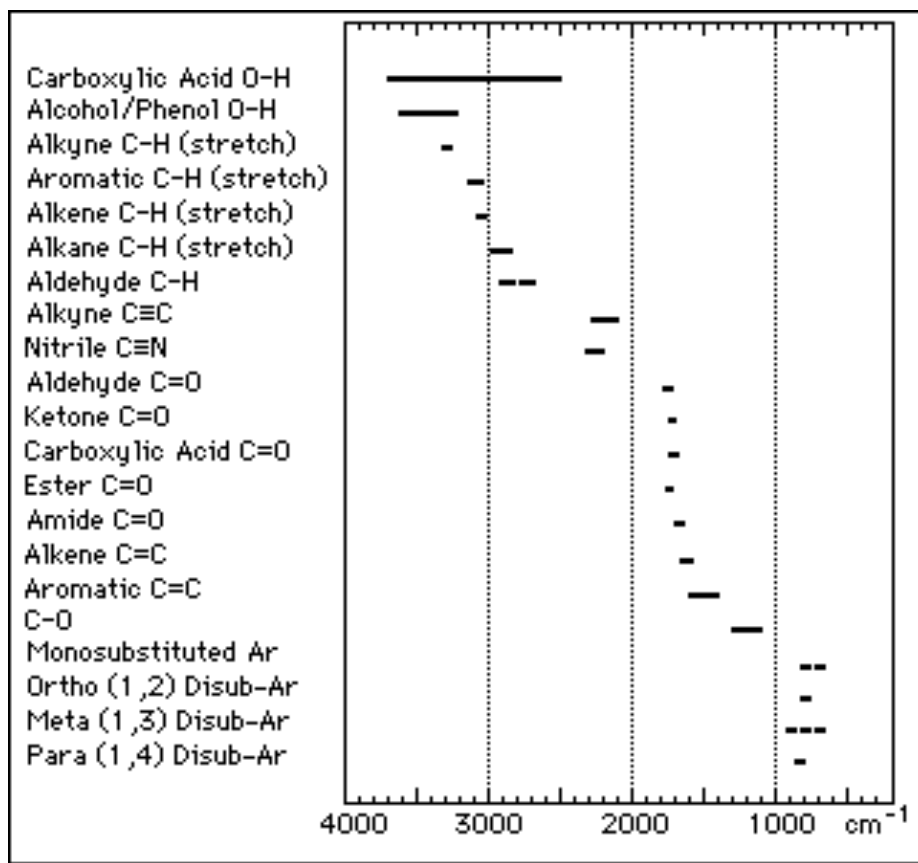


## Chapter 11. Alkenes, Infrared Spectroscopy & Mass Spectrometry

Infrared (IR) spectroscopy refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. Of greatest practical use to the organic chemist is the limited portion between 4000 and 400  $\text{cm}^{-1}$ . Infrared radiation in this region is absorbed and converted by an organic molecule into energy of molecular vibration. This absorbance is quantized, but vibrational spectra appear as bands rather than as lines because a single vibrational energy change is accompanied by a number of rotational energy changes. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds, and geometry of the atoms.

Even a very simple molecule can give an extremely complex IR spectrum. We distinguish between characteristic bands for specific functional groups and whole-molecule vibrations that are particularly pertinent between 1400 and 800  $\text{cm}^{-1}$ . The latter part of the IR spectrum is known as the “fingerprint” area, provides a complex but specific signature of a molecule, and is used for assignment of unknown compounds in comparison to reference spectra. It is unlikely that any two compounds, except enantiomers, give exactly the same IR spectrum.

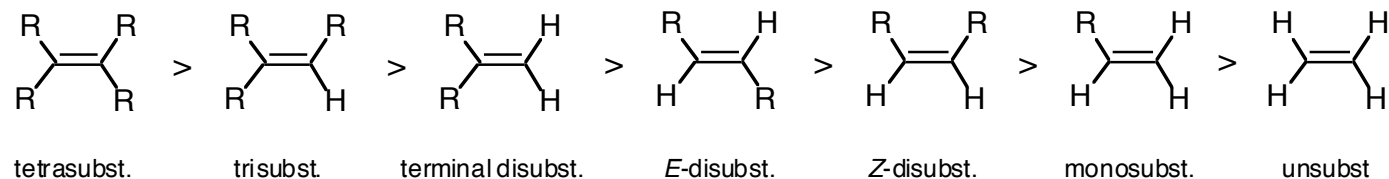
Characteristic group frequencies:



Alkenes (olefins) are important functionalized hydrocarbons with double bonds. They serve as starting materials for a wide variety of organic compounds. The nomenclature rules allocate a higher priority to double bonds, alkyl groups, and halides, but lower than oxygen-containing

functional groups such as alcohols. The index of hydrogen deficiency gives us an idea of the total unsaturation, e.g. the sum of double bonds, triple bonds, and ring systems, in a molecule with a given molecular formula.

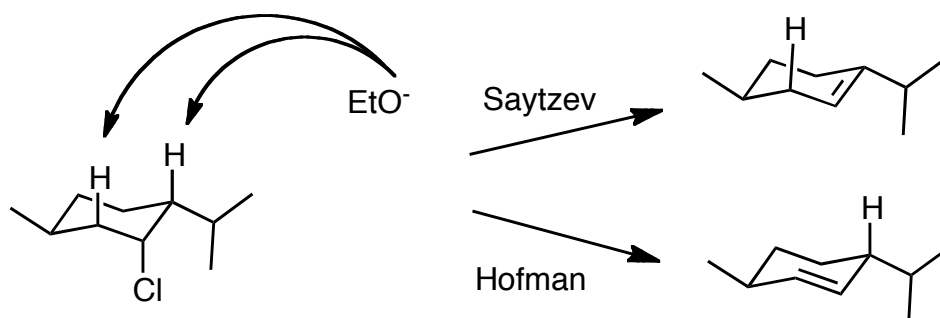
The relative stability of alkenes is revealed by analyses of heats of hydrogenation:



Methods for preparation of alkenes:

- Dehydrohalogenation (E2, E1) of alkyl halides and sulfonates. Saytzev's rule: Sterically undemanding bases and thermodynamic (equilibrating) conditions favor the more stable, more highly substituted alkenes. Hofman's rule: With bulky bases and under kinetic (non-equilibrating) conditions, the less stable, less substituted alkene is preferred.

Also, the stereochemistry of the substrate in E2 reactions (anti-elimination) has to be considered and can determine the product structure.



- Dehydration of alcohols. The ease of dehydration via E1 reactions (acidic conditions) decreases from  $3^\circ > 2^\circ > 1^\circ$  alcohols. Wagner-Meerwein rearrangements of the intermediate carbocations ([1.2] hydride or alkyl group shifts) lead to the formation of the more stable carbocation.

- Debromination of vicinal dibromides with Zn: Wurtz-coupling.

Mass spectrometry (MS) of organic compounds provides the molecular mass ( $M^+$ ) as well as the chemical formula (by HRMS). Fragmentation of the molecular ion can be used to analyze structures and determine the presence of functional groups, for example by  $\alpha$ -cleavage:

