

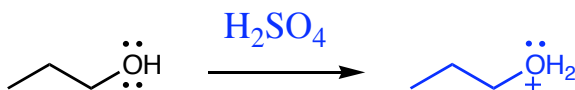
Learning Guide for Chapter 15 - Alcohols (II)

- I. Introduction to alcohol reactivity
- II. Reactions of alcohols with acids
- III. Reactions of alcohols with electrophiles
 - Halogenated phosphorus and sulfur compounds
 - Tosyl chloride
- IV. Reactions of alkoxides
- V. Reactions of alcohols and diols with oxidizing agents

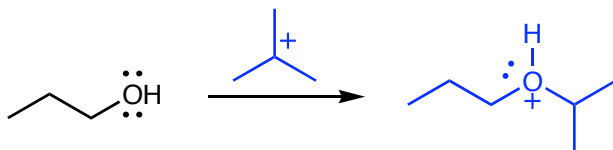
I. Introduction to alcohol reactivity

In which of the following ways can an alcohol react?

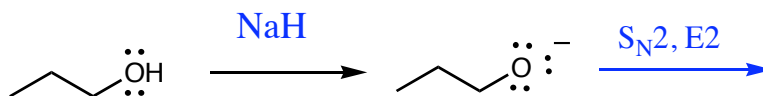
As a base: yes no if the acid has a pKa less than -2.4



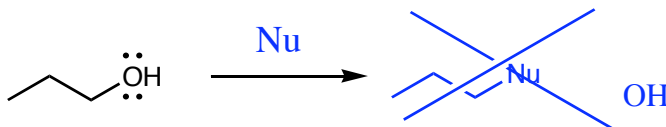
As a nucleophile: yes no if the electrophile is fairly reactive



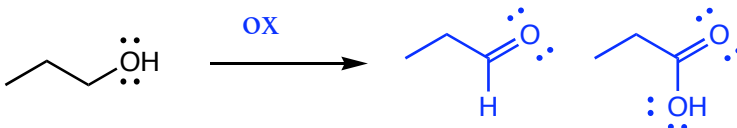
As an acid: yes no if the conjugate acid pKa is greater than 18



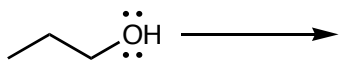
As an electrophile: yes no even though C is partially +, OH is not a good LG



Can they be oxidized? yes no can gain bonds to O - become aldehyde, ketone, COOH



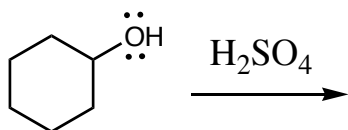
Can they be reduced? yes no



II. Reactions of Alcohols with Acids

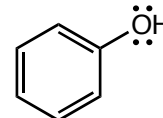
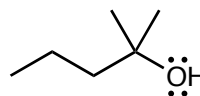
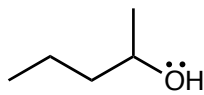
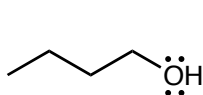
What is the first intermediate formed when an alcohol reacts with an acid?

What happens when a protonated alcohol dissociates?



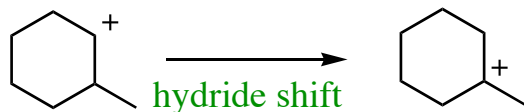
Which of the following alcohols can form a protonated alcohol that can dissociate?

What happens to the ones that can't?

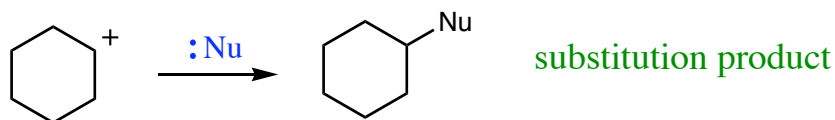


What are the three things that can happen to a carbocation?

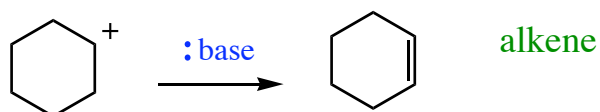
Rearrange whenever a more stable C⁺ can be formed



React w/ a Nu S_N1 - rxn



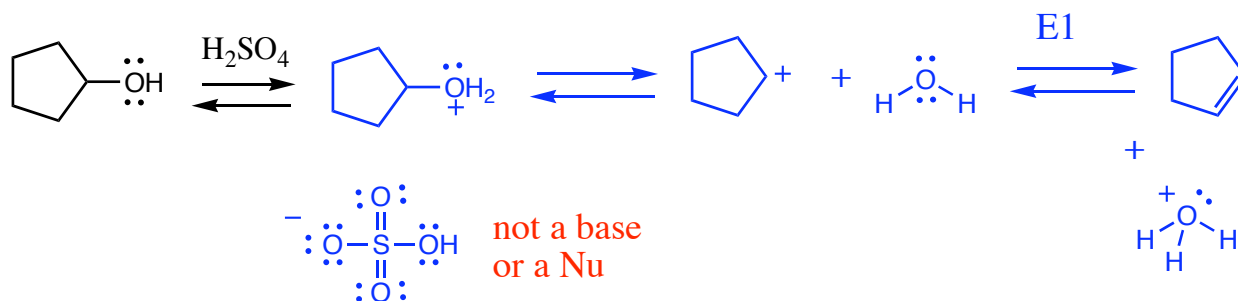
React w/ a base E1 rxn



What else do we need to know to determine if the carbocation will react as an electrophile or acid?

if the conjugate base of the acid is a nucleophile or not

What will happen when H_2SO_4 or H_3PO_4 is used as the acid?



Could this reaction give constitutional isomers and/or stereoisomers?

yes - if there are different H's, or cis/trans

Why is the acid catalytic? because H_3O^+ is formed

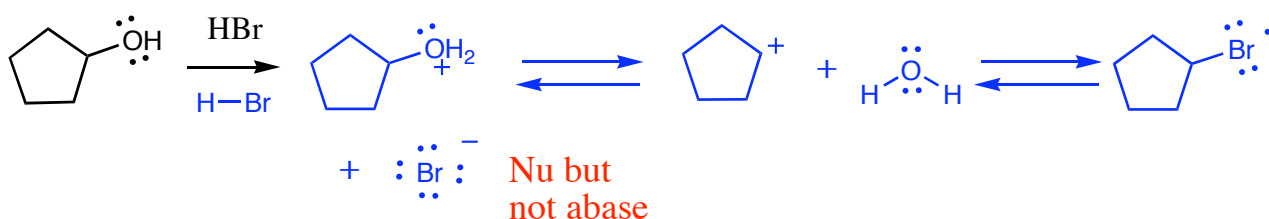
Why is heat usually required in this reaction? a C^+ is formed

Could this reaction go backward? yes - acid-catalyzed hydration of an alkene

The equilibrium constant is near 1.0 - how can we get a good yield?

high conc of alcohol - use as solvent
 remove water - absorb
 remove alkene - distill off

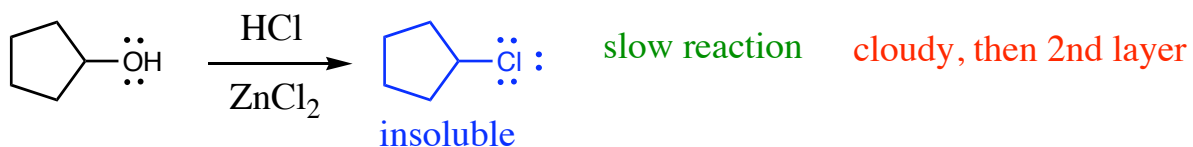
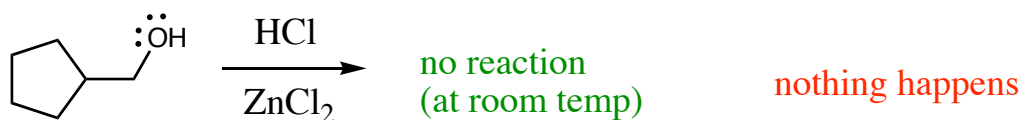
What will happen if HBr or HCl is used as the acid?



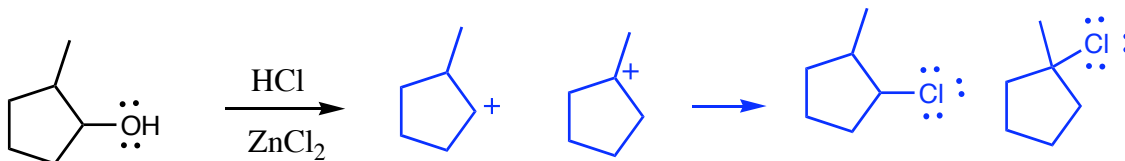
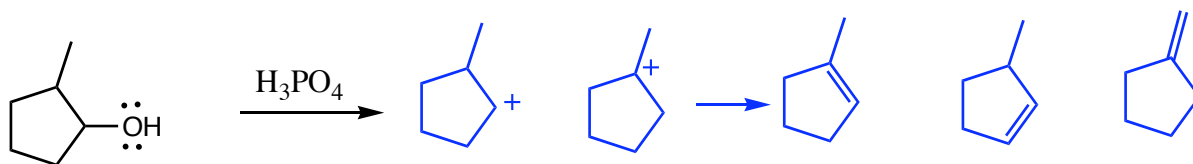
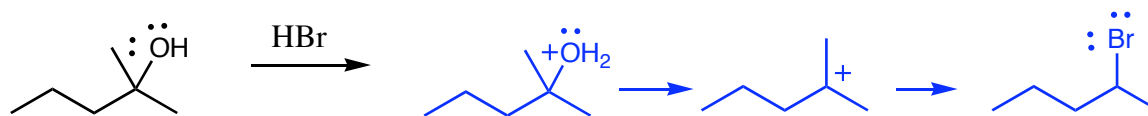
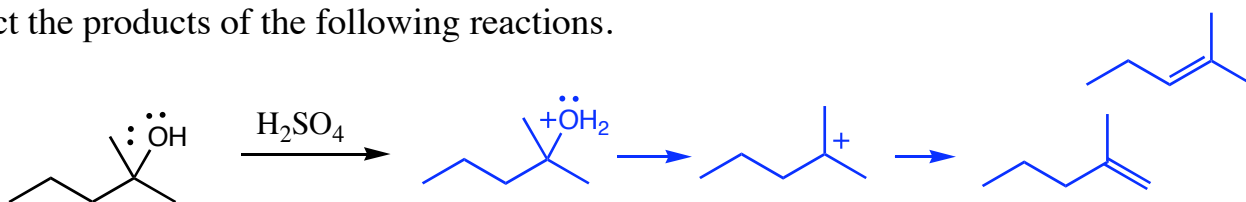
In order to make this reaction work well with HCl, what else needs to be added?

HCl, ZnCl_2 - Lucas reagent

How could you use the Lucas test to determine whether the following alcohols were 1°, 2°, or 3°?

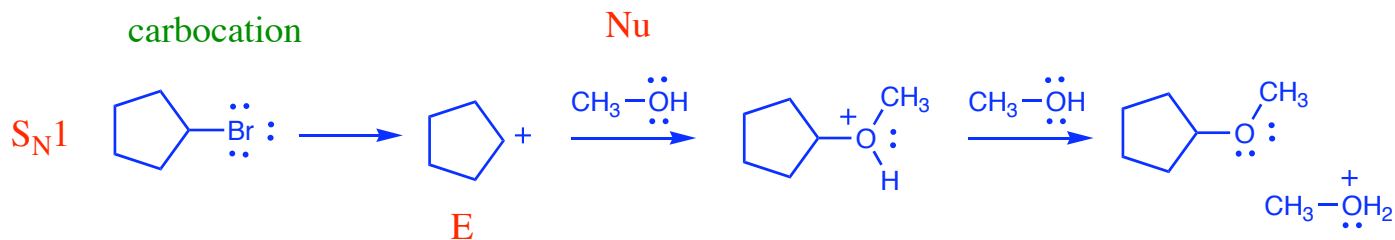


Predict the products of the following reactions.



III. Reactions of Alcohols with Electrophiles

What electrophile have we previously encountered that can react with an alcohol?



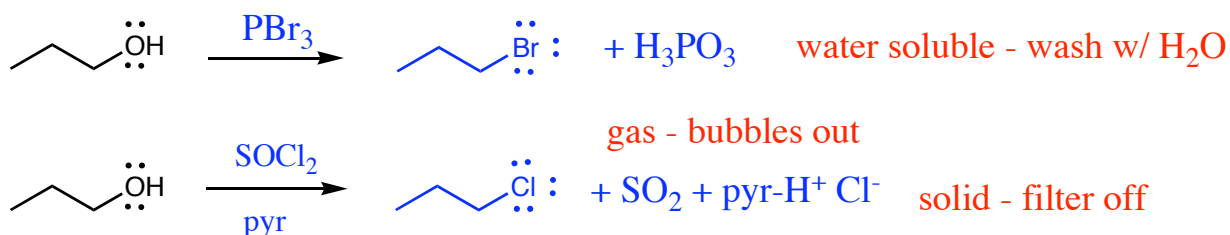
Halogenated phosphorus and sulfur compounds

What are the two most common phosphorus and sulfur reagents used as electrophiles with alcohols?

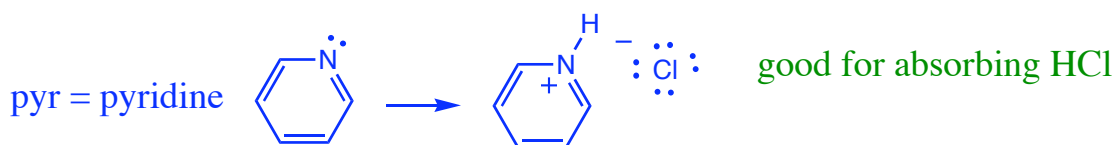
phosphorus tribromide PBr_3

thionyl chloride $SOCl_2$

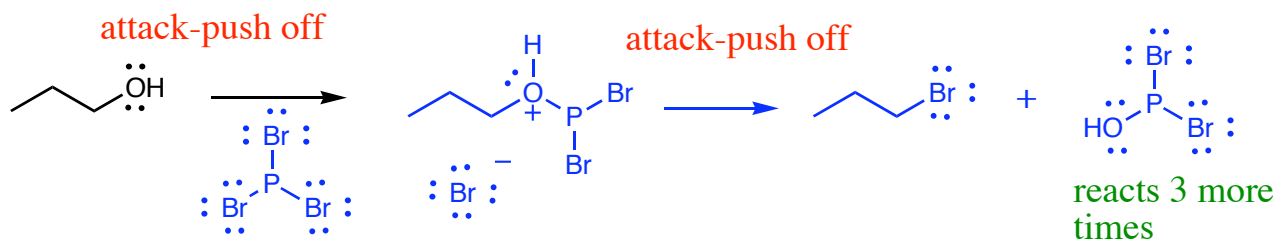
What type of compound results when they react with alcohols? alkyl halide



What advantages do these reactions have when isolating the product?



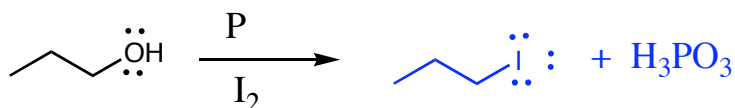
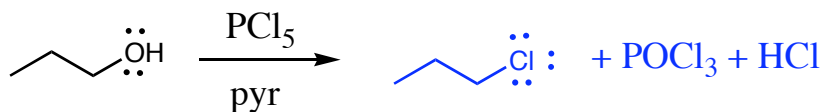
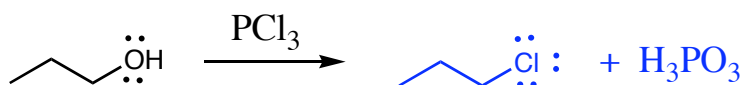
What is the mechanism of the PBr_3 reaction?



What type of alcohols work best in these reactions? Why?

1° best, 2° OK steric hindrance

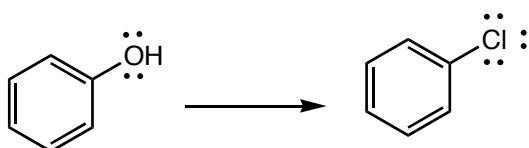
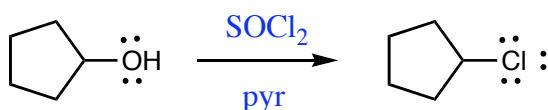
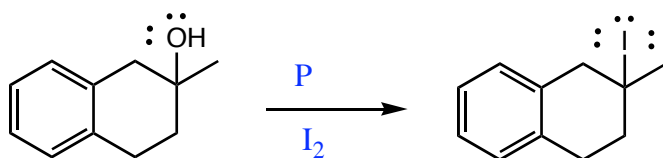
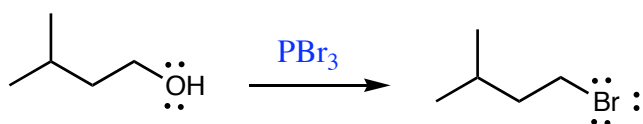
What products will the following reactions give?



If you want to convert an alcohol to an alkyl halide, which is the best way to do it?

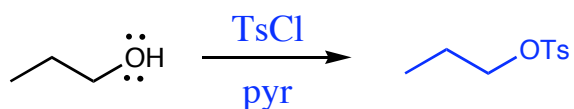
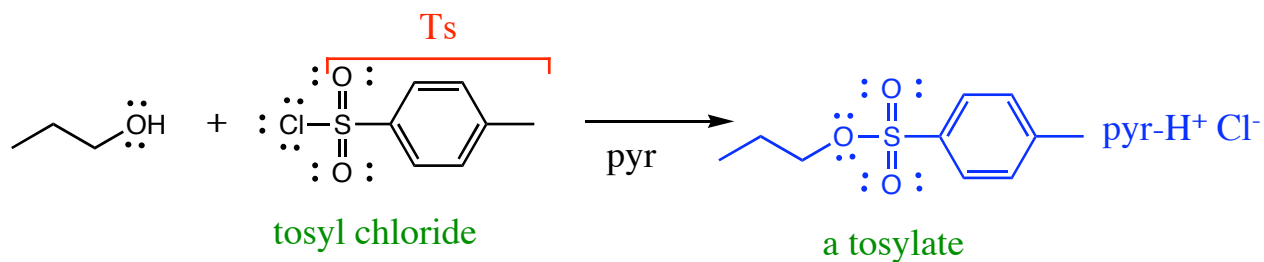
	R-Cl	R-Br	R-I
1° ROH	SOCl_2	PBr_3	P, I_2
2° ROH	HCl or SOCl_2	HBr or PBr_3	HI or P, I_2
3° ROH	HCl	HBr	HI

Convert the following alcohols to the products shown.

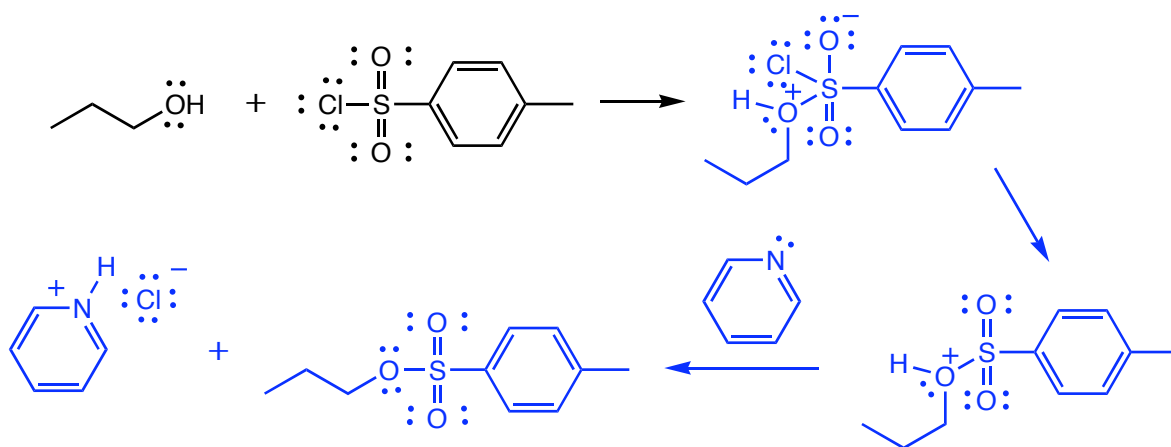


Tosyl chloride

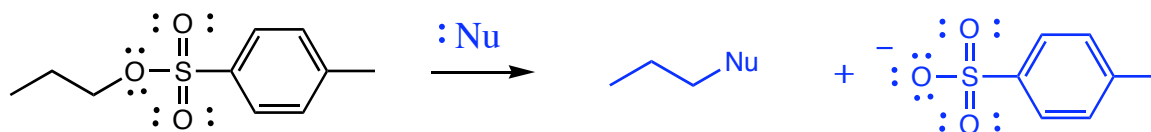
What product results when an alcohol reacts with tosyl chloride in pyridine?



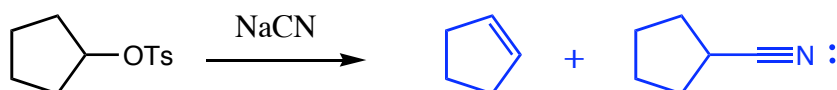
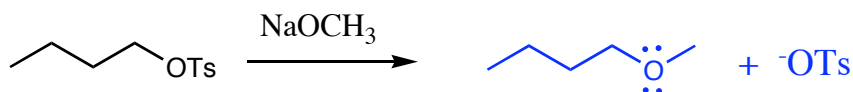
How does this reaction occur?

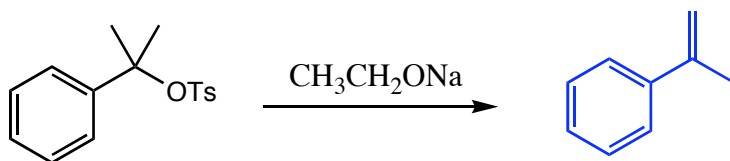


How do tosylates react? OTs is a leaving group - like Br



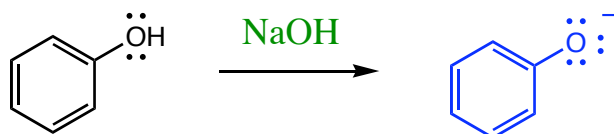
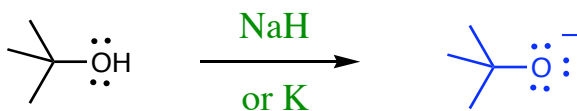
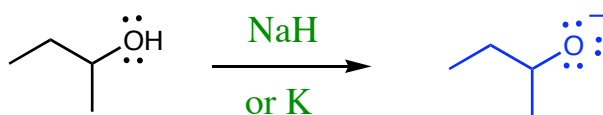
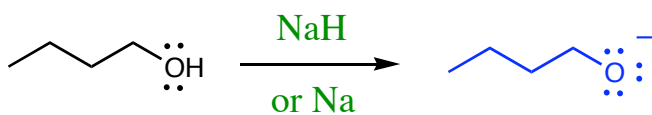
Give the products of the following reactions:



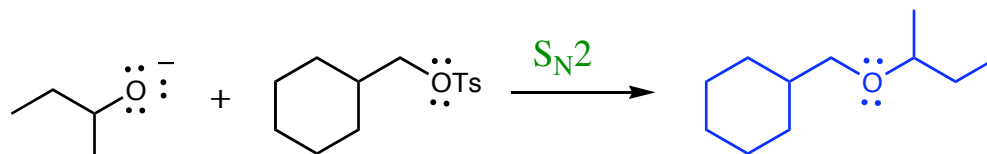
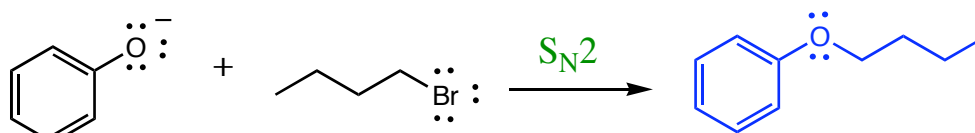
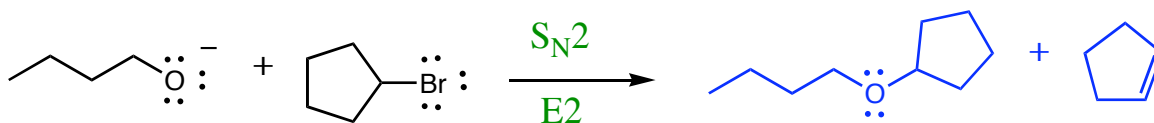


IV. Formation and reactions of alkoxides

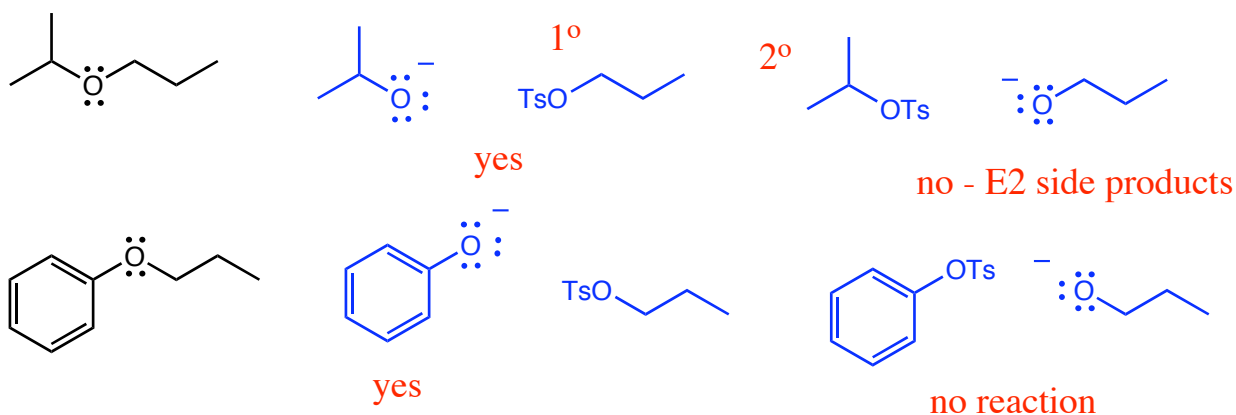
What reagents would be appropriate to form an alkoxide from the following alcohols?



Give the products of the following reactions:

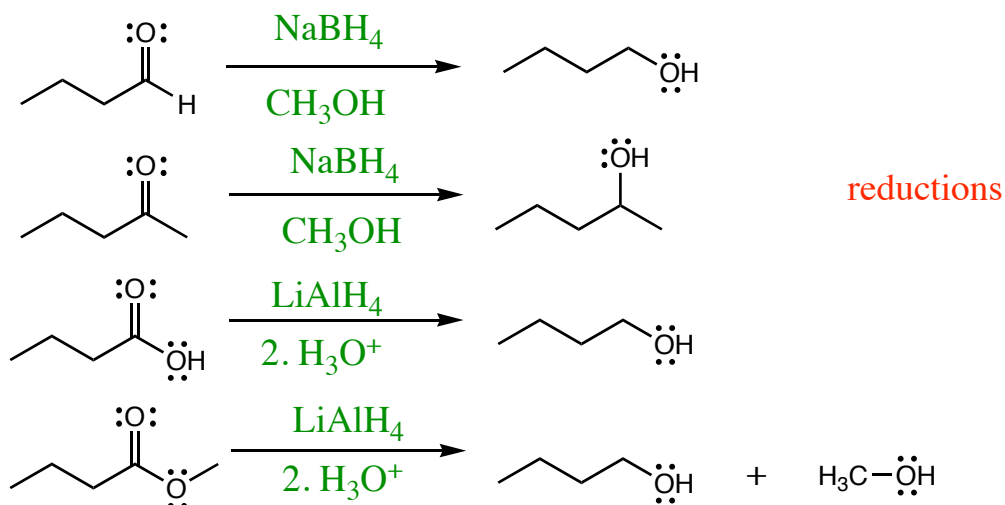


From what alkoxide and tosylate could each of the following ethers be formed?

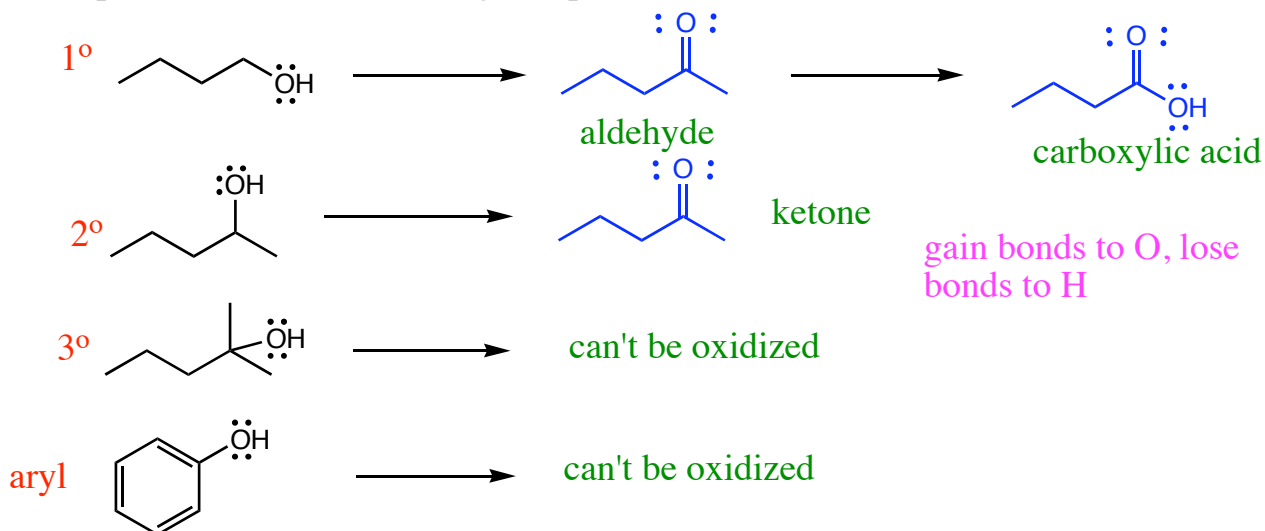


V. Oxidation of Alcohols and Diols

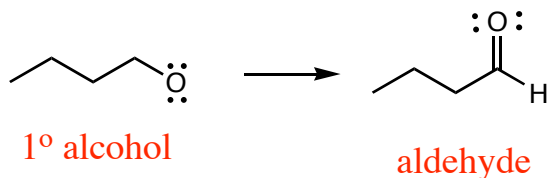
What type of reaction is represented by all of the transformations below? Give a reagent that would be effective for each.



What products can the following compounds be oxidized to?

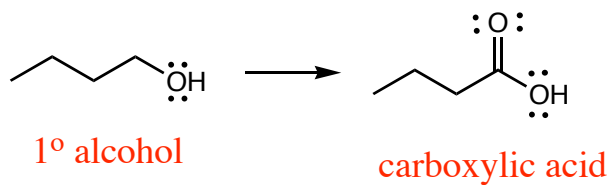


Which reagents are commonly used for the following transformations?



CrO_3 , pyridine = Collin's reagent

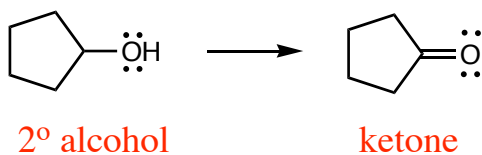
CrO_3 , pyridine, HCl = PCC



Na_2CrO_4 , H_2O , H_2SO_4

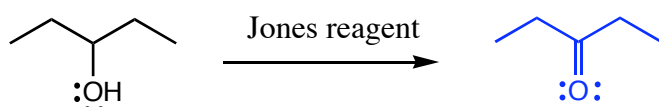
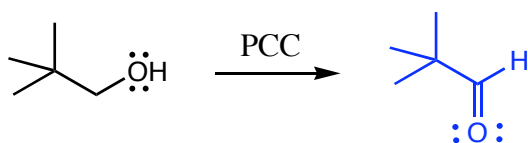
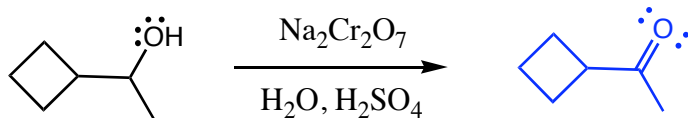
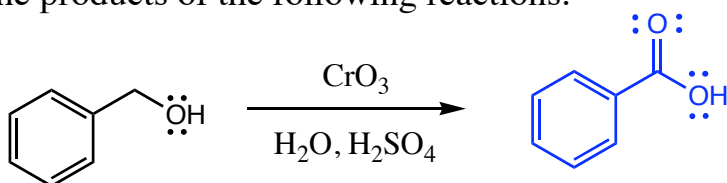
$\text{Na}_2\text{Cr}_2\text{O}_7$, H_2O , H_2SO_4

CrO_3 , H_2O , H_2SO_4 = Jones reagent

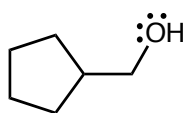


all of the above

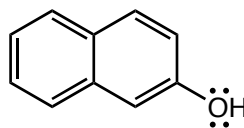
Give the products of the following reactions:



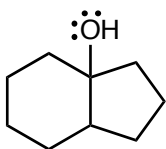
What would you observe when doing a Jones test on the following alcohols?



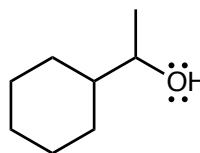
orange --> blue-green
positive test



stays orange
negative test



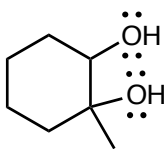
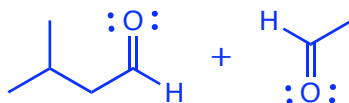
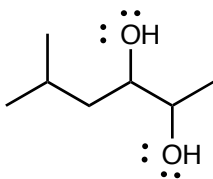
stays orange
negative test



orange --> blue-green
positive test

What reagent is needed to cleave vicinal diols? **periodic acid - HIO_4 or H_5IO_6**

What products will result from the following reactions?



What reaction of alkenes gives the same result?

ozonolysis

Summary of Alcohol Reactions