4.16 Reactive Intermediates: Stability Patterns

- Shortlived, unstable, highly reactive intermediates
- Normally lack normal bonding

These are tremendously important:

- 1. They will be the least stable intermediate in any multistep mechanism
- 2. When formed, they are **products of the rate-determining step**
- 3. Factors that stabilize them will speed up reaction rates

Thus it is very important to know their stability patterns!

<u>Class</u> Carbocations	<u>Structure</u> −¢⊕	<u>Stability Pattern</u> Allylic > 3° > 2° > 1° > methyl > alkenyl (vinyl, aryl)	Electron Poor	Electrophilic/ Acidic
Carbon Radicals	C^! •	Allylic > 3° > 2° > 1° > methyl > alkenyl (vinyl, aryl)	Electron Poor	Electrophilic/ Acidic
Carbanions	-c:	Allylic > alkenyl (vinyl, aryl) > methyl > 1° > 2° > 3°	Electron Rich	Nucleophilic/ Basic

<u>Notes</u>

- 1. Both carbocations and radicals have the same pattern. So you don't need to memorize them twice!
- 2. Carbanions are almost exactly the reverse, except that being allylic is ideal for both.
- 3. All benefit from resonance (allylic).
- 4. Cations and radicals both fall short of octet rule. As a result, they are both electron deficient. Carbanions, by contrast, are electron rich.
- 5. Alkyl substituents are electron donors. As a result, they are good for electron deficient cations and radicals $(3^{\circ} > 2^{\circ} > 1^{\circ} > \text{methyl})$ but bad for carbanions.
- 6. Alkenyl (vinyl or aryl) carbons are inherently a bit electron poor. This is excellent for carbanions, but terrible for cations or radicals.