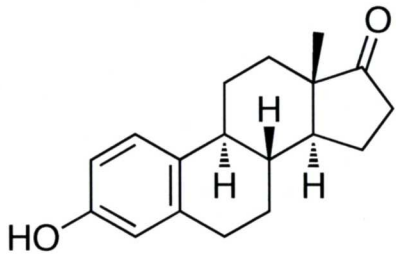
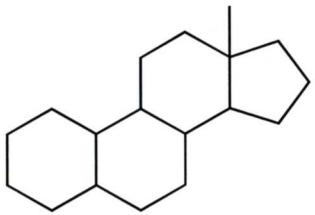
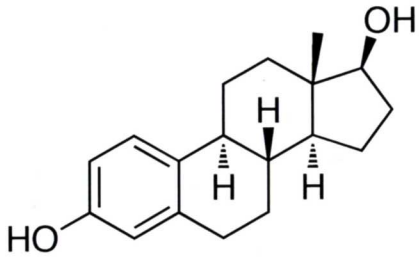
Steroids: Nomenclature



estrone



estrane



estradiol

Female Sex hormones:

12 mg estradiol was first isolated in 1929 from extraction of 4 tons of hog ovaries

Adolf Butenandt
Edward Doisy

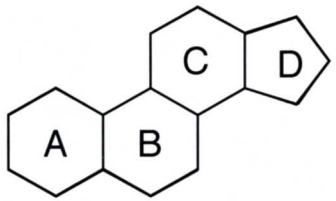
NP

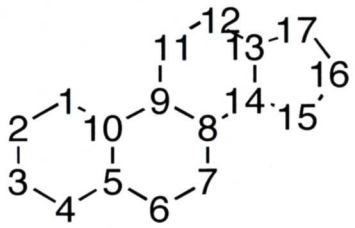
Steroids: Nomenclature

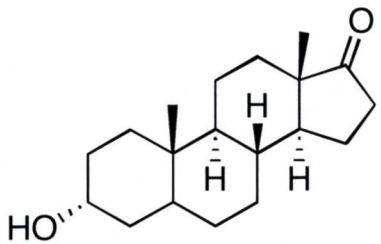
Steroids are characterized by a tetracyclic structure

rings in a steroid skeleton are designated as the A, B, C and D

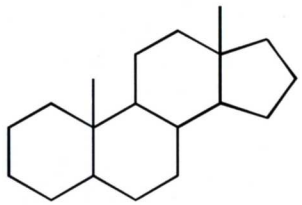
numbering as shown



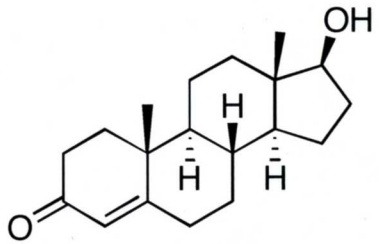




androsterone



androstane



testosterone

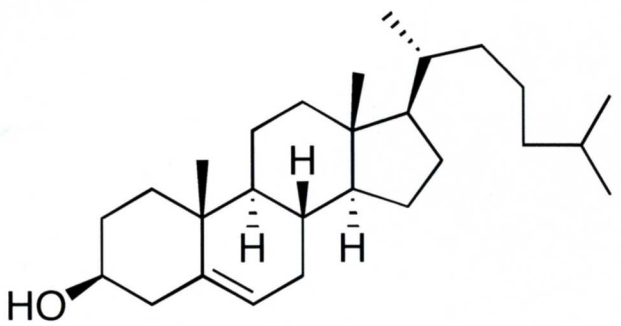
1935 Japan

Male Sex hormones:

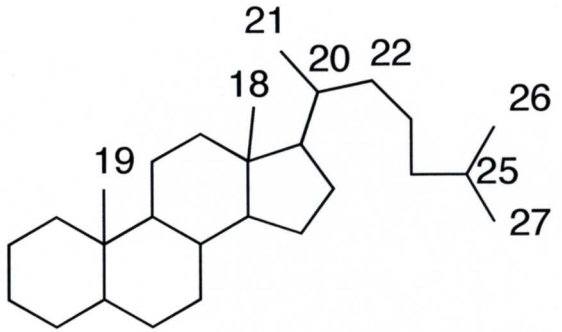
15 mg androsterone was first isolated in 1931 from extraction of 15,000 liters of urine

Butenandt

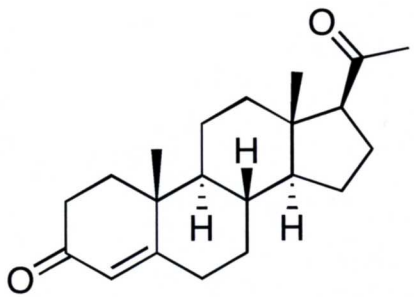
Steroids: Nomenclature



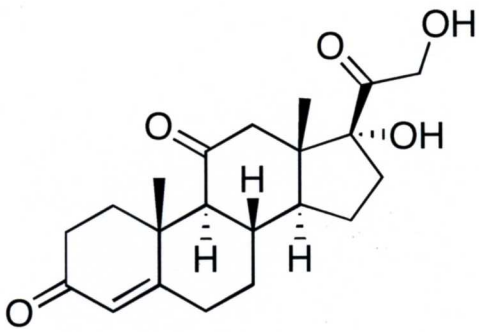
cholesterol



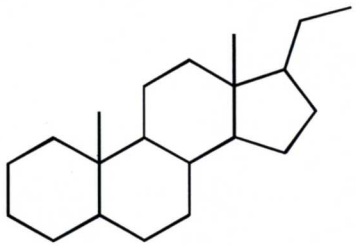
cholestane



progesterone



cortisone

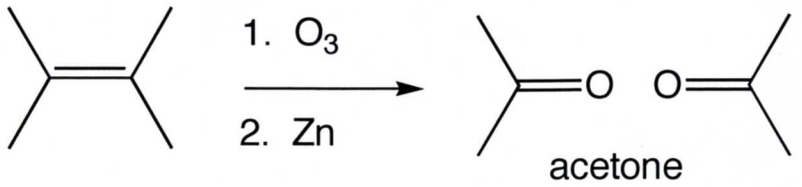


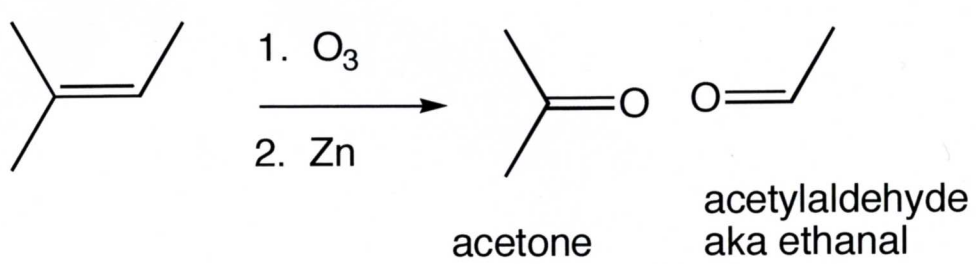
pregnane

cortisone is a hormone of the adrenal glands
progesterone required to maintain pregnancy

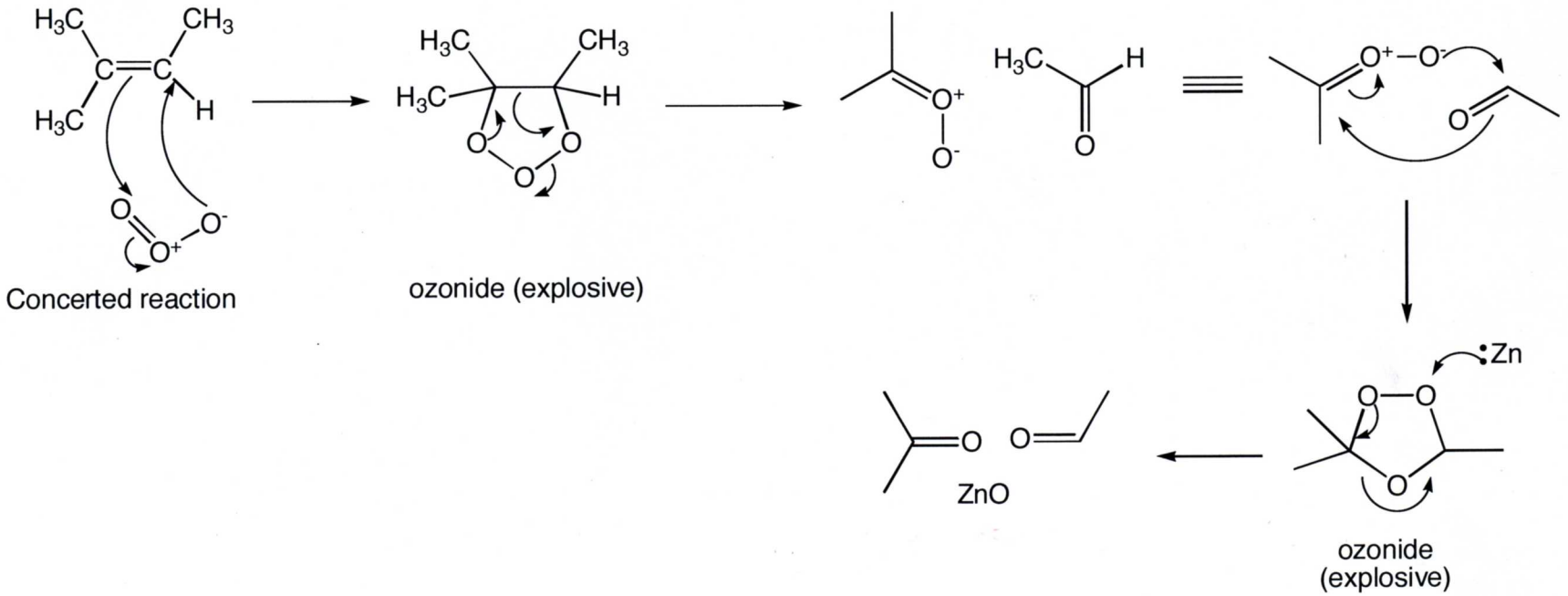
Preparation of Ketones and Aldehydes: from alkenes

Ozonolysis - an addition reaction



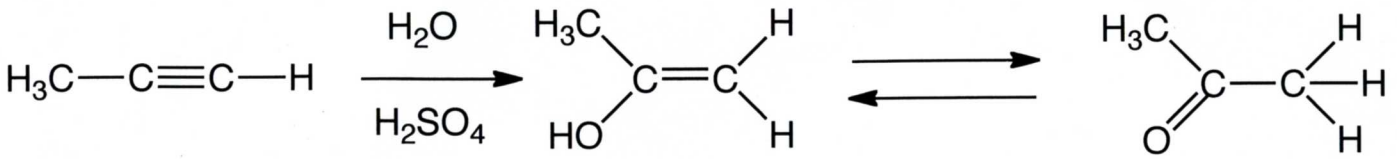


Mechanism

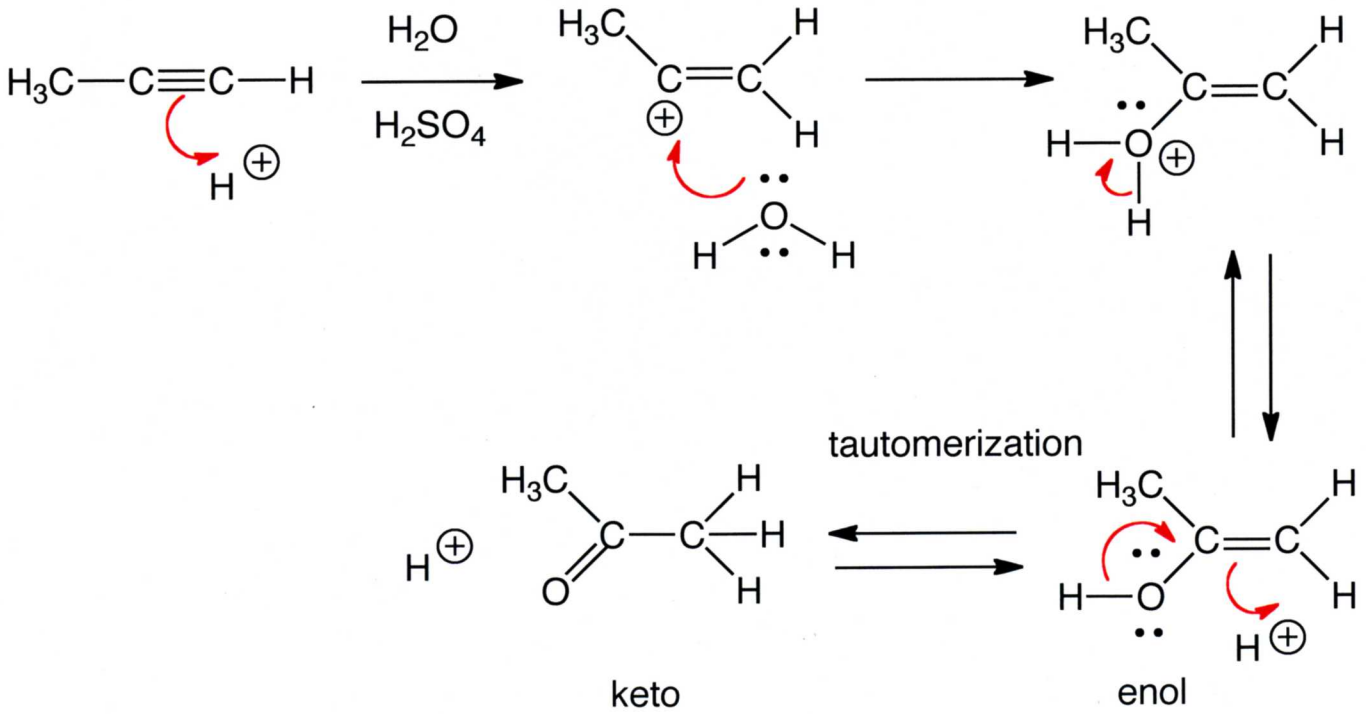


Preparation of Ketones and Aldehydes: from alkynes

Addition of water to acetylenes (Markovnikov):

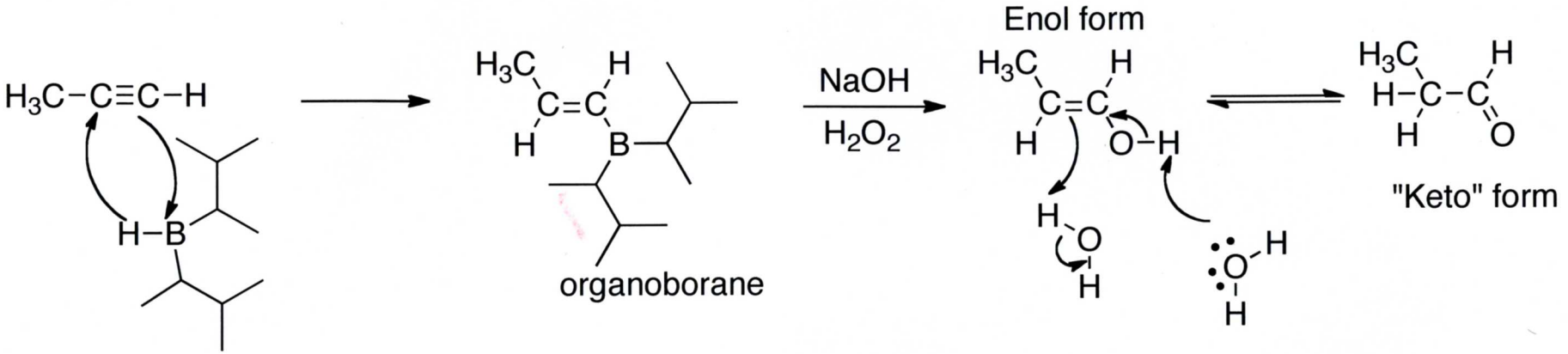


Mechanism



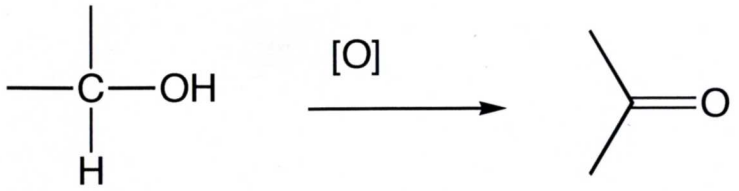
Preparation of Ketones and Aldehydes: from alkynes

Addition of water to acetylenes (via boranes - overall anti-Markovnikov):

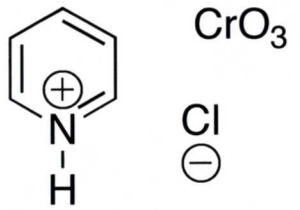


Preparation of Ketones and Aldehydes: from alcohols

Oxidation of Alcohols:



Reagents: very large variety possible - 3 given for this course:

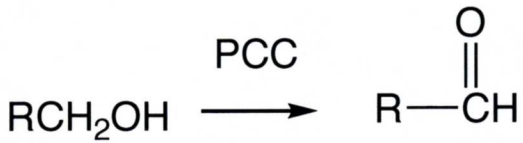


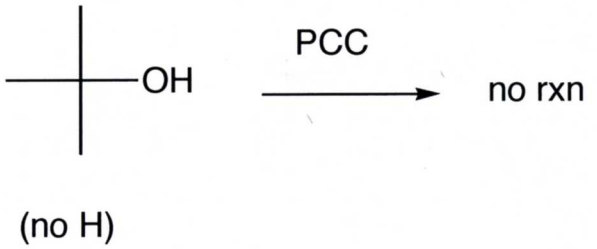
Pyridinium chlorochromate

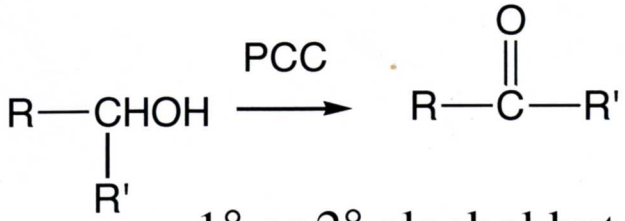
1. pyridinium chlorochromate (PCC)

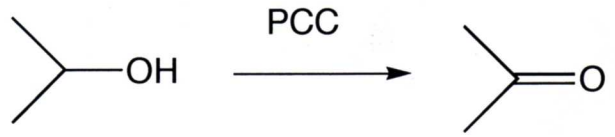
2. chromic acid (Jones reagent) (H_2CrO_4)

3. oxalyl chloride, dimethyl sulfoxide (DMSO), base (Swern oxidation)





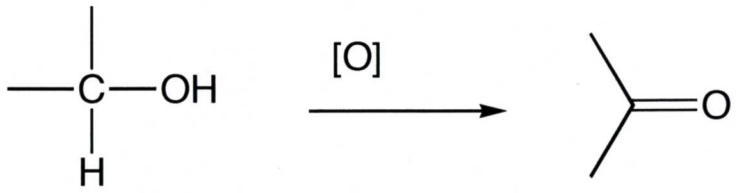




1° or 2° alcohol but not 3° alcohols

Preparation of Ketones and Aldehydes: from alcohols

Oxidation of Alcohols:



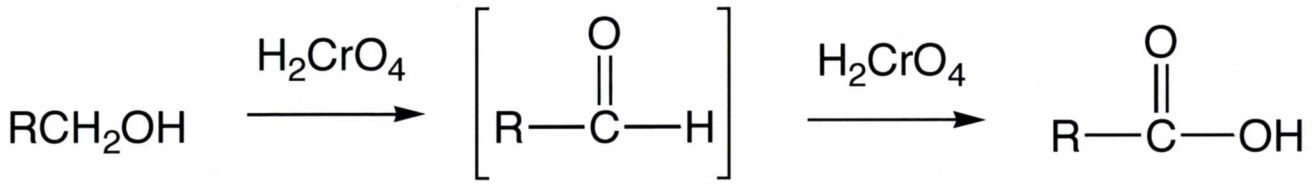
H_2CrO_4 or chromic acid, Jones reagent

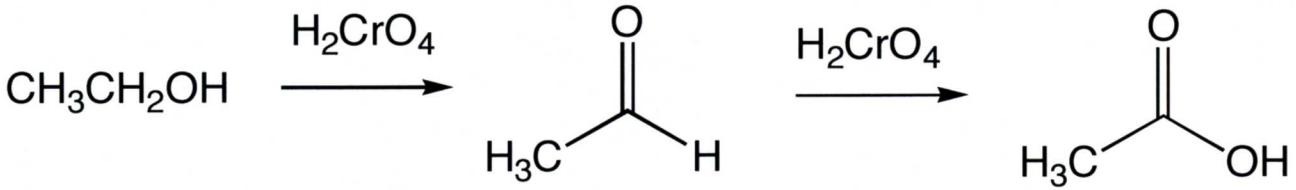
orange reagent becomes green -

converts primary alcohols to carboxylic acids because aldehyde reacts

converts secondary alcohols to ketones

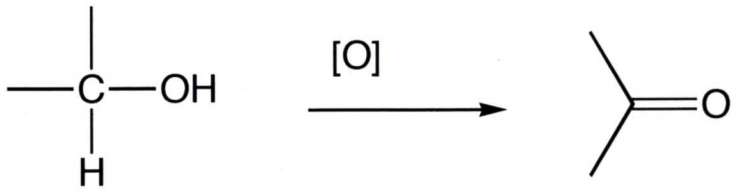
tertiary alcohols are inert





Preparation of Ketones and Aldehydes: from alcohols

Oxidation of Alcohols:



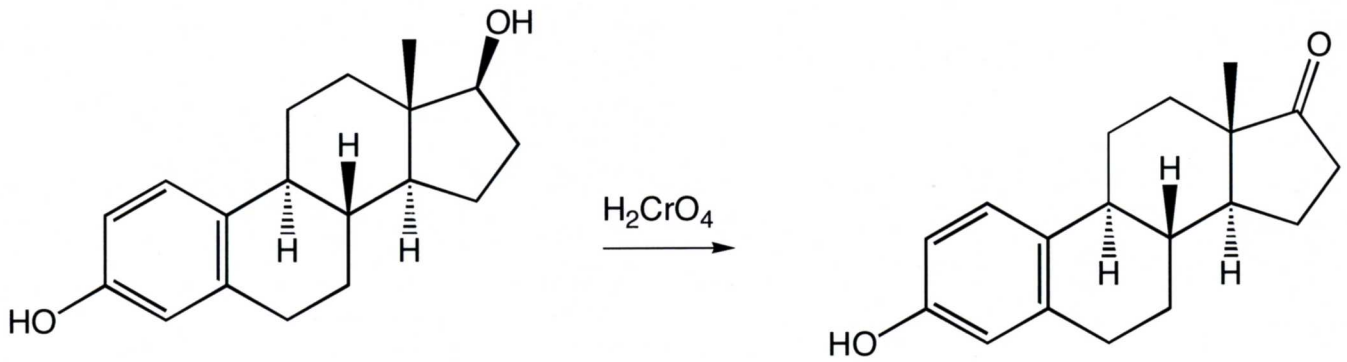
H_2CrO_4 or chromic acid, Jones reagent

orange reagent becomes green -

converts primary alcohols to carboxylic acids because aldehyde reacts

converts secondary alcohols to ketones

tertiary alcohols are inert



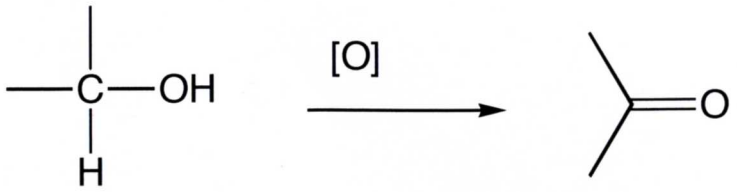
estradiol

estrone

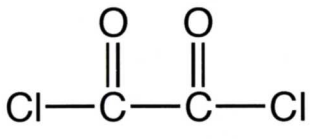
R. B. Woodward

Preparation of Ketones and Aldehydes: from alcohols

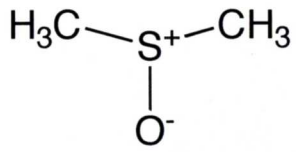
Oxidation of Alcohols:



oxalyl chloride, dimethyl sulfoxide (DMSO), base (Swern oxidation)



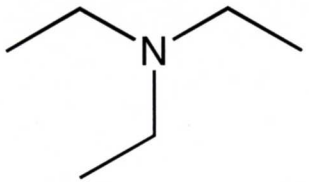
oxalyl chloride



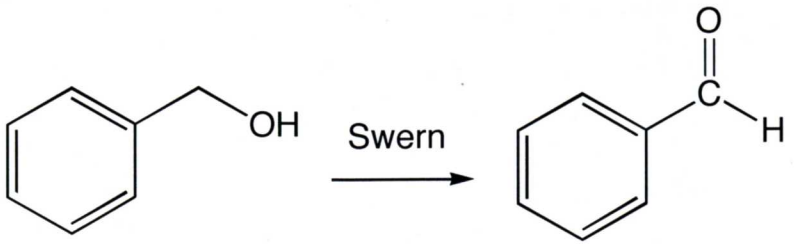
DMSO

dimethyl sulfoxide

Organic Base
eg Triethylamine
Et_3N

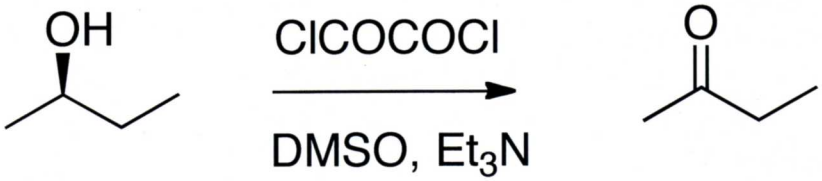


Swern Oxidation is mild and will oxidize primary alcohols to aldehydes (not to acids) and secondary alcohols to ketones, tertiary alcohols do not react

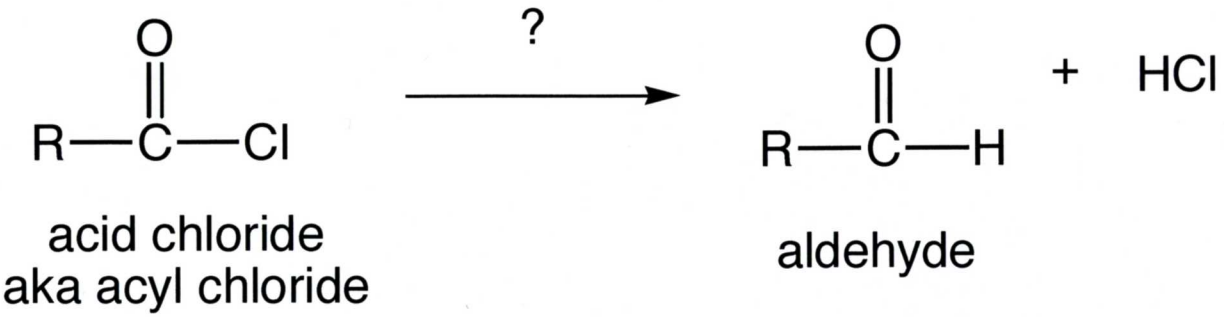


Benzyl alcohol

Benzaldehyde



Preparation of Aldehydes: from acid halides

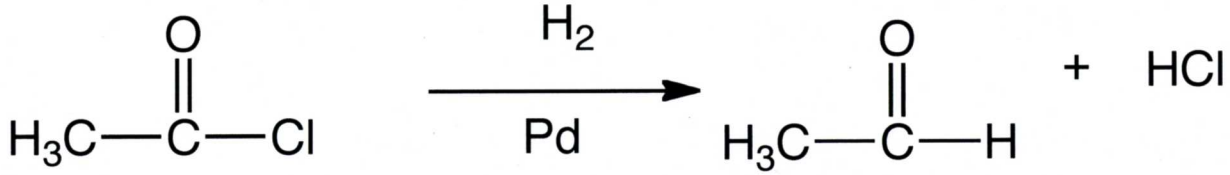


acid chloride
aka acyl chloride

aldehyde

Needed: $:H^{\ominus}$ and $H^{\oplus}$ } H_2

Actual Reagents: H_2/Pd



acetyl chloride

acetaldehyde