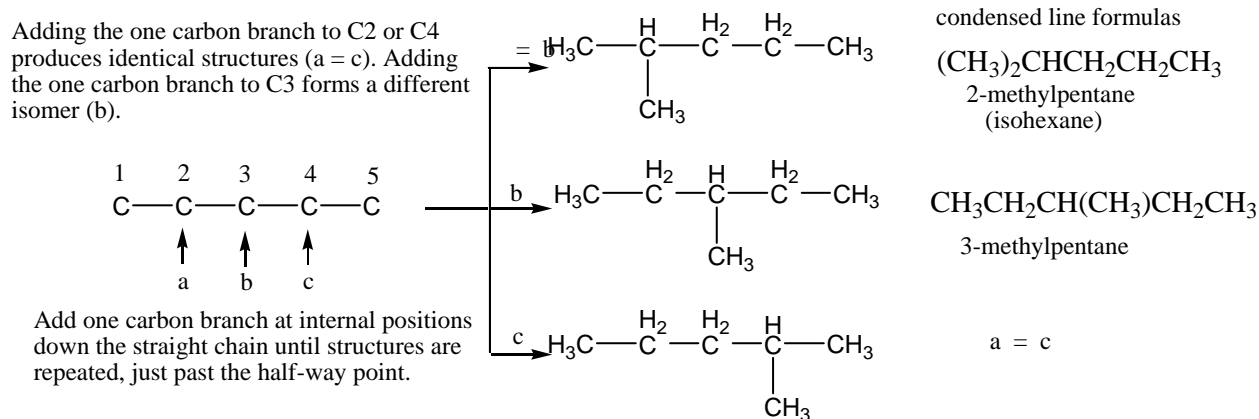
|          |          |          |             |             |
|----------|----------|----------|-------------|-------------|
| $CH_4$   | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ | $C_5H_{12}$ |
| 1 isomer | 1 isomer | 1 isomer | 2 isomers   | 3 isomers   |

6. hexane isomers:  $C_6H_{14}$ 

From this point on we have to be extra careful to be systematic in our approach. Following steps similar to our above examples we first write out the six carbon atom chain with its 14 additional bonding sites, all filled with hydrogen (saturated with hydrogen atoms).



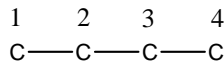
Next, we shorten this by one carbon and attach that carbon to nonequivalent, internal positions. There are two additional isomers with a longest chain of five carbons.



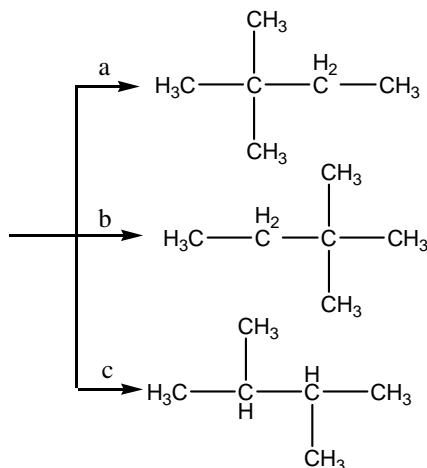
Next, we shorten our six carbon chain by two carbon atoms so that the longest carbon chain is four carbon atoms long. There are two carbon atoms left to add, which can be attached as a single two carbon branch or two one carbon branches. Adding a two carbon branch produces a five carbon chain that we already considered. However, adding two one carbon branches will produce new isomers. As before, we have to avoid the terminal carbon atoms. We can put both one carbon branches at the second carbon (or third carbon, which would be identical). Finally, we can keep one carbon branch in place and move the other carbon branch down the chain (avoiding the other end, of course).

## Lecture 6

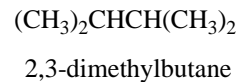
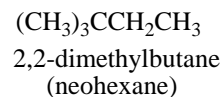
Structures "a" and "b" are identical. Structure "c" is a different isomer.



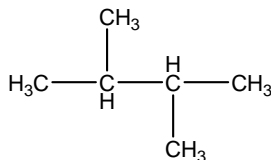
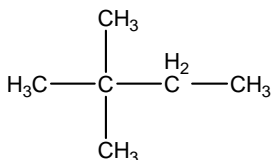
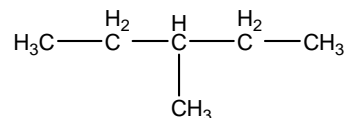
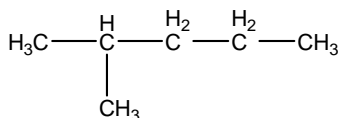
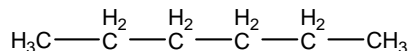
Adding two one carbon branches to C2 is the identical to adding two one carbon branches to C3. Adding a one carbon branch to C2 and C3 forms a different isomer.



condensed line formulas



We cannot shorten the carbon chain any more (i.e., a three carbon chain). When we try to add on the additional three carbons we are forced to draw at least a four carbon chain, which we just considered. So our six carbon atom formula produced five different skeletal isomers. This still seems like a reasonable result.



There are five  $\text{C}_6\text{H}_{14}$  skeletal isomers.

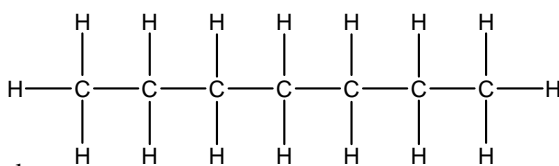
## 7. heptane isomers: $\text{C}_7\text{H}_{16}$

As a final example, we will look at the isomers of heptane in a more abbreviated form. We begin with the straight chain isomer.

condensed formula  
(ambiguous)



2D formula

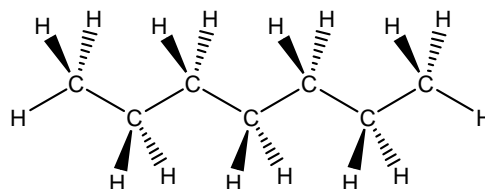


condensed line formulas



heptane

3D formula



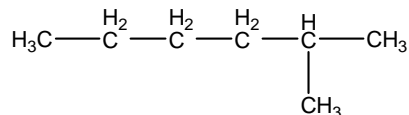
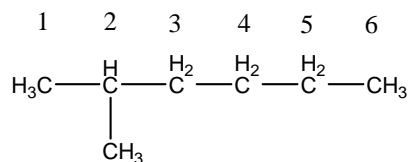
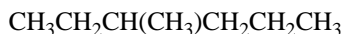
Rotation is possible about any of the carbon-carbon single bonds, generating different conformations. Build a model and try it.

Next, we shorten by one carbon and move that one carbon to unique internal positions on the six carbons chain. Notice substitution on C2 duplicates substitution on C5, while substitution on C3 duplicates substitution on C4.

## Lecture 6

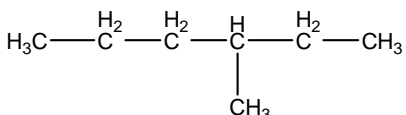
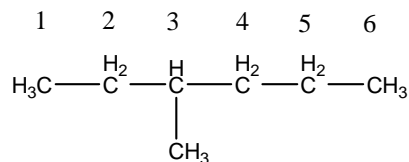
condensed formula  
(ambiguous)

condensed line formulas



2-methylhexane

These two structures are identical.



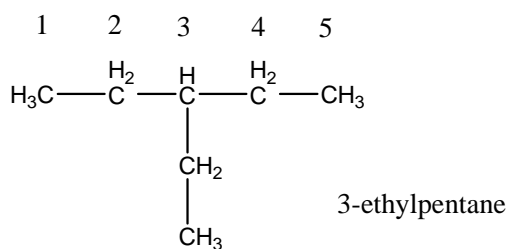
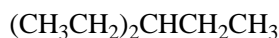
3-methylhexane

These two structures are identical.

We shorten the carbon chain to five carbon atoms, leaving two carbons to add on as a single two carbon branch or two one carbon branches. The two carbon branch can only be added to C3, or else a six carbon chain is formed (already considered above).

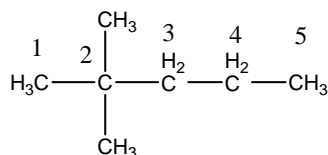
condensed formula  
(ambiguous)

condensed line formula

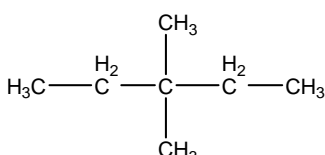


3-ethylpentane

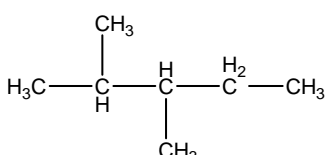
We can also add the extra two carbon atoms as two one-carbon branches. Beginning with both of them on C2 and moving them together to C3 forms a different isomer. Moving them both to C4 duplicates the C2 isomer. Leaving one of the one carbon branches at C2 and moving the other one carbon branch to C3 and then to C4 generates two additional isomers. All together this produces four additional isomers.



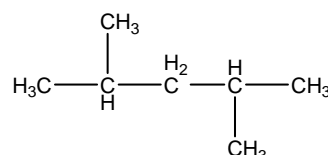
2,2-dimethylpentane



3,3-dimethylpentane



2,3-dimethylpentane



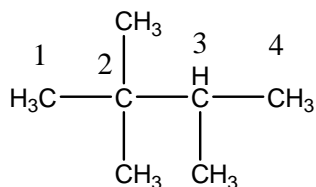
2,4-dimethylpentane



condensed line formulas

We next shorten the chain to four carbon atoms, leaving three carbon atoms to add on. Addition of a three carbon branch or a two carbon branch is not possible because either chain formed is too long (and already considered above). There is one extra isomer having three one carbon branches at C2 and C3. This is as far as we can go with a formula of  $C_7H_{16}$ .

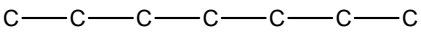
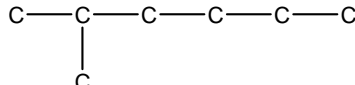
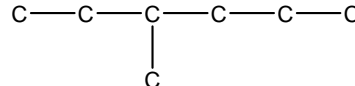
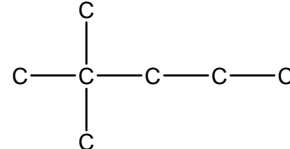
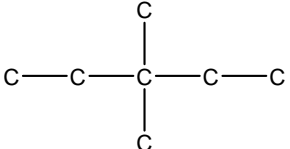
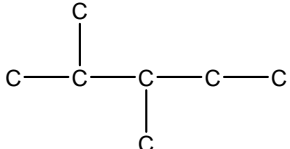
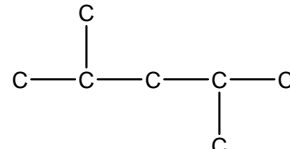
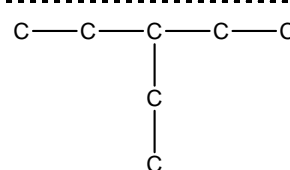
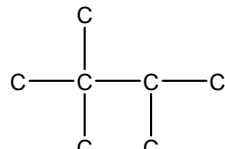
condensed line formula



2,2,3-trimethylbutane

## Lecture 6

There are nine different structural isomers. Their physical properties are different showing they are, in fact, distinct structures.

| C <sub>7</sub> H <sub>16</sub> alkane isomers |   | name                  | melting point (°C) | boiling point (°C) | density (g/cm <sup>3</sup> ) | refractive index | heat of formation (kcal/mole) |
|---|---|-----------------------|--------------------|--------------------|------------------------------|------------------|-------------------------------|
| 1.  |    | heptane               | -91                | 98                 | 0.684                        | 1.3878           | -44.88                        |
| 2.  |    | 2-methylhexane        | -118               | 90                 | 0.677                        | 1.3848           | -41.66                        |
| 3.  |    | 3-methylhexane        | -119               | 92                 | 0.686                        | 1.3887           | -41.02                        |
| 4.  |    | 2,2-dimethylpentane   | -124               | 79                 | 0.674                        | 1.3822           | -49.27                        |
| 5.  |    | 3,3-dimethylpentane   | -134               | 86                 | 0.694                        | 1.3909           | -48.17                        |
| 6.  |   | 2,3-dimethylpentane   | –                  | 90                 | 0.695                        | 1.3919           | -47.62                        |
| 7.  |  | 2,4-dimethylpentane   | -119               | 81                 | 0.673                        | 1.3815           | -48.28                        |
| 8.  |  | 3-ethylpentane        | -119               | 94                 | 0.698                        | 1.3934           | -45.33                        |
| 9.  |  | 2,2,3-trimethylbutane | -24                | 81                 | 0.690                        | 1.3894           | -48.95                        |

As the number of carbons goes up, the number of isomers grows beyond comprehension. Take a look at the numbers below.

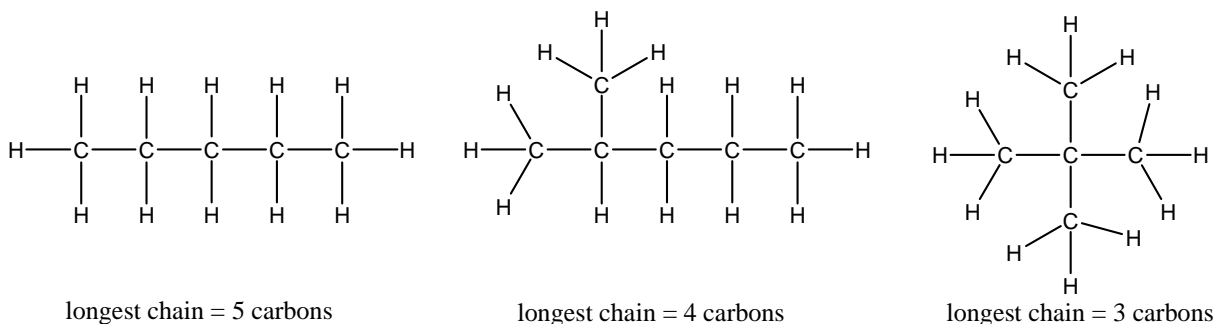


## Lecture 6

| formula                      | number of structural isomers                     |
|------------------------------|--|
| $\text{CH}_4$                | 1  |
| $\text{C}_2\text{H}_6$       | 1  |
| $\text{C}_3\text{H}_8$       | 1  |
| $\text{C}_4\text{H}_{10}$    | 2  |
| $\text{C}_5\text{H}_{12}$    | 3  |
| $\text{C}_6\text{H}_{14}$    | 5  |
| $\text{C}_7\text{H}_{16}$    | 9  |
| $\text{C}_8\text{H}_{18}$    | 18   |
| $\text{C}_9\text{H}_{20}$    | 35   |
| $\text{C}_{10}\text{H}_{22}$ | 75   |
| $\text{C}_{20}\text{H}_{42}$ | 366,319  |
| $\text{C}_{30}\text{H}_{62}$ | 4,111,846,763 (that's billion)                   |
| $\text{C}_{40}\text{H}_{82}$ | around 62,000,000,000,000 (and that's trillion!) |

Problem 1 - Generate the 18 possible structural isomers of  $\text{C}_8\text{H}_{18}$ . (We'll save  $\text{C}_{40}\text{H}_{82}$  for another lifetime. If you generated one isomer per second, it would take you about 2,000,000 years. We better make that several lifetimes.)

All we've been looking at are molecules that have only carbon and hydrogen and we are talking 2,000,000 years to do a problem. What happens if one little hydrogen atom is replaced with a halogen atom? This seems like a pretty minor change. After all, halogen atoms only form one bond, just like hydrogen atom? No pi bonds or rings can form because of one. We want an example that is complex enough to demonstrate the logic of what is changing, but not so complicated that we have to invest 2,000,000 years.  $\text{C}_5\text{H}_{12}$  should give us the insight we need, yet only has three different structural formulas.



### Adding a Chlorine to an Alkane Skeleton

The five carbon atom chain has three different bonding positions where we could switch out a hydrogen atom for a halogen atom (let's use a chlorine atom). The chlorine atom can bond at C1 (identical to C5), or at C2 (identical to C4), or at C3 (unique). There are four different kinds of bonding positions in the four carbon chain (C1 = C5, C2, C3 and C4). Finally, there is only one kind of bonding position in the three carbon chain (...that's right, all 12 C-H bonds are equivalent).

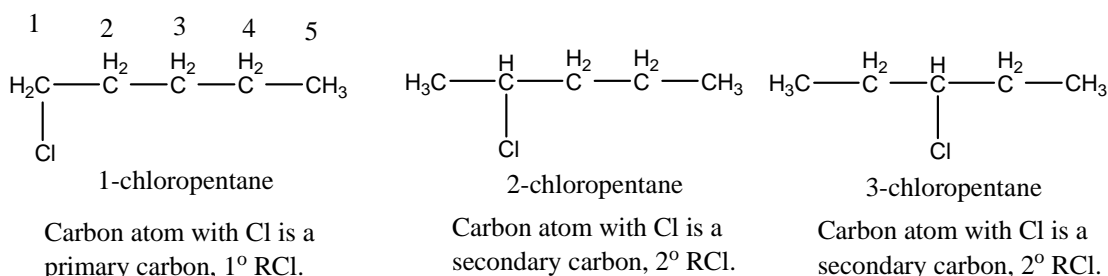
Carbon atoms are sometimes categorized by the number of other carbon atoms attached to them. If only one carbon is attached to a carbon of interest, it is classified as a primary carbon and sometimes symbolized by " $1^\circ$ ". If two carbons are attached to a carbon of interest, the classification is secondary ( $2^\circ$ ). When three carbons are attached to a carbon of interest the classification is tertiary ( $3^\circ$ ) and finally, if four carbons are attached to a carbon of interest the classification is quaternary ( $4^\circ$ ). Each of the  $\text{C}_5\text{H}_{12}$

## Lecture 6

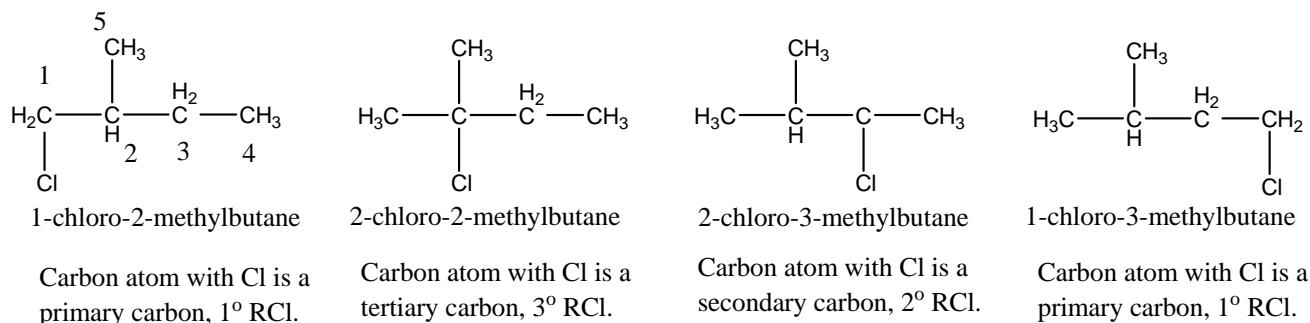
isomers is shown below with designation of primary, secondary or tertiary for the carbon atom bonded to the chlorine atom. The simple little chlorine atom changed three isomers into eight isomers.

**Eight chloroalkane isomers.**

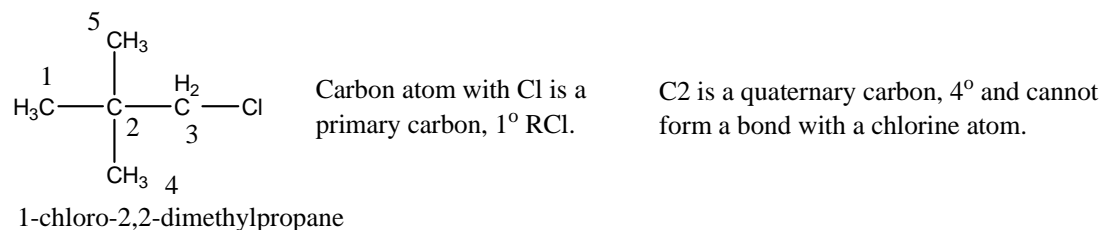
Five carbon chain. C1 = C5 and C2 = C4



Four carbon chain. C1 = C5



Three carbon chain. C1 = C3 = C4 = C5



**Problem 2** – Draw all of the possible isomers of  $\text{C}_4\text{H}_9\text{Br}$ . Hint: There should be four. If you feel ambitious, try and draw all of the possible isomers of  $\text{C}_6\text{H}_{13}\text{F}$ . There should be about 17 of them.

What happens when an oxygen is added to a formula? Oxygen forms two bonds, so there is a new possibility we haven't had to consider thus far. First, when an oxygen atom bonds to the surface of the carbon skeleton, by inserting itself between a carbon atom and a hydrogen atom, an alcohol functional group is created (ROH). Since the "OH" substituent, as a group, only forms one bond, the number of isomers possible is no different than the chlorine example above. If we used the same five carbon skeletons above, there would be eight possible isomeric alcohols.

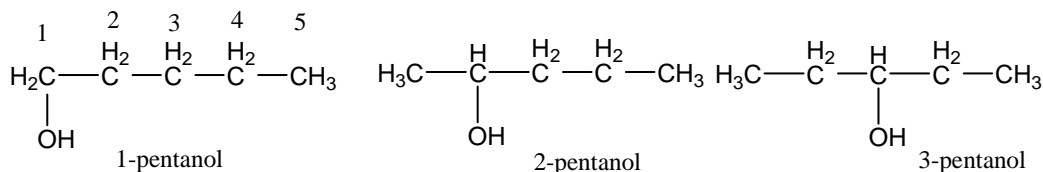
Oxygen atoms don't have to bond to the surface of a carbon skeleton, they can insert themselves in between two carbon atoms. It gets a little trickier to try and consider all of the possibilities for inserting oxygen between two carbons, since one carbon skeleton is becoming two carbon skeletons. When oxygen is surrounded on both sides by a simple carbon atom, the functional group is an ether (ROR).

The alcohol and ether functional groups are shown below, along with the classification of primary, secondary or tertiary for the carbon atoms bonded to the oxygen atom. An isolated  $\text{CH}_3$  substituent does not fall under any of the classifications (1°, 2°, 3° or 4°).  $\text{CH}_3$  groups go by the name of methyl.

## Lecture 6

**Eight alcohol isomers.**

Five carbon chain. C1 = C5 and C2 = C4

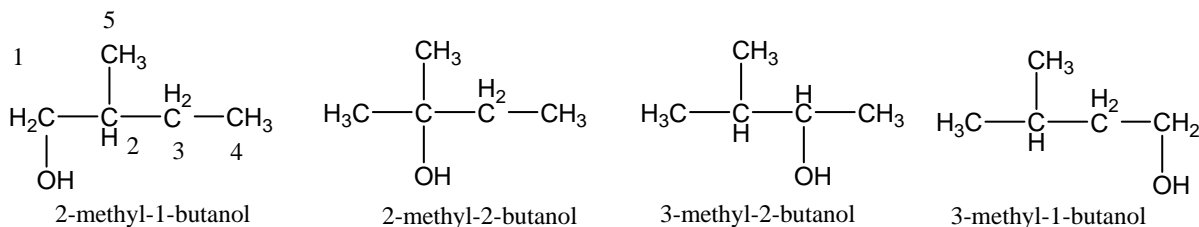


Carbon atom with OH is a primary carbon, 1° ROH.

Carbon atom with OH is a secondary carbon, 2° ROH.

Carbon atom with OH is a secondary carbon, 2° ROH.

Four carbon chain. C1 = C5



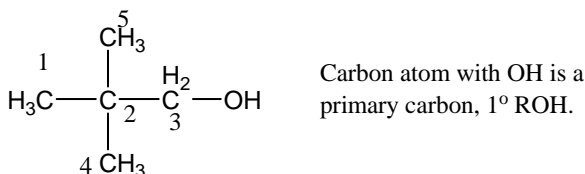
Carbon atom with OH is a primary carbon, 1° ROH.

Carbon atom with OH is a tertiary carbon, 3° ROH.

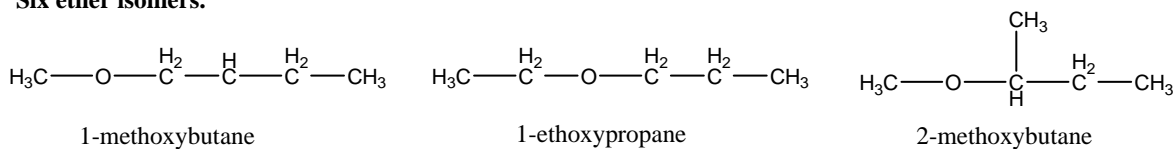
Carbon atom with OH is a secondary carbon, 2° ROH.

Carbon atom with OH is a primary carbon, 1° ROH.

Three carbon chain. C1 = C3 = C4 = C5



2,2-dimethyl-1-propanol

**Six ether isomers.**

Insert oxygen between C1 and C2 (same as between C4 and C5).

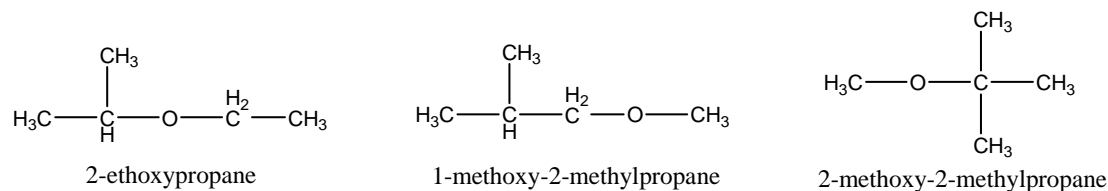
Insert oxygen between C2 and C3 (same as between C4 and C3).

Insert oxygen between C1 and C2 (same as between C5 and C2).

carbon to left of oxygen is methyl, carbon to right of oxygen is a primary carbon

carbon to left of oxygen is primary, carbon to right of oxygen is also a primary carbon

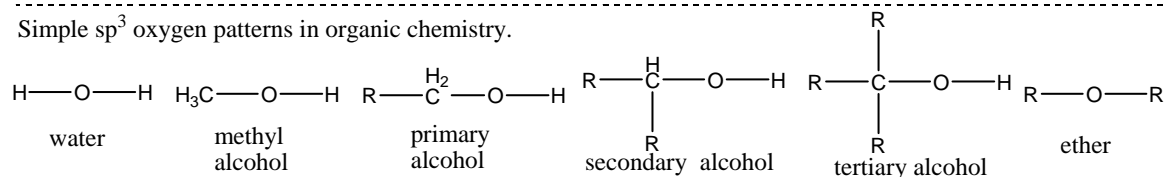
carbon to left of oxygen is methyl, carbon to right of oxygen is a secondary carbon



Insert oxygen between C2 and C3. carbon to left of oxygen is secondary, carbon to right of oxygen is a primary carbon

Insert oxygen between C3 and C4. carbon to left of oxygen is primary, carbon to right of oxygen is a methyl

Insert oxygen between C1 and C2. carbon to left of oxygen is a methyl, carbon to right of oxygen is tertiary

Simple sp<sup>3</sup> oxygen patterns in organic chemistry.

What happens when a nitrogen is added to the formula? Nitrogen forms three bonds, so there is again a new possibility we haven't had to consider before. When simple carbon atoms are bonded to simple nitrogen atoms with only single bonds between them, the functional group is called an amine. Amine nitrogen atoms are also classified by how many carbon atoms are attached to the nitrogen atom. Amines can be primary, secondary or tertiary depending on whether one carbon atom, two carbon atoms or three carbon atoms are attached to the nitrogen atom. If four carbon atoms are attached, a positive formal charge is required and the nitrogen is identified as a quaternary ammonium ion. As with oxygen, amine nitrogen atoms can be attached to the surface of a carbon skeleton as primary amines,  $\text{RNH}_2$ . If the nitrogen atom is inserted between carbon atoms, it will be a secondary,  $\text{R}_2\text{NH}$ , or tertiary amine,  $\text{R}_3\text{N}$ . If we use the same five carbon structures above, there will be 17 possible isomeric amines (quite a change from the simple carbon skeletons we started with)! These are drawn below, along with the classifications of primary, secondary or tertiary amine.

## primary amines

primary amine, 1° RNH<sub>2</sub>

primary amine, 1° RNH<sub>2</sub>

primary amine, 1° RNH<sub>2</sub>

primary amine, 1° RNH<sub>2</sub>

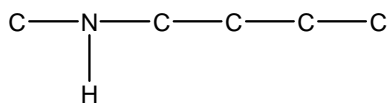
primary amine, 1° RNH<sub>2</sub>

primary amine, 1° RNH<sub>2</sub>

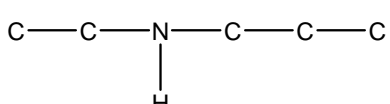
primary amine, 1° RNH<sub>2</sub>

2,2-dimethyl-1-propanamine

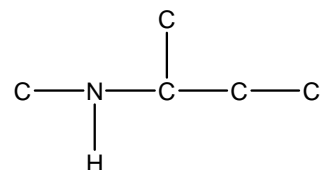
## Lecture 6

**secondary amines**

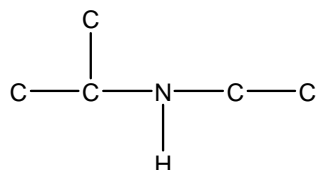
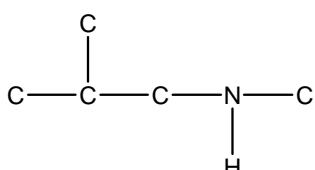
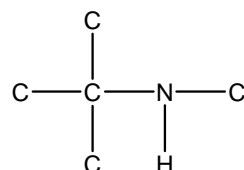
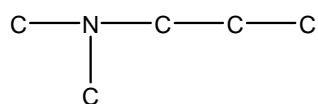
N-methyl-1-butanamine

secondary amine,  $2^\circ \text{R}_2\text{NH}$ .

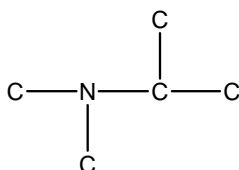
N-ethyl-1-propanamine

secondary amine,  $2^\circ \text{R}_2\text{NH}$ .

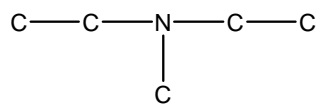
N-methyl-2-butanamine

secondary amine,  $2^\circ \text{R}_2\text{NH}$ .N-ethyl-2-propanamine  
secondary amine,  $2^\circ \text{R}_2\text{NH}$ .2,N-dimethyl-1-propanamine  
secondary amine,  $2^\circ \text{R}_2\text{NH}$ .2,N-dimethyl-2-propanamine  
secondary amine,  $2^\circ \text{R}_2\text{NH}$ .**tertiary amines**

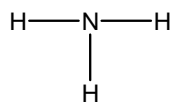
N,N-dimethyl-1-propanamine

tertiary amine,  $3^\circ \text{R}_3\text{N}$ .

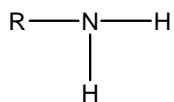
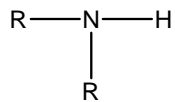
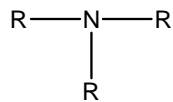
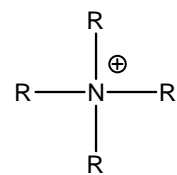
N,N-dimethyl-2-propanamine

tertiary amine,  $3^\circ \text{R}_3\text{N}$ .

N-ethyl-N-methylethanamine

tertiary amine,  $3^\circ \text{R}_3\text{N}$ .Simple  $\text{sp}^3$  nitrogen patterns in organic chemistry.

ammonia

primary  
aminesecondary  
aminetertiary  
amine

ammonium ion

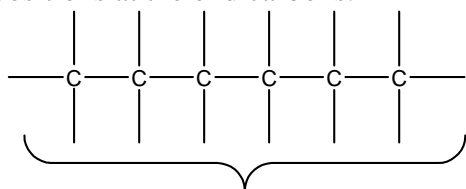
## Lecture 6

Problem 4 – Draw all of the possible isomers of  $C_4H_{11}N$ . Hint: There should be eight. If you feel ambitious, try and draw all of the possible isomers of  $C_6H_{15}N$ . There should be about 39 of them.

All of the bonding patterns above have full saturation, meaning every bonding position possible is filled with an individual atom (usually hydrogen atoms, but sometimes a halogen atom).

### Degrees of Unsaturation (or Hydrogen Deficiency)

Alkanes are an example of saturated molecules. Every single bonding position on the carbon skeleton is filled with a hydrogen atom. If a halogen atom or an OH of an alcohol or  $NH_2$  of an amine are substituted in for one of the hydrogen atoms, the molecule is still saturated. The number of bonding positions on an alkane carbon skeleton is easy to calculate. There are two positions on every carbon atom plus two additional positions at the end carbons.



Two bonding positions on every carbon, plus two more at the end positions.

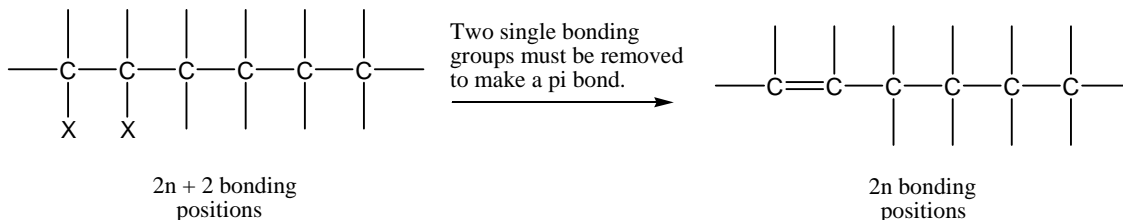
Maximum number of bonding positions on a saturated carbon skeleton =  $2n + 2$

$n$  = the number of carbon atoms in the structure

Maximum number of bonding positions on a six carbon skeleton =  $2(6) + 2 = 14$

When a pi bond or a ring is present, the number of single bonding groups will be less than this maximum number ( $2n + 2$ ). To make a pi bond, two hydrogen atoms must be removed from adjacent atoms, so that a second bond can form between those two atoms. Making a ring also requires that two hydrogen atoms be removed in order for the chain of atoms to connect back on itself. The maximum number of bonding decreases by two for every degree of unsaturation. A pi bond or a ring, in turn, is also referred to as a degree of unsaturation.

#### Pi Bonds

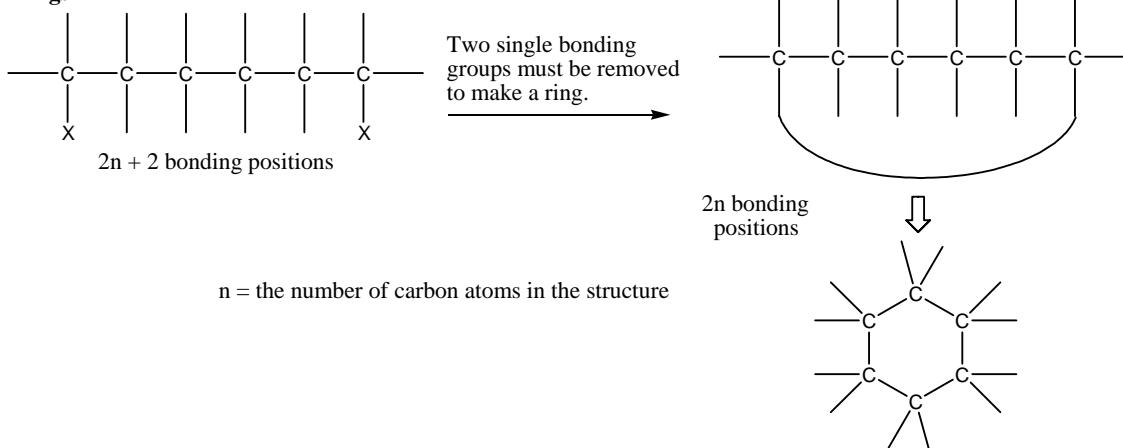


$2n + 2$  bonding positions

$2n$  bonding positions

$n$  = the number of carbon atoms in the structure

#### Rings



$2n + 2$  bonding positions

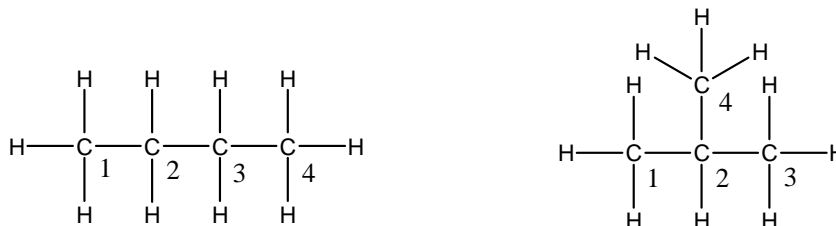
$2n$  bonding positions

$n$  = the number of carbon atoms in the structure

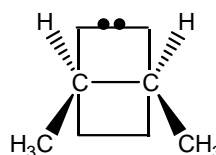
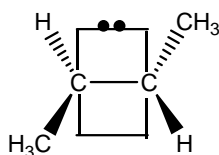
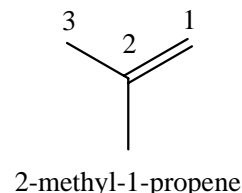
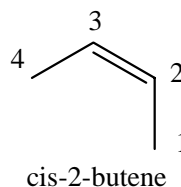
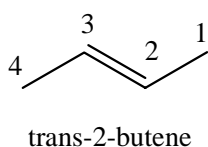
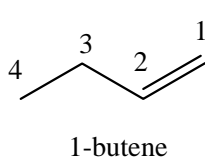
## Lecture 6

We restricted ourselves in the initial examples, above, to saturated structures in order to limit the number of possible isomers. Adding just a single degree of unsaturation will greatly increase this number.

Let's see what happens to the  $C_4H_{10}$  formula when a single degree of unsaturation is introduced, either as a pi bond or as a ring? The new formula will have two fewer hydrogen atoms,  $C_4H_8$ . There are two different alkane carbon skeletons and we can use those as starting points to decide where pi bonds and rings can be placed.

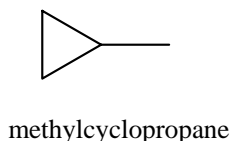
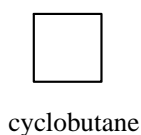


Either the straight chain or the branched chain will allow a pi bond between any two adjacent atoms. In the straight chain a pi bond between C1 and C2 is identical to a pi bond between C4 and C3. A pi bond between C2 and C3 actually generates two different isomers, because of the restricted rotation about the pi bond. If the two  $CH_3$  groups (methyl groups) are on the same side of the pi bond, the isomer is a cis alkene and if the two methyl groups are on opposite sides of the pi bond, the isomer is a trans alkene. Three alkenes are possible from the straight chain skeleton. In the branched carbon skeleton, a pi bond of C2 with any of the other carbon atoms forms an identical alkene, having two methyl groups on one carbon and two hydrogen atoms on the other carbon. No cis/trans isomers are possible when two identical groups are on a single carbon.



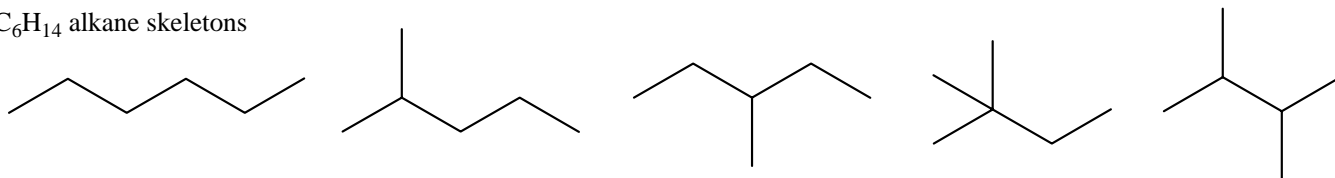
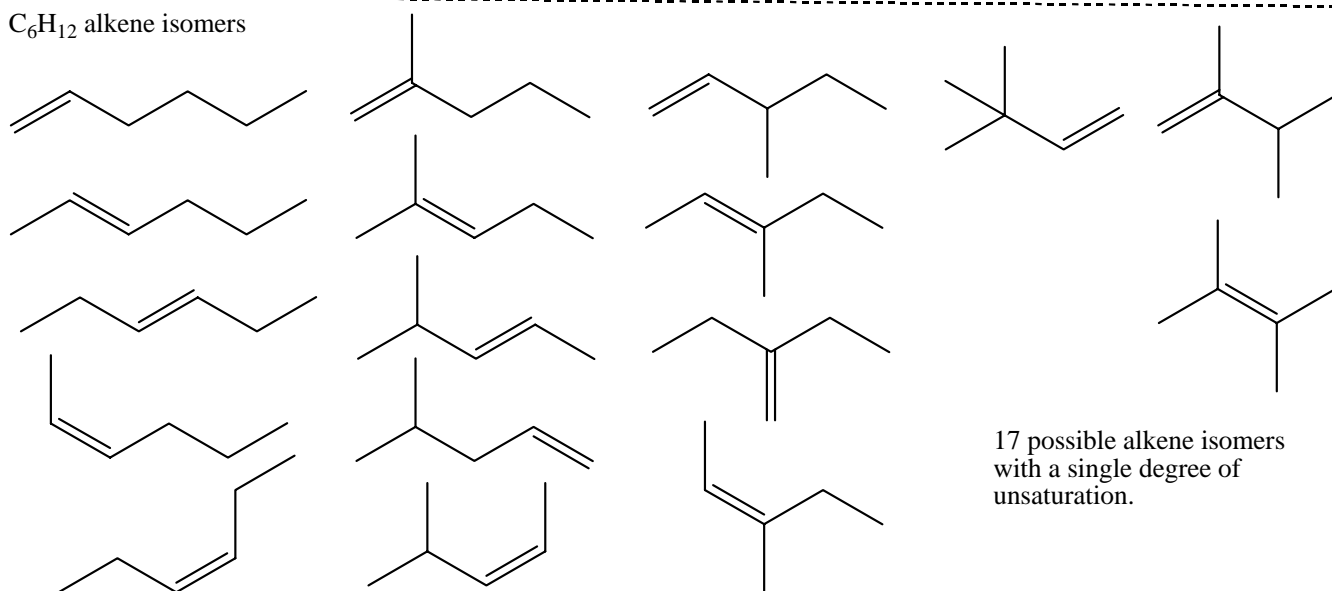
No rotation is possible without breaking the pi bond. This is too energetically expensive at room temperature. Restricted rotation about the pi bond makes these two alkenes different.

There are two possible ways to make one ring using the four carbon atoms. All four carbon atoms will form a four carbon ring (cyclobutane) and three of the carbon atoms can form a ring having a one carbon branch (methylcyclopropane). The two carbon skeletons of  $C_4H_{10}$  becomes six carbon skeletons of  $C_4H_8$ .

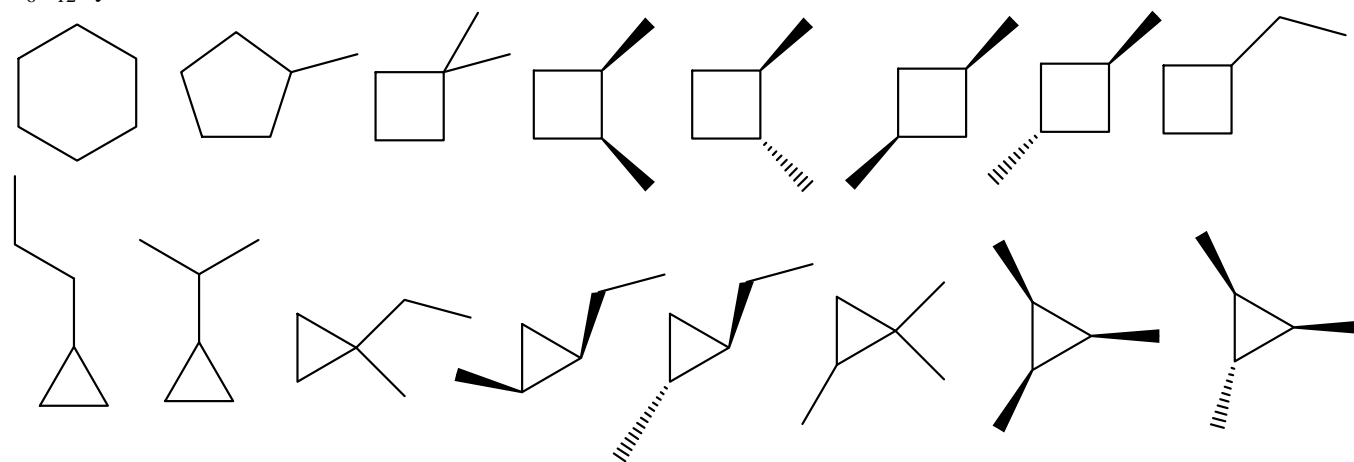


The five alkane isomers of  $C_6H_{14}$  becomes 17 alkene isomers and 15 cycloalkane isomers (..if I found them all). These are presented below without comment. A single degree of unsaturation really changes things.

## Lecture 6

 $C_6H_{14}$  alkane skeletons $C_6H_{12}$  alkene isomers

17 possible alkene isomers  
with a single degree of  
unsaturation.

 $C_6H_{12}$  cycloalkane isomers

16 possible cycloalkane isomers with a single degree of unsaturation. There are actually more, but only cis/trans stereoisomers are included.

Problem 5 – Calculate the degree of unsaturation in the hydrocarbon formulas below. Draw one possible structure for each formula.

a.



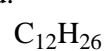
b.



c.



d.



e.



f.



g.



h.



i.



j.



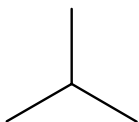
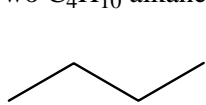
Problem 6 – Draw all of the alkene and cycloalkane isomers of  $C_5H_{10}$ . I calculate that there should be six alkenes and six cycloalkanes.



## Lecture 6

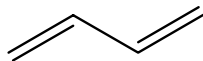
What would two degrees of unsaturation do to the four carbon alkane? We have to consider more possible combinations, including two pi bonds, a pi bond and a ring or two rings. Each is possible as is shown below.

Two  $C_4H_{10}$  alkane skeletons

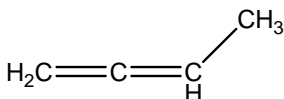


| pi bonds | rings |
|----------|-------|
| 2        | 0     |
| 1        | 1     |
| 0        | 2     |

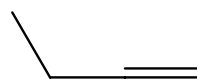
Four  $C_4H_6$  isomers having two pi bonds



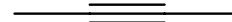
1,3-butadiene



1,2-butadiene  
(an allene)

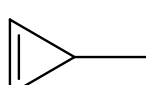
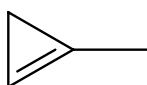
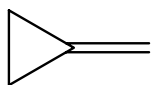


1-butyne

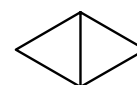


2-butyne

Four  $C_4H_6$  isomers having one pi bond and one ring

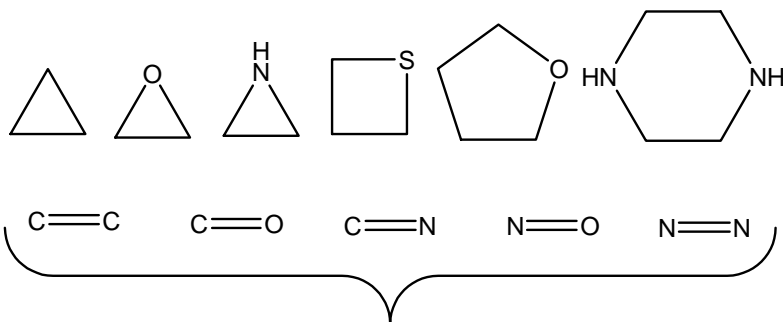


One  $C_4H_6$  isomer having two rings

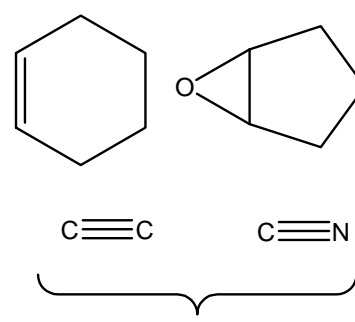


Problem 7 – If you feel daring, try and draw some of the isomers of  $C_5H_8$ . I found four dienes (2 pi), three alkynes (2 pi), three allenes (2 pi), ten ring and pi bond isomers and four isomers with two rings. It's quite possible that I missed some. Why not shoot for two of each possibility.

Any pi bond or ring uses up two bonding positions and introduces a degree of unsaturation, no matter what atoms are bonded together.



These all count as one degree of unsaturation.

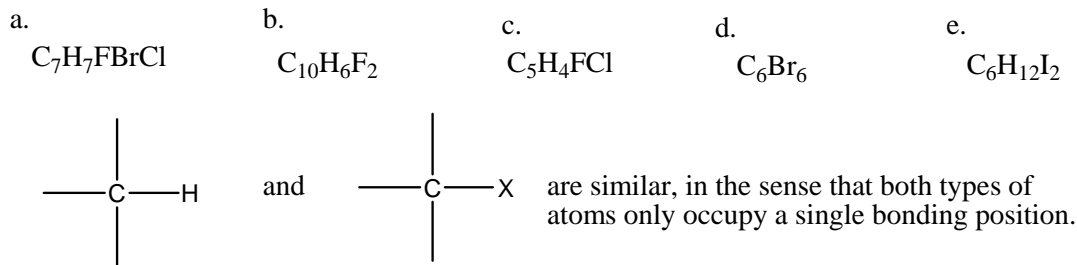


These all count as two degrees of unsaturation.

Halogen atoms are similar to hydrogen atoms in that they only form single bonds. They are added to the hydrogen atom count to obtain a total number of single bonding groups and this number is compared to the maximum number of single bonding positions ( $2n + 2$ ). Every two groups short of the maximum number of bonding positions is a degree of unsaturation.

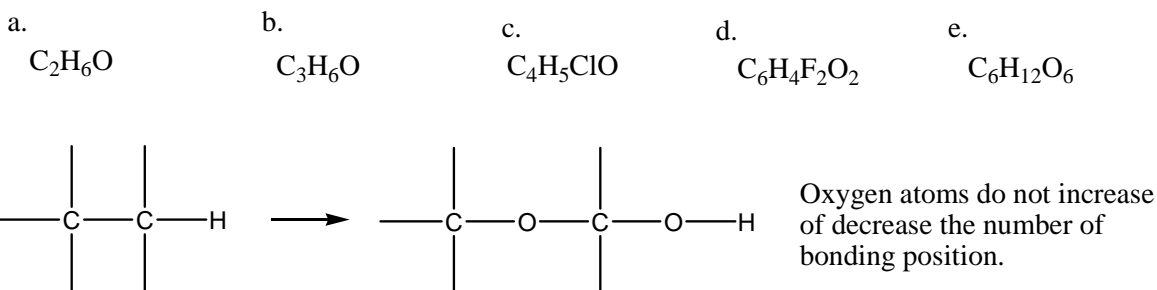
Problem 8 – Calculate the degree of unsaturation in the formulas below. Draw one possible structure for each formula.

## Lecture 6



How do oxygen atoms change the calculation of degree of unsaturation? The answer is oxygen atoms do not change the calculation at all. Because oxygen atoms form two bonds, the bond they take away by connecting to the carbon skeleton they give back through their second bond. Oxygen atoms act like spacers between carbon and hydrogen atoms or between two carbon atoms. Just act like the oxygen atoms aren't there and perform the calculation just as you did above.

Problem 9 – Calculate the degree of unsaturation in the formulas below. Draw one possible structure for each formula.



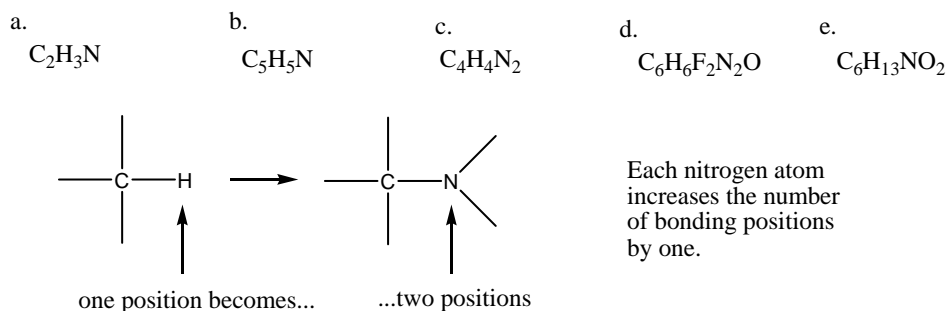
How do nitrogen atoms change the calculation of degree of unsaturation? Nitrogen atoms add an extra bonding position for every single nitrogen atom present. Nitrogen atoms make three bonds. One bond is used in connection to the carbon skeleton. Nitrogen atoms give back two additional bonds in the place of that single bond, so there is one extra bond that wasn't there before. For every nitrogen atom present, you have to add an extra bonding position. The formula we use to calculate degrees of unsaturation has to be modified as follows.

Maximum number of single  
 bonding groups on a carbon skeleton =  $2(\#C) + 2 + \#N$

$\#C$  = the number of carbon atoms

$\#N$  = the number of nitrogen atoms

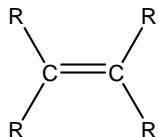
Problem 10 – Calculate the degree of unsaturation in the formulas below. Draw one possible structure for each formula.



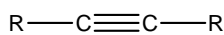
## Lecture 6

Problem 11 – The following functional groups are unsaturated. Draw as many structures as you can for each of the examples below.

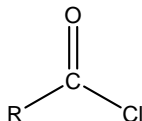
alkene isomers of  $C_5H_{10}$ , at least six, don't forget cis and tran possibilities



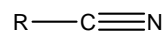
alkyne isomers of  $C_5H_8$ , at least three



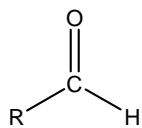
acid chloride isomers of  $C_5H_9OCl$ , at least four



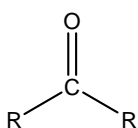
nitrile isomers of  $C_5H_9N$ , at least four



aldehyde and ketone isomers of  $C_5H_{10}O$ , at least seven

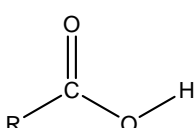


aldehyde

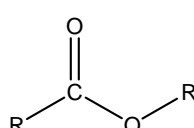


ketone

carboxylic acid and ester isomers of  $C_5H_{10}O_2$ , at least 13

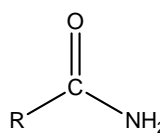


carboxylic acid

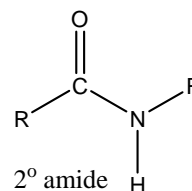


ester

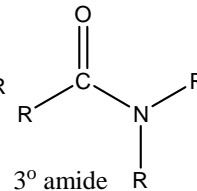
primary, secondary and tertiary amide isomers of  $C_5H_{11}NO$ , at least 17



1° amide



2° amide



3° amide