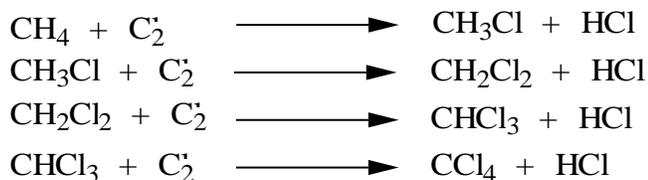


1. Free radical halogenation of alkanes.

Alkane + halogen + uv, ROOR, or 300°C+.



R-H + F₂ Not useful, too fast, not specific

R-H + Cl₂ Useful, controllable, somewhat nonspecific (3° > 2° > 1° > CH₄)

R-H + Br₂ Useful, controllable, specific for 3° if present (3° » 2° > 1° > CH₄)

R-H + I₂ Not useful, too Slow

Determine the number of constitutional isomers produced when a halogen is reacted with a higher alkane (more complex than simple alkane).

2. Combustion of alkanes.



3. Dehydrogenation of an alkane to give an alkene.

Alkane + metal catalyst (Pt, Ni, Pd) + heat yields an alkene.



Usefull for ethane, propane, and isobutane only. Others give multiple products.

4. Addition to alkenes.



Adding agent can be symmetrical or asymmetrical. Ex. H₂ vs. HCl

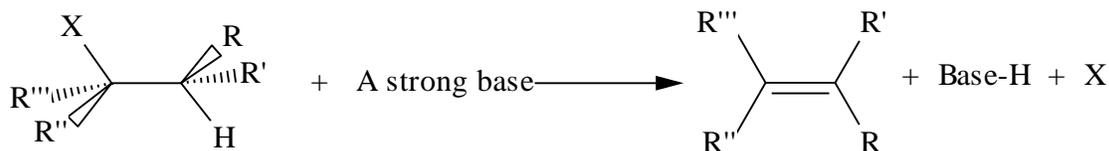
Symmetrical: H₂, Cl₂, Br₂, and I₂ (I₂ slow and readily reversible)

Asymmetrical: HCl, RBr, HOH (H₂O)

Addition of symmetrical agents may be anti or syn depending on mechanism or catalyst. Addition of asymmetrical agents follows Markovnikov's Rule except for addition of HBr in the presence of peroxides which adds anti-Markovnikov (only works with HBr).

5. Dehydrohalogenation of alkyl halides to give alkenes.

Elimination reactions favored by strong bases and heat.

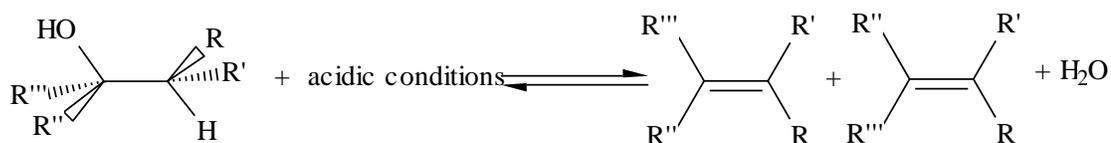


Halogen and hydrogen must be anticoplanar. Hindered bases favor elimination (E2) over substitution (SN₁ and SN₂). Higher temperatures favor elimination.

Bases that favor elimination: Alcoholic KOH, alkoxides (t-butoxide commonly used), NH₂⁻ will cause elimination.

6. Dehydration of alcohols to yield alkenes. Acid catalyzed and reversible reaction.

Proceed through a carbocation intermediate. Skeletal rearrangements possible.

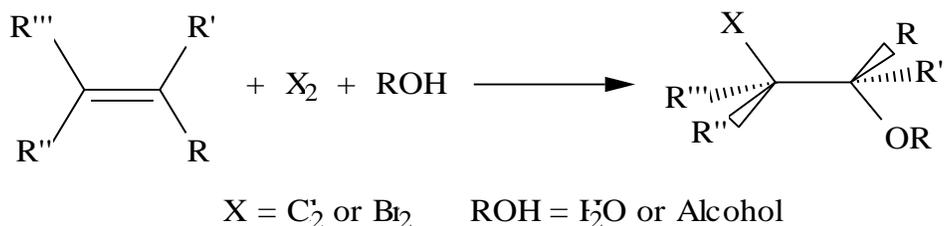


3° ROH easier than 2° ROH easier than 1° ROH. Typical conditions include:

3°	20% H ₂ SO ₄ at 30-40°C
2°	85% H ₃ PO ₄ at 60-100°C
1°	Conc. H ₂ SO ₄ at +140°C

7. Halohydrin Reaction.

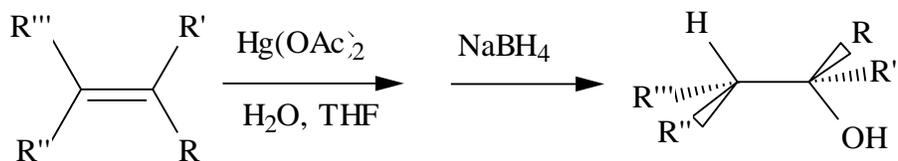
The reaction of an alkene with a halogen in the presence of water.



X⁺ is the electrophile followed by water or ROH acting as a nucleophile.

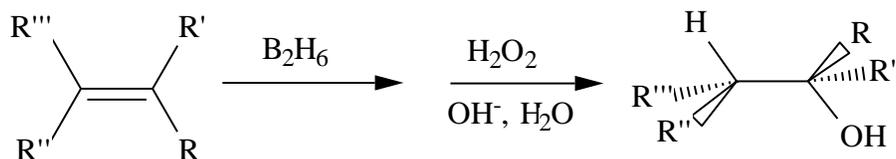
8. **Oxymercuration of an alkene to yield an alcohol.**

Oxidation followed by borohydride reduction. Anti addition that follows Markovnikov's Rule.

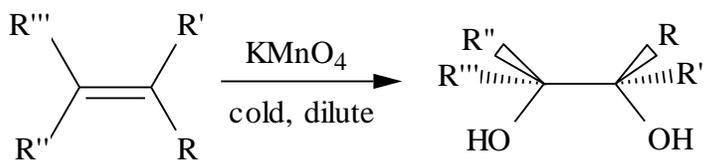


A carbon-mercury covalent bond is formed in the intermediate of the reaction. Alkoxymercuration is the reaction when ROH is used instead of water.

9. **Hydroboration of an alkene to yield an alcohol. Syn addition that follows anti-Markovnikov mechanism.**



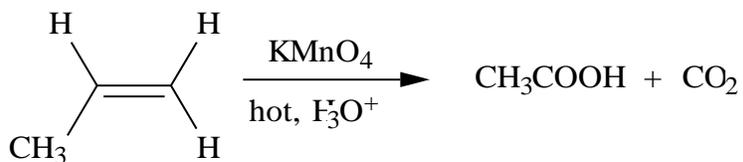
10. **Dihydroxylation of alkenes (Oxidation). Uses cold, alkaline permanganate or OsO₄ in pyridine to make a vicinyl diol.**



Syn (*cis*) addition of OH's. Used as a test for alkenes (Bayer's Test, brown MnO₂ detected).

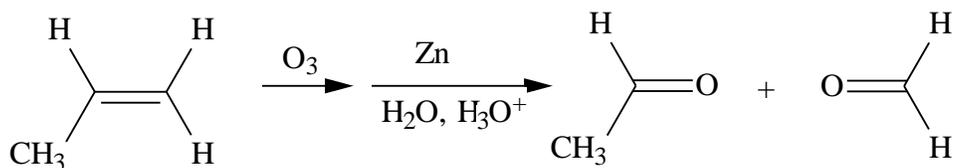
11. **Oxidative cleavage of alkenes by hot permanganate.**

Alkaline or acidic permanganate causes oxidation.



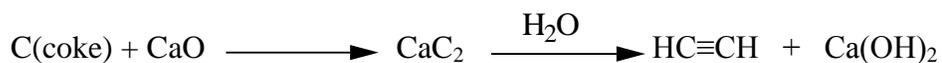
If C on C=C is 2°, C is oxidized to -COOH. If C on C=C is 3°, C is oxidized to ketone. If C is =CH₂ (terminal C), C is oxidized to CO₂. Works with alkynes as well to yield acids and CO₂.

12. **Ozonolysis (Oxidative cleavage by ozone).** Uses O_3 followed by moist, acidic zinc.

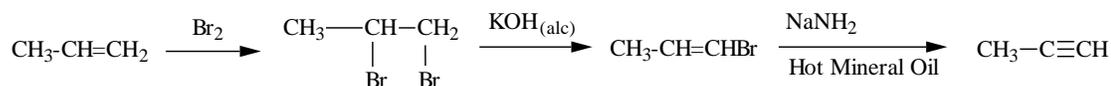


The carbons of the double bond are oxidized to carbonyls (aldehydes or ketones). Works with alkynes as well with acids as the products.

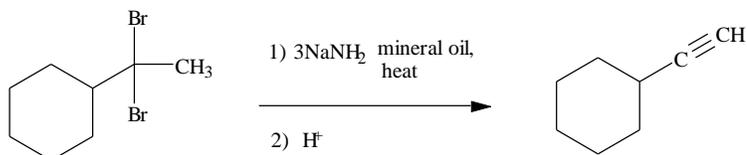
13. **Synthesis of acetylene from coke via calcium carbide.**



14. **Synthesis of alkynes by the double dehydrohalogenation of *vic* dibromides.**

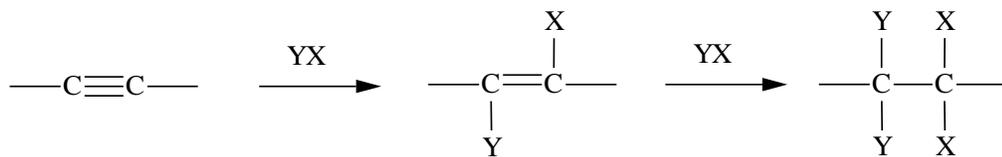


15. **Synthesis of alkynes by the double dehydrohalogenation of *gem* dibromides.**



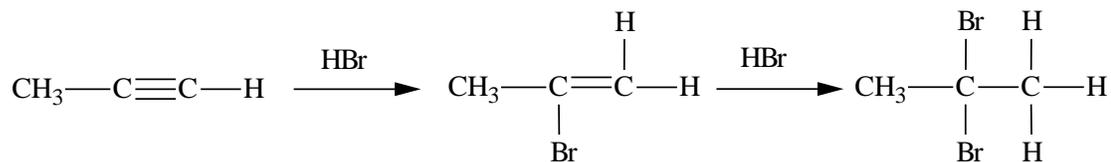
16. **Addition of YX to alkynes.**

Similar to alkenes and follows Markovnikov Rule.

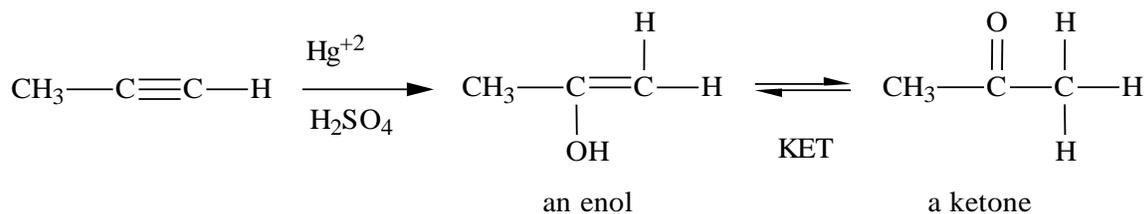


$YX = \text{H}_2, \text{Br}_2, \text{Cl}_2, \text{HCl}, \text{HBr}$

Example:



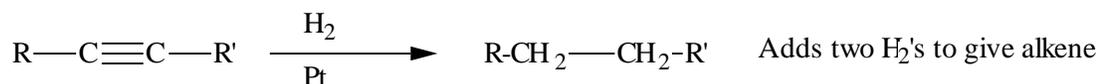
17. Hydration of alkynes (addition of water by refluxing with Hg^{+2}).



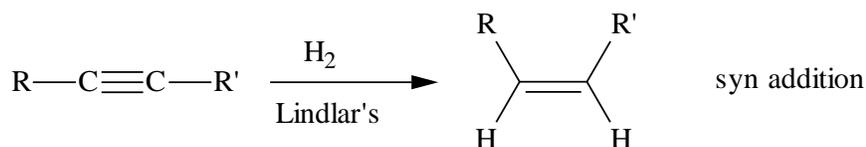
Intermediate is an unstable enol, Keto-enol tautomerism favors keto form.

18. Addition of hydrogen (reduction) of alkynes.

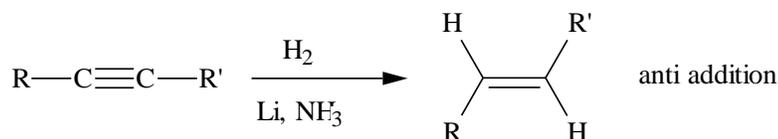
If partial reduction, *cis* or *trans* product depends on catalyst used.



Using a Lindlar catalyst:

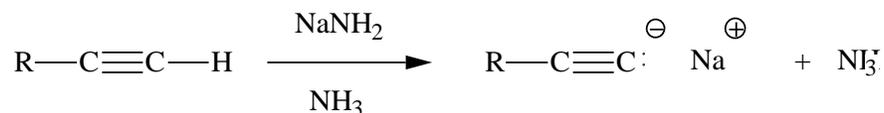


Using lithium in NH_3 or EtNH_2 .



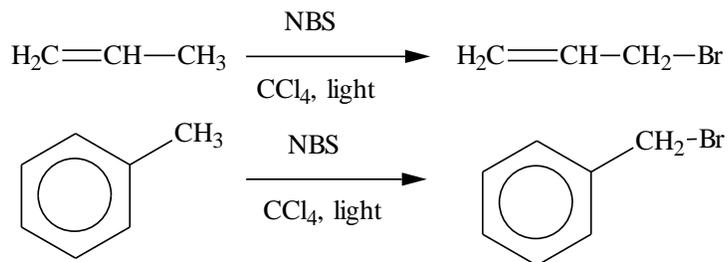
19. Formation of the acetylide anion.

Must use a base stronger than acetylide (pK_a of acetylene = 25)

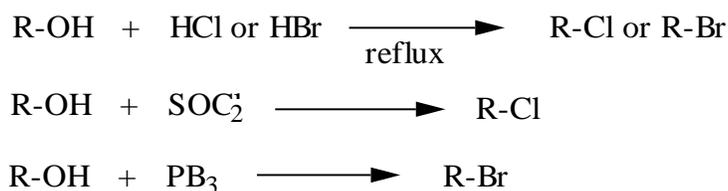


The acetylide ion is a strong base that can act as a nucleophile in an $\text{S}_\text{N}2$ reaction as long as the substrate is not susceptible to elimination or does not contain acidic protons. With 3° substrates you get all elimination as 3° don't do $\text{S}_\text{N}2$.

20. **Allylic and benzylic bromination using NBS (N-bromosuccinimide).**
Adds a bromine atom to the allylic or benzylic carbon of a compound.



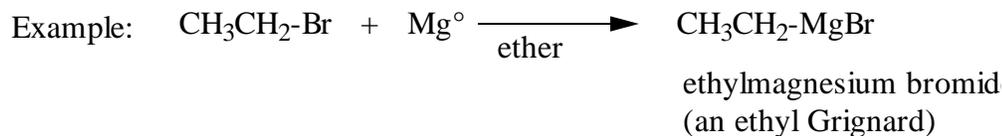
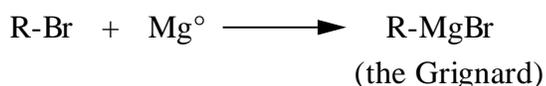
21. **Synthesis of alkyl halides from alcohols.**
Reaction of alcohols with HX* and heat, SOCl₂ with heat or PBr₃.



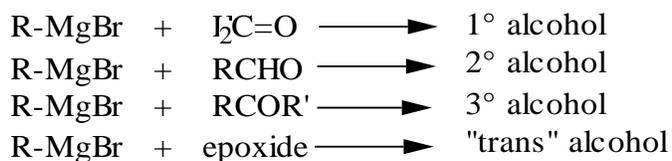
* Rearrangements may occur with the carbocation intermediate.

22. **Grignard Reactions - Alcohols from carbonyls and epoxides.**

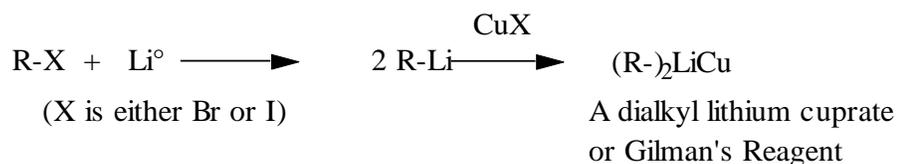
Formation of the Grignard



Reaction of the Grignard with a carbonyl or epoxide .

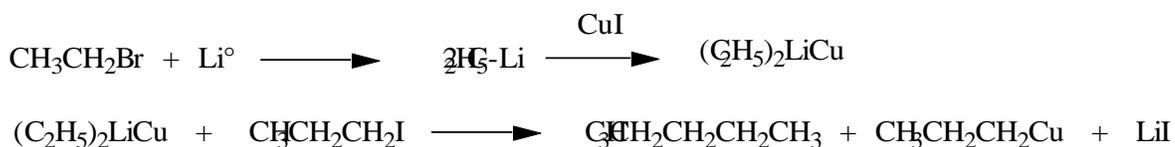


23. **Dialkyl lithium Cuprate Reaction - A way to make alkanes. A coupling reactions that makes C-C bonds.**



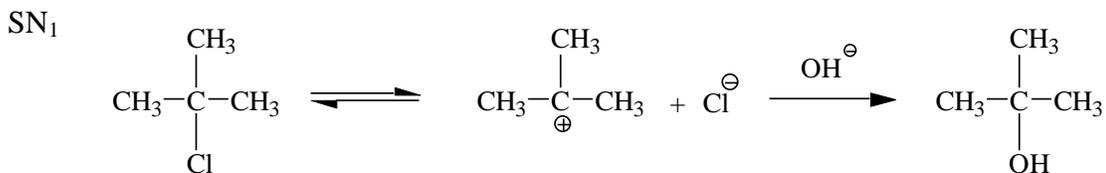
R' may be 1°, 2°, vinylic, or aromatic but not 3°

Example:

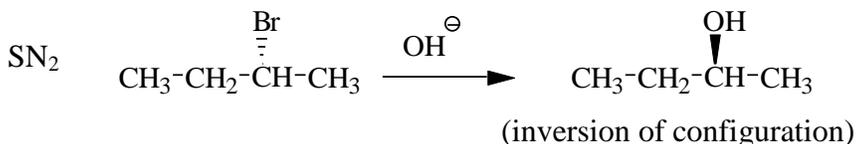


24. **SN₁, SN₂, E₁, and E₂ Reactions.**

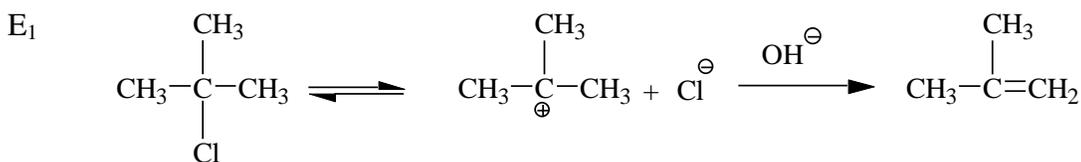
Elimination favored by strong hindered bases and heat. These reactions compete.



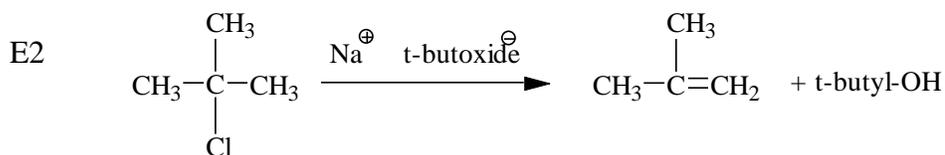
3° and allylic mainly, racemization, sp² intermediate, competes with E₁.



1° & 2° substrates, inversion, competes with E₂, polar aprotic solvents.



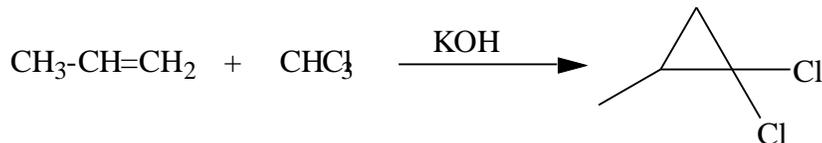
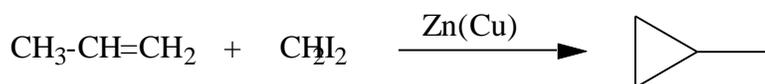
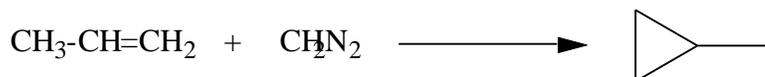
3° and allylic mainly, alkene formed, competes with SN₁, polar protic solvents.



(H and Cl must be antiperiplanar)

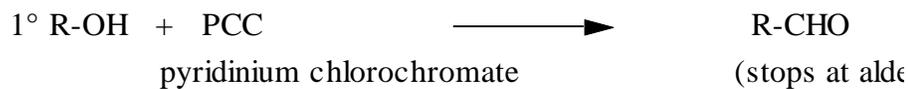
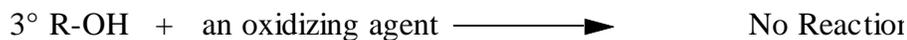
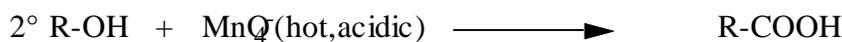
2° and 3° best (get SN₂ with 1°), competes with SN₂, favored by strong hindered bases and heat

25. Carbenes – The formation of cyclopropyl rings.



26. Oxidation and Reduction Reactions.

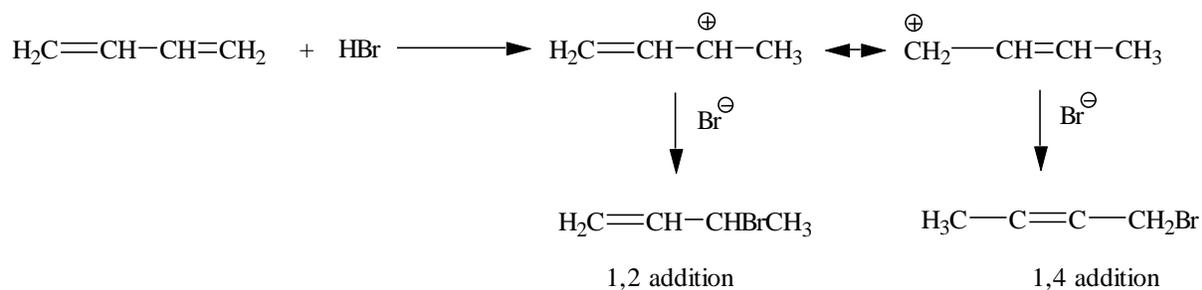
For oxidation use Cr(VI) or Mn(VII) compounds. For reduction use Hydrides.



27. Reactions of Ethers - Formation and cleavage.



28. 1,2 and 1,4 Addition to Conjugated Dienes (Allylic addition).



1,2 addition produces the most stable intermediate but the least stable product.

1,4 addition produces the least stable intermediate but the most stable product.

29. Diels - Alder Reaction. The 1,4 cycloaddition of a diene to a dienophile.

