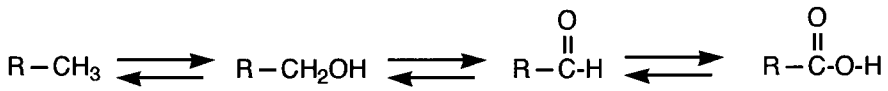
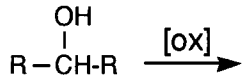
Chapter 11: Reactions of Alcohols

I. Oxidations:

oxidation increases # of bonds to O, N, or halogens or decreases # of bonds to H
reduction increases # of bonds to H or decreases # of bonds to O, N, or halogens
neither oxidation or reduction if HX or H_2O is gained or lost



A. Oxidation of 2° alcohols:



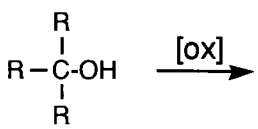
[ox] :
1. chromic acid reagents
   a. $Na_2Cr_2O_7$ / H_2SO_4 / H_2O
   b. CrO_3 / H_2SO_4 / H_2O / acetone / 0°C (Jones reagent)
2. $KMnO_4$
3. HNO_3
4. pyridinium chlorochromate / CH_2Cl_2 (written as: PCC/CH_2Cl_2 or CrO_3 pyridine HCl / CH_2Cl_2)

B. Oxidation of 1° alcohols:

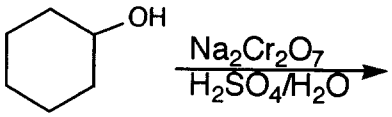
[ox-b] : 1-3 above

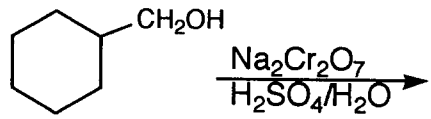
[ox-a] : PCC ONLY

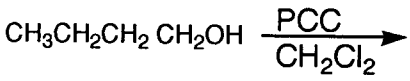
C. Oxidation of 3° alcohols:

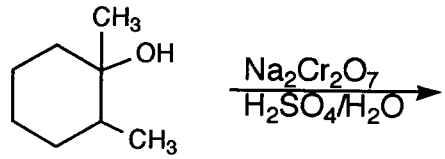


Examples:

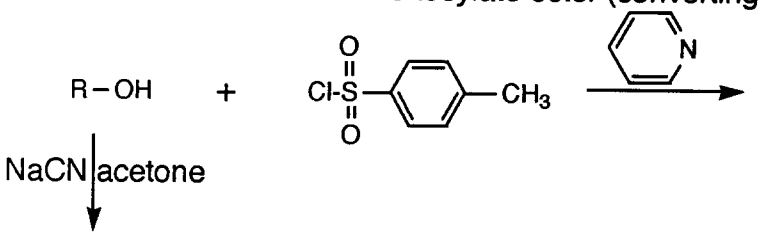


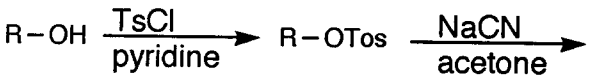






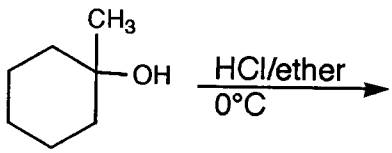
II. Formation and uses of the tosylate ester (converting the OH group to a better leaving group)





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

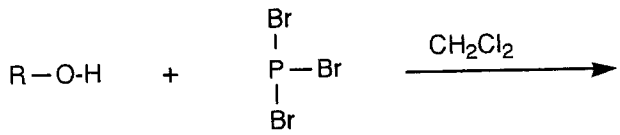
A. Formation of 3° alkyl halides from 3° alcohols: use hydrohalic acids (HBr, HCl)



- for 1° and 2° alcohols, treatment of alcohol with HX is not the best method of forming alkyl halides
- addition of catalyst (Lucas reagent) improves results

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

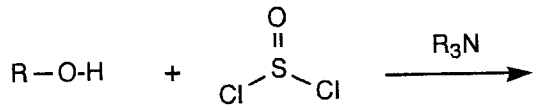
1. Bromides: use PBr_3



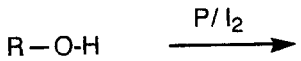
2. Chlorides

a. PCl_3 or PCl_5

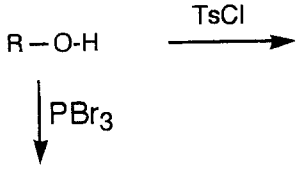
b. $SOCl_2$ - NOTE: The mechanism given on page 474 (p. 449 of 3rd ed.) occurs only under "special conditions." The more typical mechanism is the following:



3. Iodides: use P/I_2



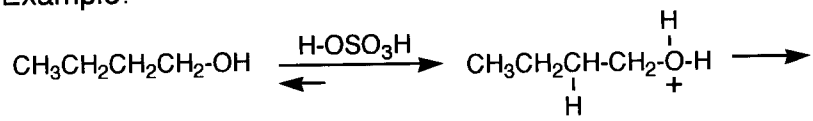
Stereochemistry of Indirect Substitution of ROH:



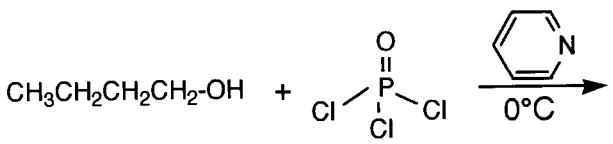
IV. Acid-catalyzed dehydration to alkene (first discussed in Ch. 7)

Mechanism : E1
Intermediate : C+
Major product : formed according to Saytzeff's rule (more stable alkene is major product)

Example:

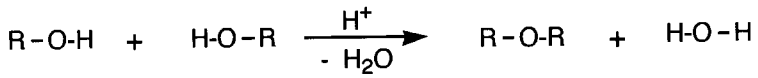


Acid-catalyzed dehydratons of 1° alcohols do NOT give good yields of terminal alkenes.
Phosphorous oxychloride ($POCl_3$) - a good dehydrating agent for 1°, 2°, and 3° alcohols



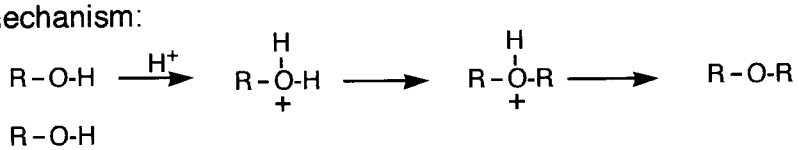
V. Formation of Ethers

A. Symmetrical ethers through intermolecular dehydration



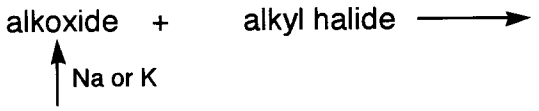
EX: 2 $CH_3CH_2-O-H \xrightarrow[140°C]{H_2SO_4} CH_3CH_2-O-CH_2CH_3 + H-O-H$

Mechanism:



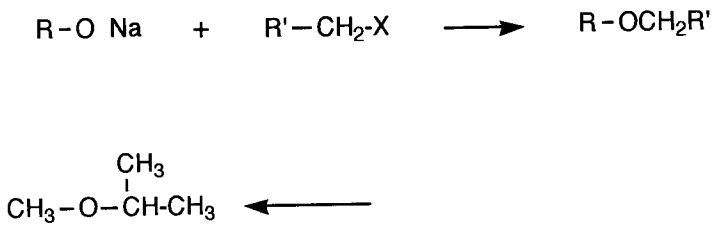
NOT for unsymmetrical ethers! $CH_3CH_2-O-H + CH_3-O-H \xrightarrow[140°C]{H_2SO_4}$

B. Williamson Ether Synthesis (symm. or unsymmetrical ethers)



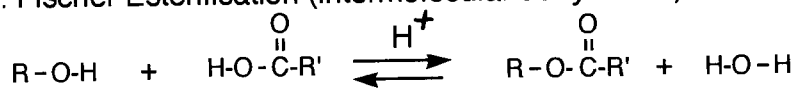
R-O-H order of reactivity of ROH in alkoxide formation : Me > 1° > 2° > 3°

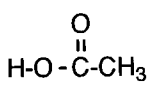
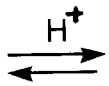
Williamson Ether Synthesis continued:



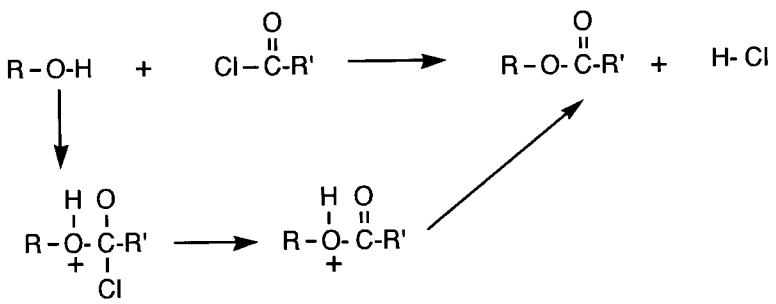
VI. Ester Formation

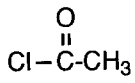
A. Fischer Esterification (intermolecular dehydraton) - mechanism next semester!



Ex: CH_3CH_2-O-H +  

B. Nucleophilic acyl substitution of acid chloride



Ex: CH_3CH_2-O-H +  

VII. Unique reactions of 1,2-diols

A.Periodic acid cleavage