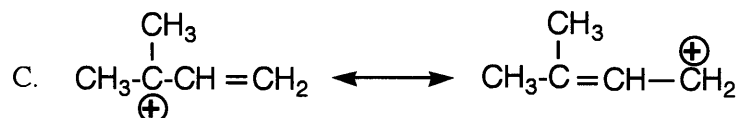
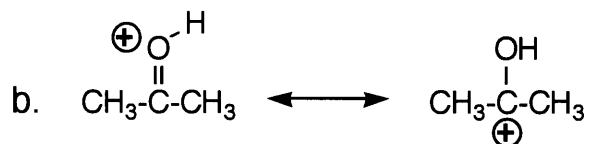
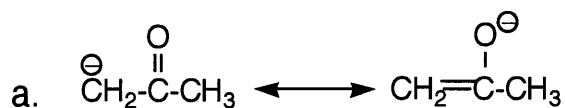


I. Lewis Structure/Formal Charge:

Write an acceptable Lewis structure for CO_3 . Indicate any formal charges.

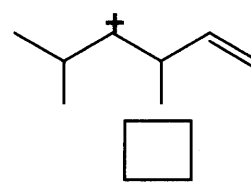
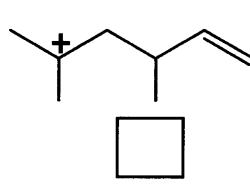
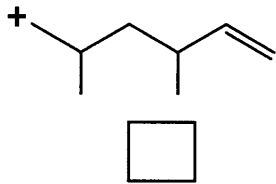
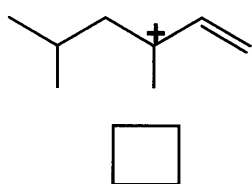
II. Resonance:

Circle the more stable resonance contributor in each pair.

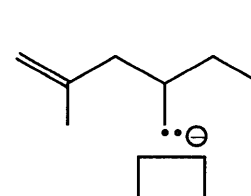
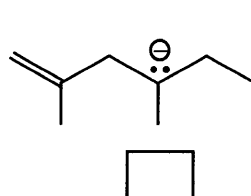
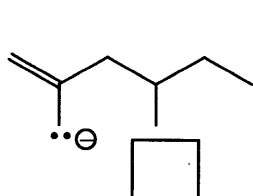
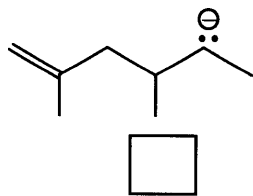


III. Stability of Intermediates:

Rank the carbocations in order of increasing stability (1=least stable, 4=most stable).



Rank the carbanions in order of increasing stability (1=least stable, 4=most stable).



A Brief Review of Organic I - Reactions and Mechanisms

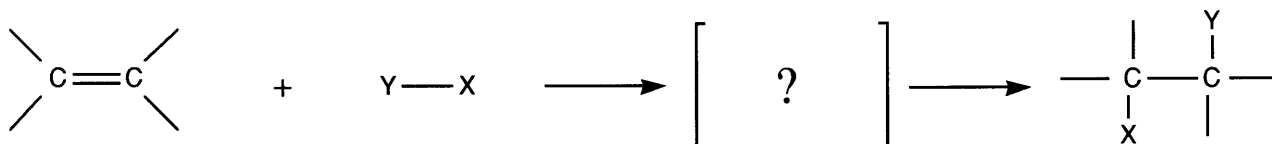
I. Additions

II. Eliminations

III. Substitutions

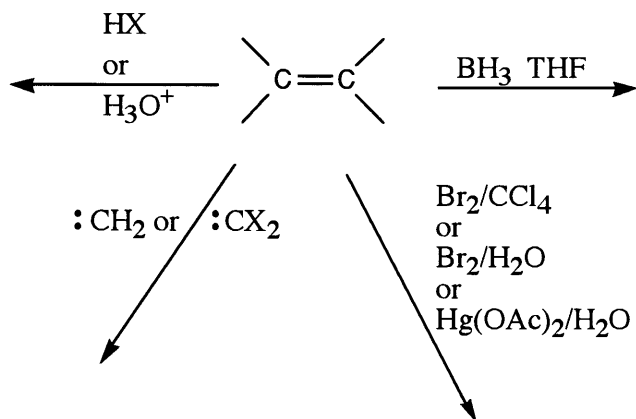
IV. Rearrangements

I. Additions: (alkene example, X more EN than Y)



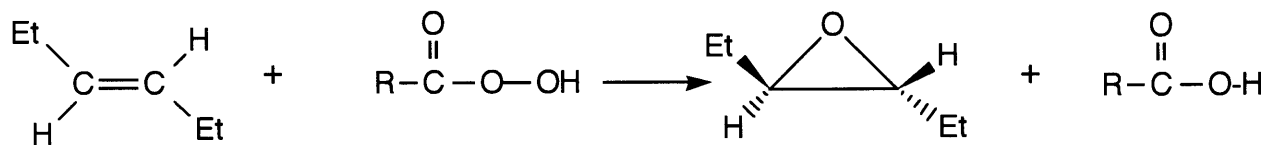
Mechanism Tips and Reminders:

- identify nucleophile (Nu) and electrophile (E^+)
- electron flow is always from electron rich (Nu) to electron poor (E^+); never the reverse
- arrow always drawn from a lone pair or bond to a positive or $\delta+$ atom
- mechanism arrows do not show where atoms "go"
- in the presence of strong acids or strong electrophiles, do not form strong bases or strong nucleophiles
- in the presence of strong bases or strong nucleophiles, do not form strong acids or strong electrophiles

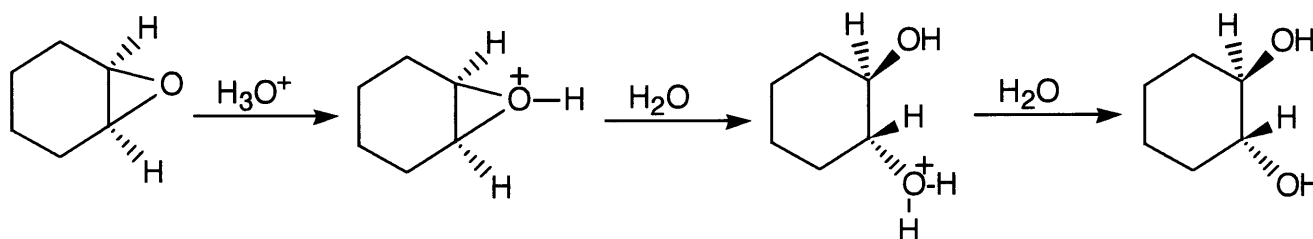


Alkene oxidations: (addition of oxygen)

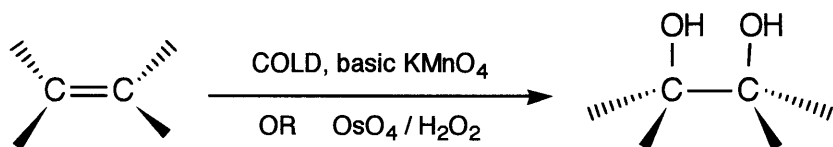
A. Epoxidation with peroxyacids:



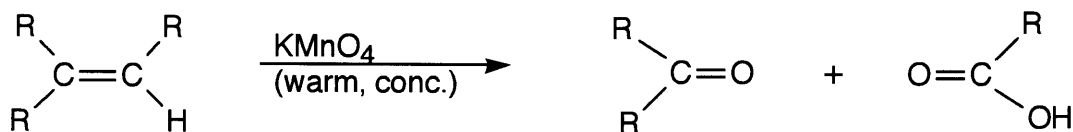
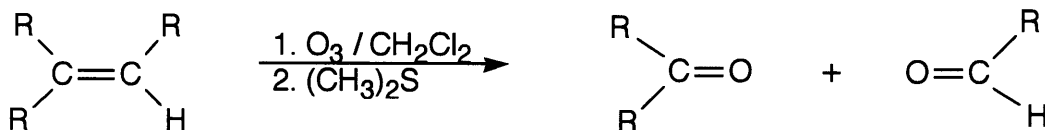
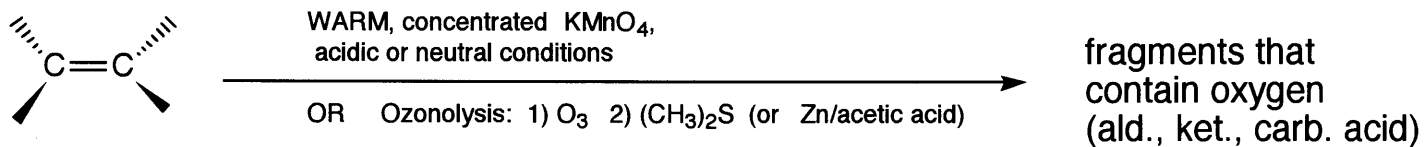
Acid-catalyzed ring opening of epoxides:



B. Hydroxylation



C. Oxidative Cleavage



Addition Mechanisms Continued: Additions to Alkynes

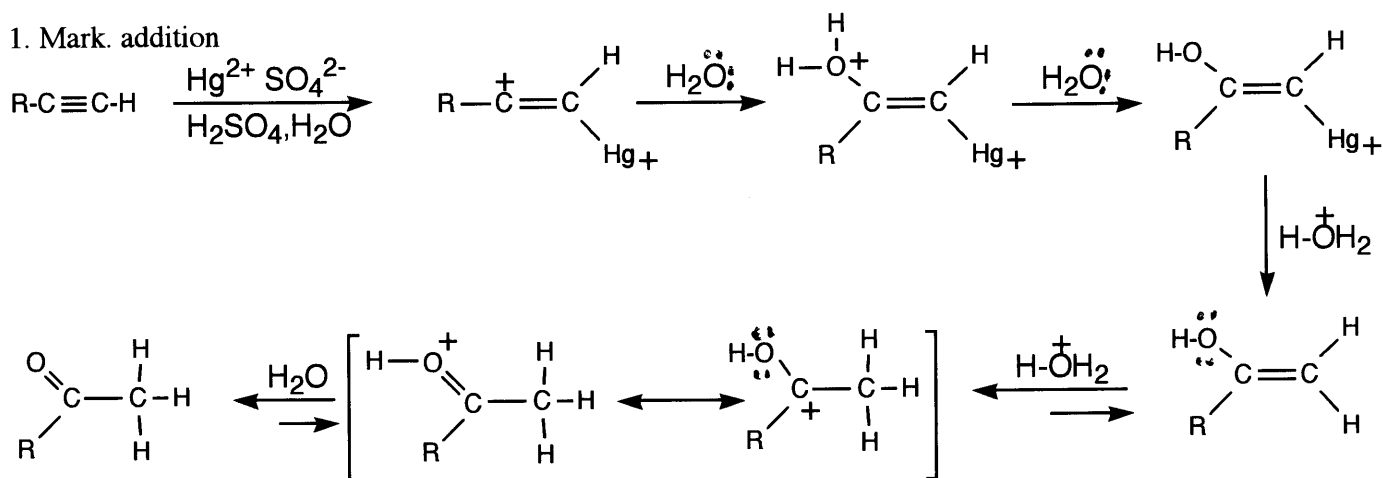
A. Addition of H-X: similar to addition to alkenes - intermediate is more stable C⁺ (Mark's Rule)

B. Addition of X₂: 3-membered ring intermediate probably too strained; forms more stable C⁺
addition of first eq. of X₂ gives cis and trans products

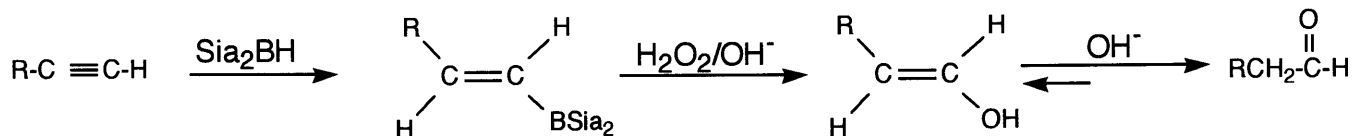
C. Addition of H₂: 3 choices - 1) gives alkane with H₂ and active catalyst (Pt, Pd, Ni)
2) gives cis-alkene with H₂ and Pd/BaSO₄/quinoline (Lindlar's cat)
3) gives trans-alkene with Na or Li in liquid ammonia

D. Addition of H-OH: Does not give alcohols!

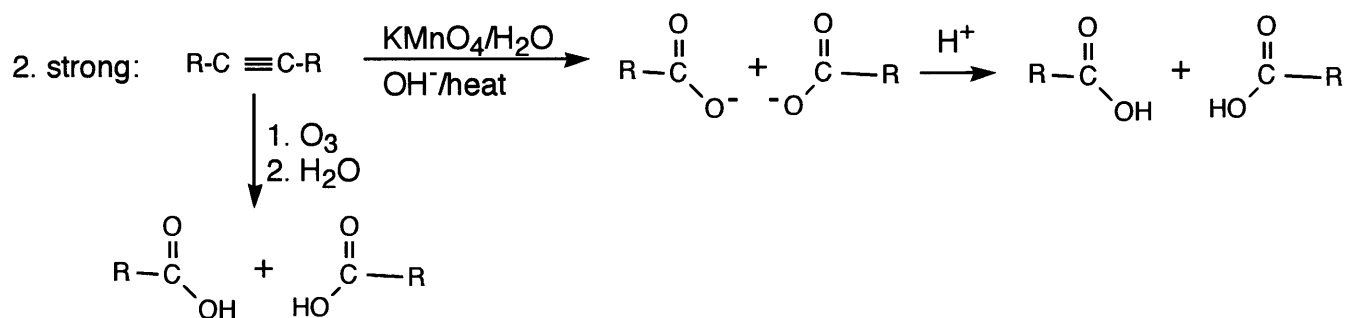
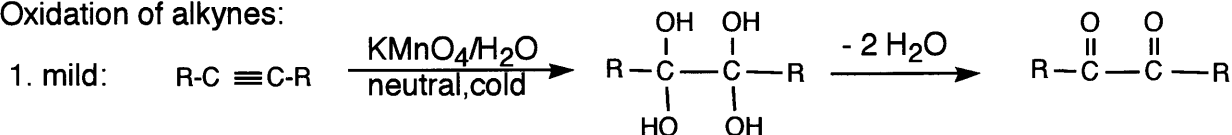
1. Mark. addition



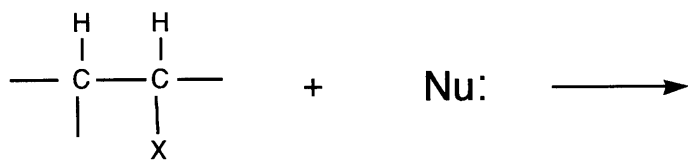
2. Non-Mark. addition



Oxidation of alkynes:



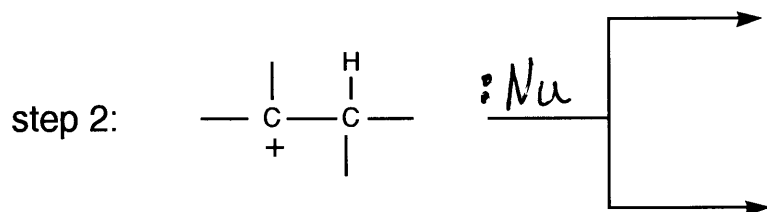
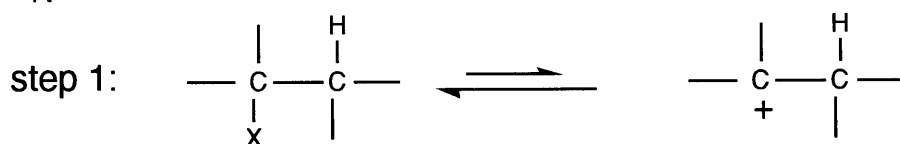
II./III. Elimination/Substitution Reactions:



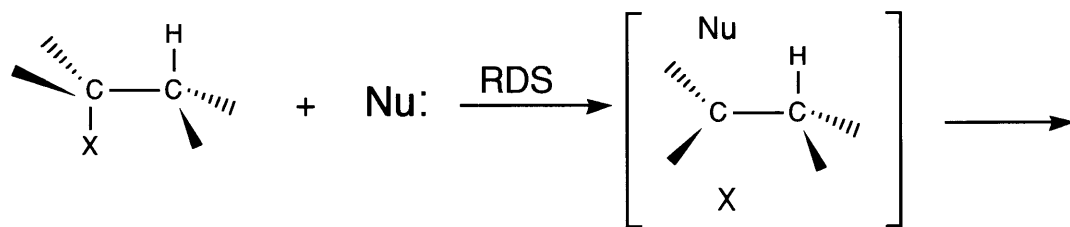
For Pathway A, E⁺ is _____

For Pathway B, E⁺ is _____

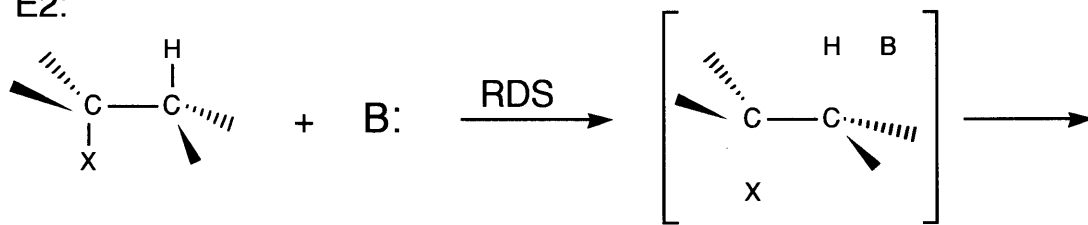
S_N1/E1:



S_N2:



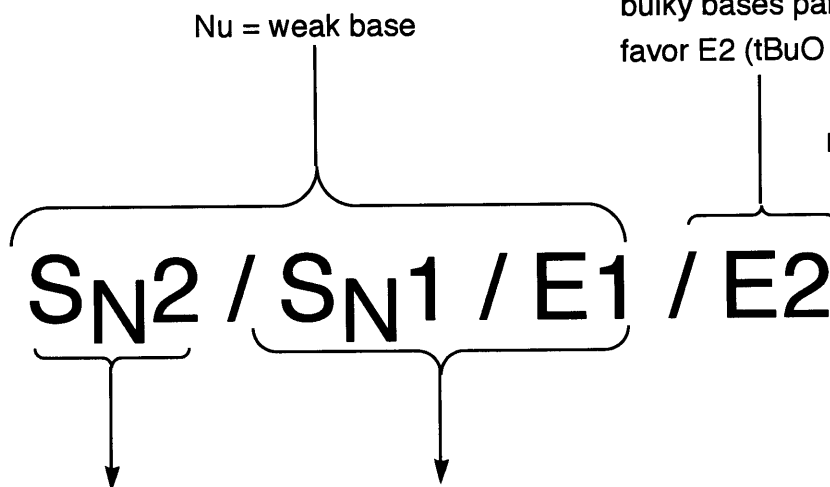
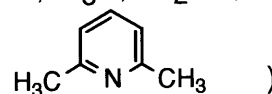
E2:



Pathway that has the fastest rxn. rate (lowest E_a /lowest E TS) forms major product.

Substitution vs Elimination (Wade summaries: sections 6-16 and 6-22)

Nu = strong base
 (OH^- , RO^- , NH_2^- , $\text{RC}\equiv\text{C}^-$)
 bulky bases particularly
 favor E2 (tBuO^- , Et_3N , iPr_2NH , and

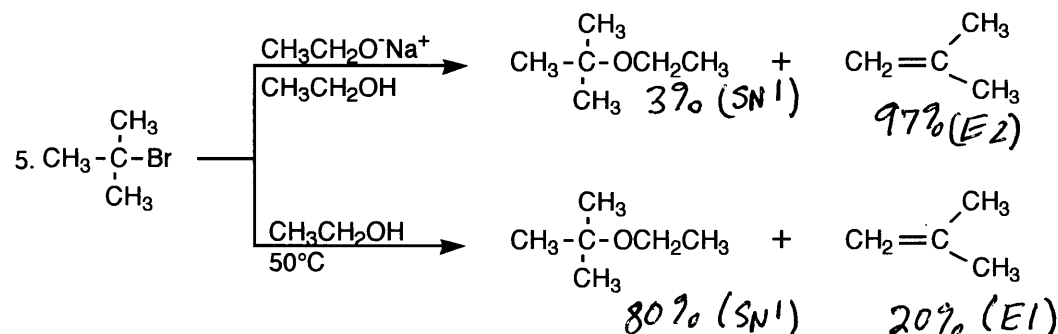
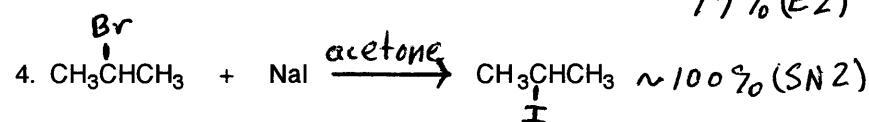
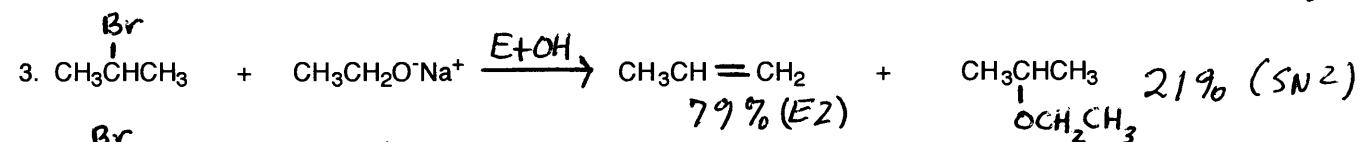
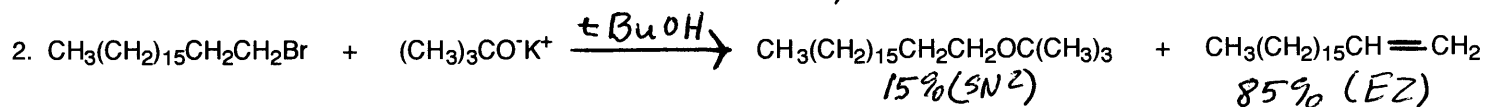
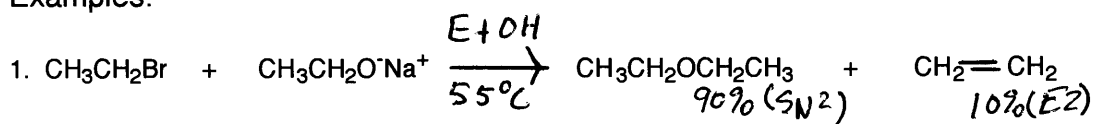


- CH_3 , 1° , 2° , allylic/benzylic
- Strong Nu, but weak base such as iodide, HS^- , RS^- , or CN^-
- faster rate in aprotic solvents

- 3° , 2° , allylic/benzylic
- Weak Nu
- ionizing solvent is necessary
- $\text{S}_{\text{N}}1$ usually major process
- high T increases E1

Exception: 1° halide with a strong, unhindered base - $\text{S}_{\text{N}}2$ gives major product

Examples:



SYNTHESIS OF ALCOHOLS

I. From Alkyl Halides: Ch. 6



II. From Alkenes: Ch. 8

A. Hydration (H_3O^+)

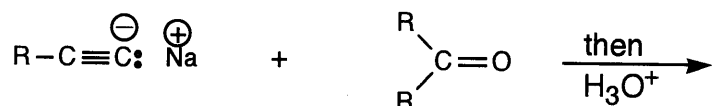
B. Oxymercuration/Demercuration: 1. $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$ 2. NaBH_4

C. Hydroboration: 1. $\text{BH}_3 \cdot \text{THF}$ 2. $\text{H}_2\text{O}_2/\text{OH}^-$

D. Epoxidation followed by acidic hydrolysis: 1. MCPBA 2. H_3O^+ or $\text{CH}_3\text{CO}_3\text{H}/\text{H}_3\text{O}^+$

E. Hydroxylation: $\text{OsO}_4/\text{H}_2\text{O}_2$ or cold, basic KMnO_4

III. From Acetylide Anion and Carbonyl Compound: Ch. 9



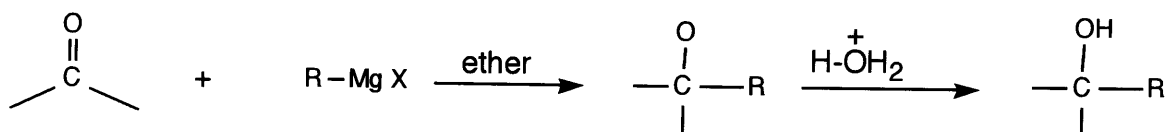
IV. Organometallic Reagents + Carbonyl Compounds \longrightarrow R-OH : *ch. 10*

A. Preparation of Reagents

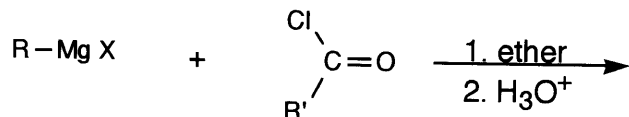


B. Mechanism of Grignard Reaction (mechanism of organolithium reaction is similar)

1. with aldehydes and ketones:



2. with esters or acid halides:



V. Reduction of Carbonyls

A. Hydride reductions

Reducing agents:

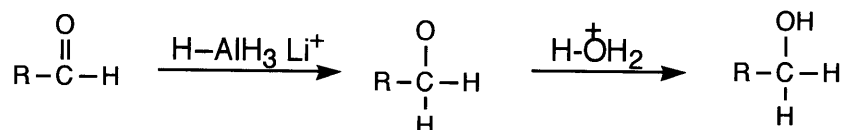
NaBH_4 - the milder choice; usually chosen for aldehydes and ketones

- may use H_2O or alcohol as solvents
- very slow reduction of esters; will not reduce acid chlorides or carboxylic acids

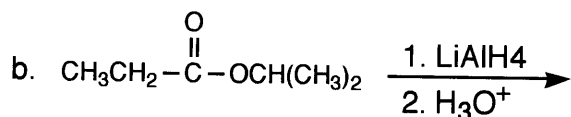
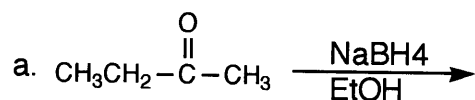
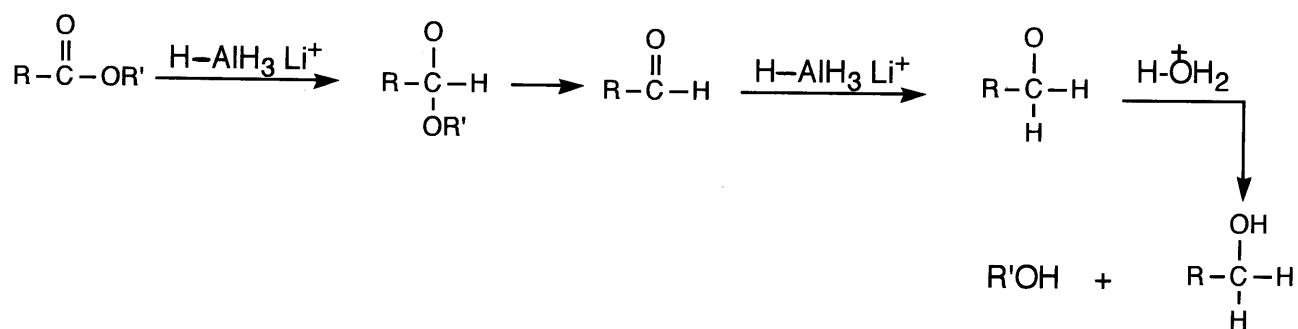
LiAlH_4 - more reactive than NaBH_4

- reduces aldehydes, ketones, esters, acid halides and carboxylic acids
- CAUTION: reacts violently with H_2O and alcohols! Must use ethers as solvents.

1. reduction of aldehydes and ketones:



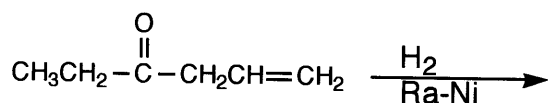
2. reduction of esters, acid halides and carboxylic acids:



B. Catalytic Hydrogenation of Aldehydes and Ketones:



- catalytic reduction of carbonyl is slower than reduction of carbon-carbon double bond
- Raney Ni is best catalyst



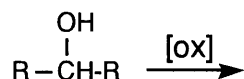
Reactions of Alcohols

I. Oxidations:

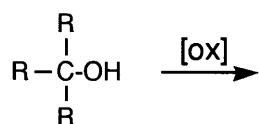
A. Oxidation of 1° alcohols:



B. Oxidation of 2° alcohols:

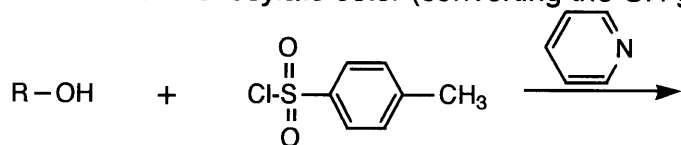


C. Oxidation of 3° alcohols:



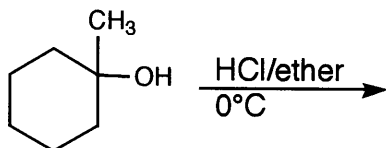
- [ox] :
1. chromic acid reagents
 - a. $\text{Na}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4 / \text{H}_2\text{O}$
 - b. $\text{CrO}_3 / \text{H}_2\text{SO}_4 / \text{H}_2\text{O} / \text{acetone} / 0^\circ\text{C}$ (Jones reagent)
 2. pyridinium chlorochromate / CH_2Cl_2 (written as: PCC/ CH_2Cl_2 or CrO_3 pyridine HCl / CH_2Cl_2)

II. Formation of the tosylate ester (converting the OH group to a better leaving group)



III. Conversion of alcohols to alkyl halides - The BEST methods

A. Formation of 3° alkyl halides from 3° alcohols: use hydrohalic acids (HBr, HCl)



B. Formation of 1°/2° alkyl halides from 1°/2° alcohols:

1. Bromides: use PBr_3

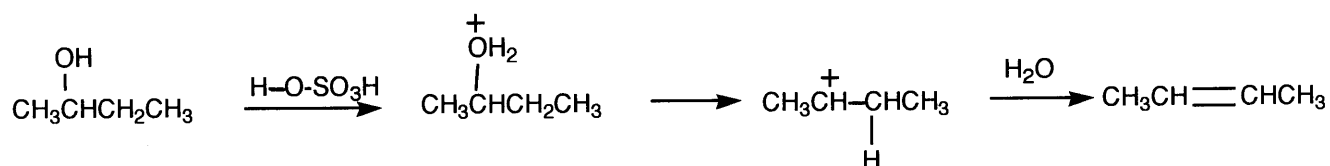
2. Chlorides

a. PCl_3 or PCl_5

b. SOCl_2 - NOTE: The mechanism given on page 463 occurs only in solvents like dioxane. The more typical mechanism is $\text{S}_{\text{N}}2$.

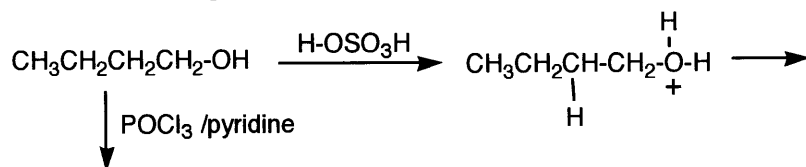
IV. Dehydration of alcohols to alkenes (first discussed in Ch. 7)

A. for 3°, 2° alcohols use H₂SO₄(conc.)/heat (Be careful! E1, so may rearrange.)



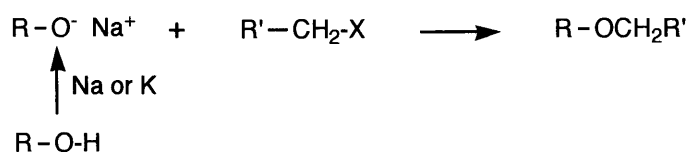
B. for 1° (and 3°, 2° that may rearrange) use POCl₃/pyridine - E2, so no carbocations

Note: this reagent is given by Wade in a chapter problem



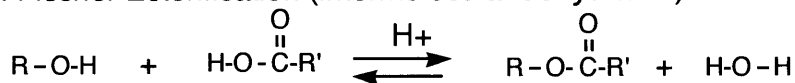
V. Formation of Ethers

Williamson Ether Synthesis (symm. or unsymmetrical ethers)

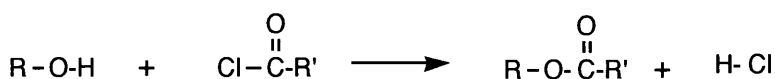


VI. Ester Formation

A. Fischer Esterification (intermolecular dehydration) - mechanism this semester!

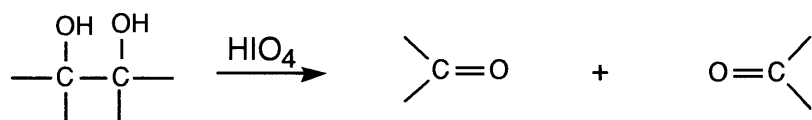


B. Nucleophilic acyl substitution of acid chloride



VII. Unique reactions of 1,2-diols

A. Periodic acid cleavage



B. Pinacol-Pinacolone Rearrangement

