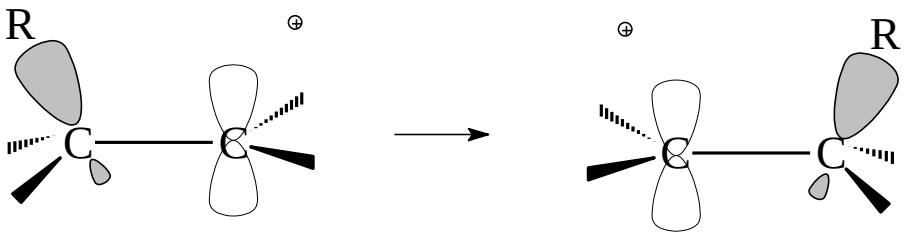
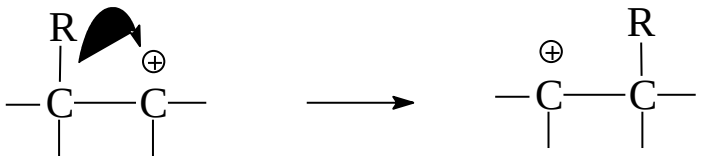
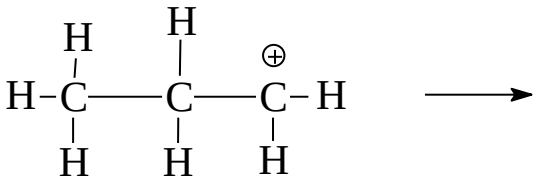
CARBOCATION REARRANGEMENTS



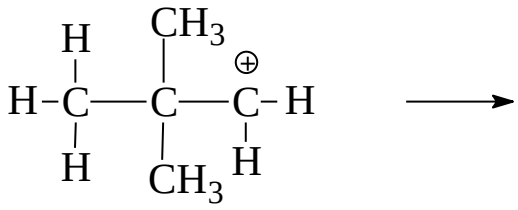
The general example of a 1,2-shift:



An example of a 1,2-hydride shift: (the two methylene H's are equivalent and so either can shift)



An example of a 1,2-methyl shift: (the three methyl groups are equivalent and so any of them can shift)



SUGGESTED PROBLEMS (Answers on the next page.)

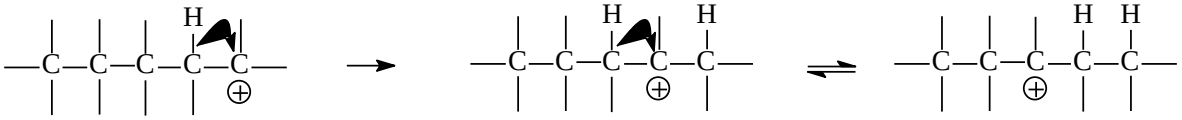
Draw all carbocations of formula $(C_5H_{11})^+$. [Hint: Begin by drawing structures for all 3 pentane isomers, and then determine how many carbocations can be generated for each isomer. Remember to look for equivalent CH's.]

a. Classify each carbocation carbon as primary, secondary or tertiary.

b. For each carbocation that could potentially rearrange to a more stable carbocation, use arrows to show either a hydrogen or methyl shift and the structure of the newly-formed carbocation.

c. Where possible, show two or more sequential shifts that result in a more stable carbocation.

Three carbocations are derived from *n*-pentane [$CH_3CH_2CH_2CH_2CH_3$]. If you draw the 1° first, then it can be shown how to generate the two 2°'s from it by sequential shifts.



primary

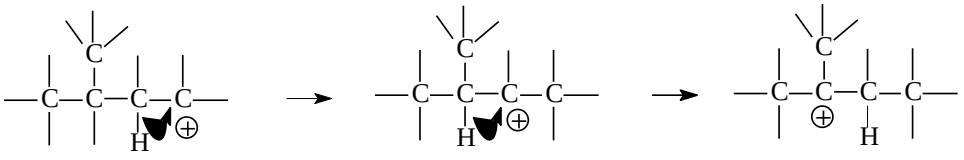
secondary

secondary

(About the same stability. The two 2^o carbocations can interconvert by hydrogen shifts.)

Four carbocations are derived from isopentane [$(CH_3)_2CHCH_2CH_3$]. (Remember, the two Me groups on the left are equivalent.)

<u>Draw a 1° first</u>. A 2° and 3° carbocation can be generated in sequential shifts.



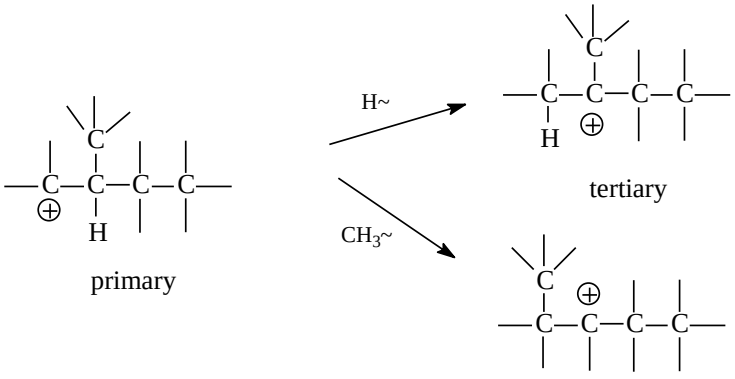
primary

secondary

tertiary

(Stable; no rearrangement.)

<u>Draw the other possible 1°</u>. It can rearrange by either a H-shift or a CH_3-shift from the tertiary carbon.



primary

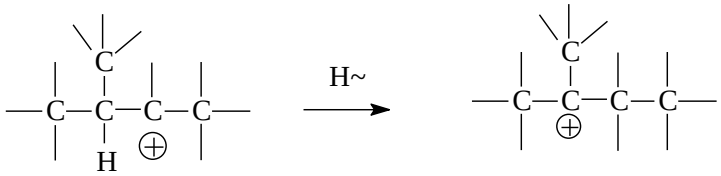
tertiary

secondary

(This carbocation is the same as the 2^o generated from n-pentane, above.)

The secondary carbocation cannot rearrange to a more stable 3°, but it can rearrange to another secondary carbocation of ~ same stability (see the ones generated from *n*-pentane, above).

<u>The third carbocation is the 2° carbocation</u>. It can rearrange to the more stable tertiary.



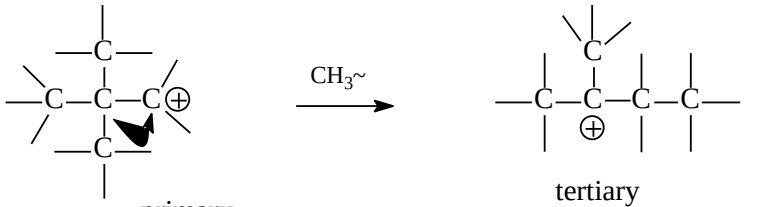
secondary

tertiary

(Same as tertiary, above.)

The fourth carbocation derived from isobutane is the tertiary carbocation, shown above, which will not rearrange since it is the most stable.

One carbocation is derived from neopentane



primary

tertiary

(Same as tertiary, above.)