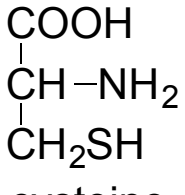
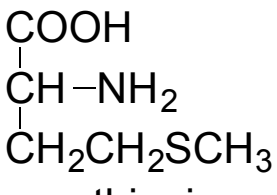
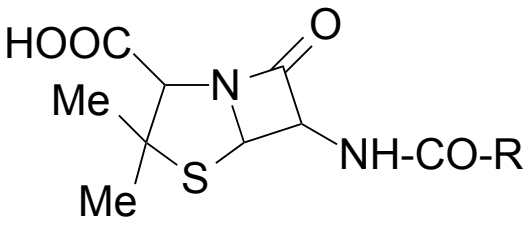
Sulfur containing compounds



cysteine

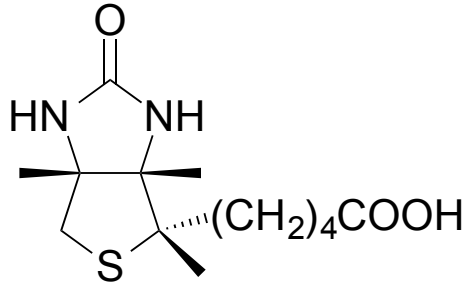


methionine

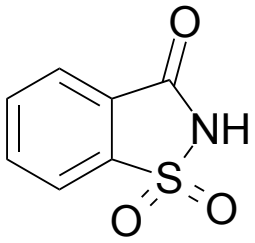


penicilline (Fleming, 1928)

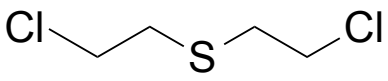
1941: isolation of sodium salt
1945: structure determination
1952: synthesis (Woodward)



biotine (H vitamin, Kˆgl, 1936)



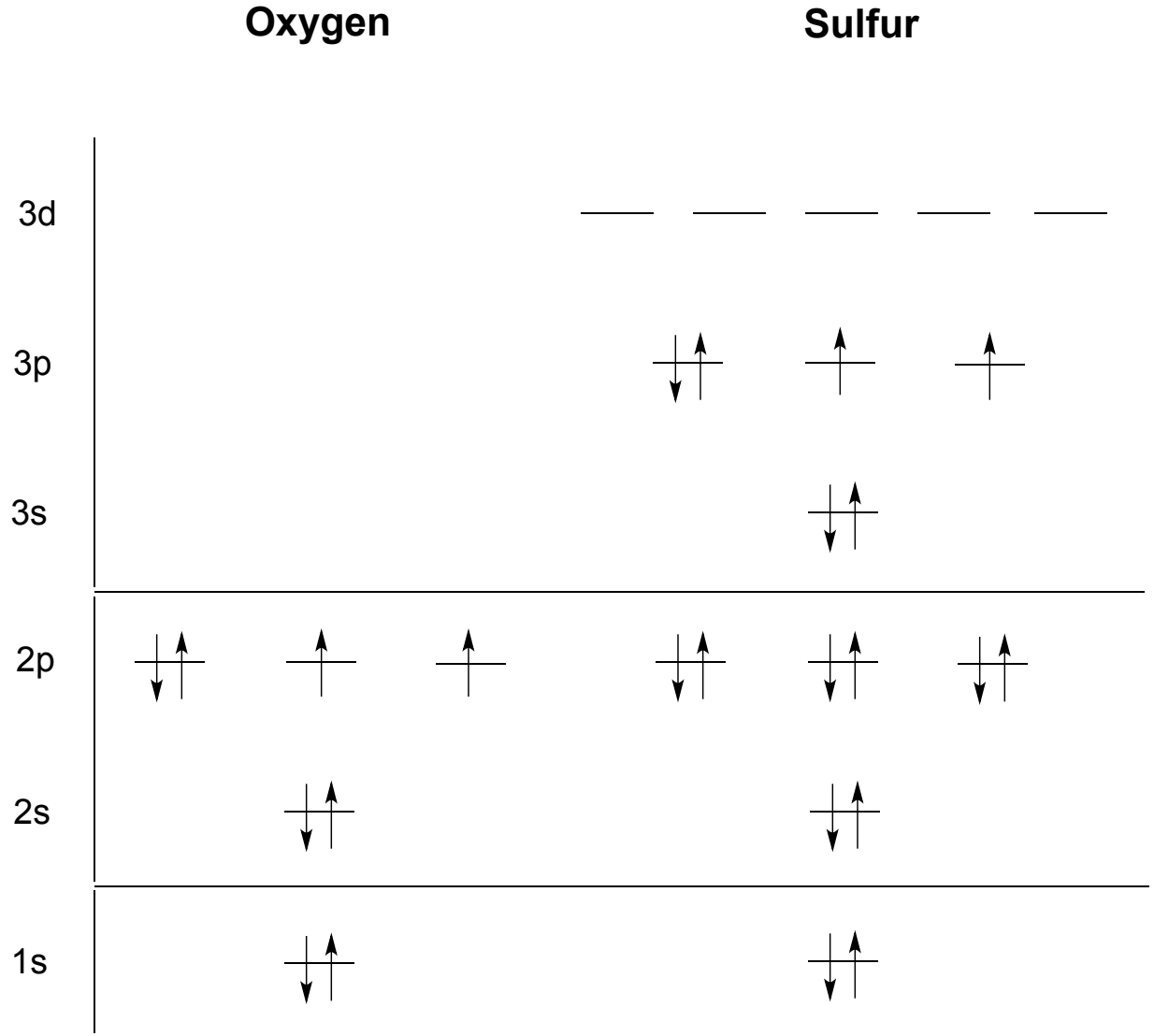
sacharine



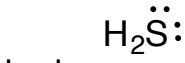
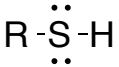
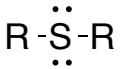
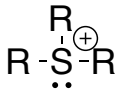
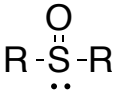
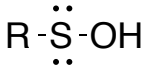
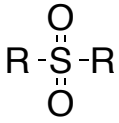
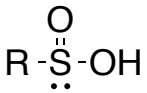
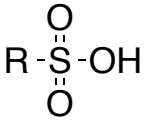
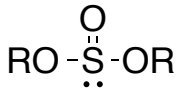
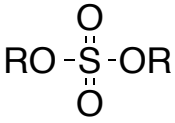
mustard gas
fp. 218 ^{o}C

Sulfur containing compounds

Electronstructure

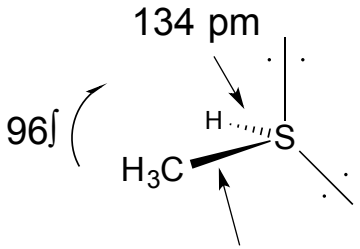


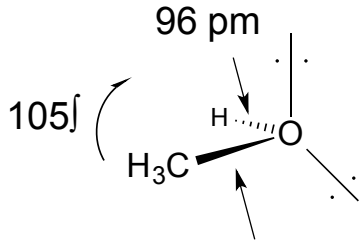
Sulfur-containing compounds

oxidation state	compounds
-2	 hydrogen sulfide;  thiols;  sulfides;  sulfonium salts
-1	 disulfides
0	 sulfoxides;  sulfenic acids
+2	 sulfones;  sulfinic acids
+4	 sulfonic acids;  sulfite esters
+6	 sulfate esters

THIOLS

Structure





Electronegativity

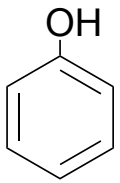
C 2.5 H 2.2 O 3.5 S 2.5

Bonding energy

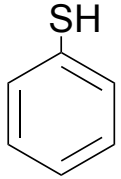
S-H 330 kJ/mol O-H 440 kJ/mol

Acidity (pK)

CH_3OH 17 CH_3SH 11



10

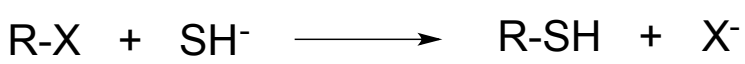


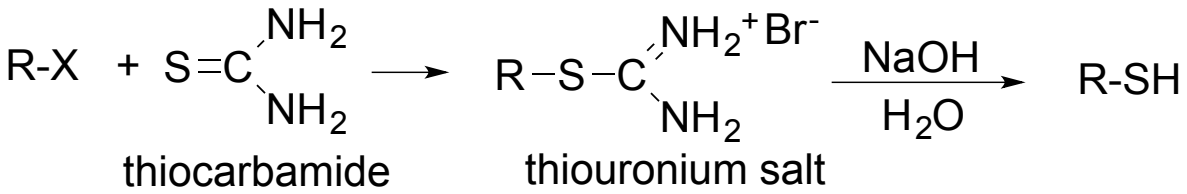
6,6

$R\text{-}OH + OH^- \rightleftharpoons R\text{-}O^- + H_2O$

$R\text{-}SH + OH^- \longrightarrow R\text{-}S^- + H_2O$

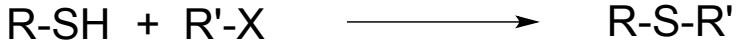
Synthesis



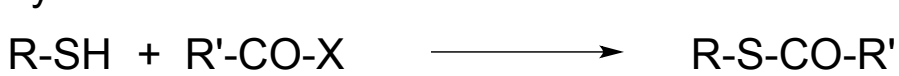


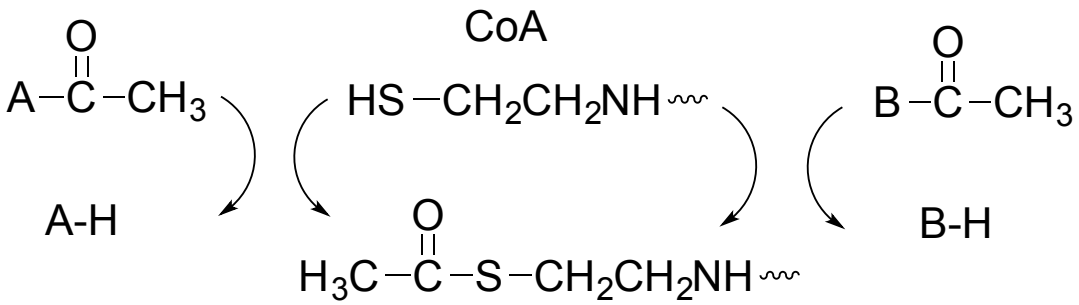
Reactivity

alkylation (S_N)

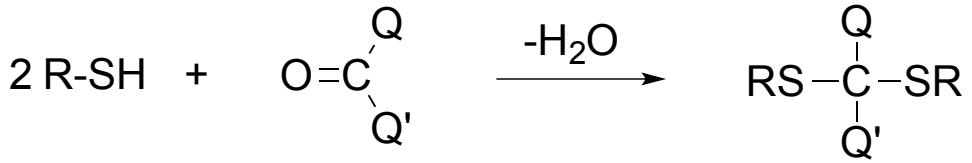


acylation

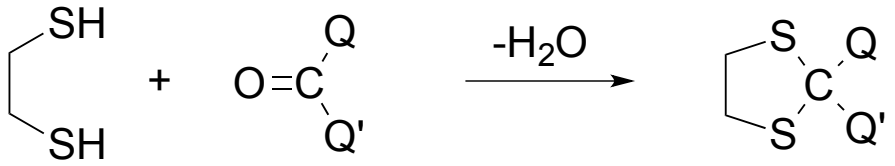




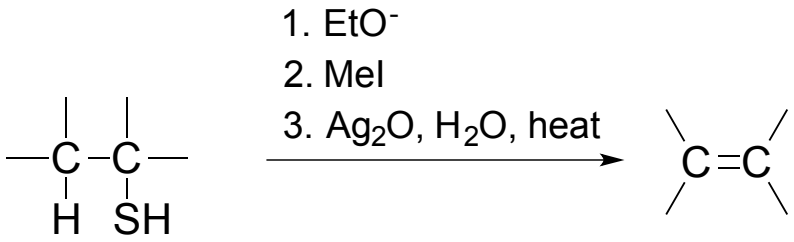
Addition with oxo compound



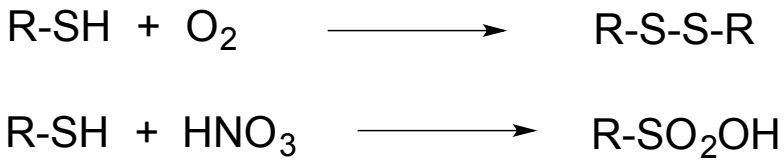
thioacetal



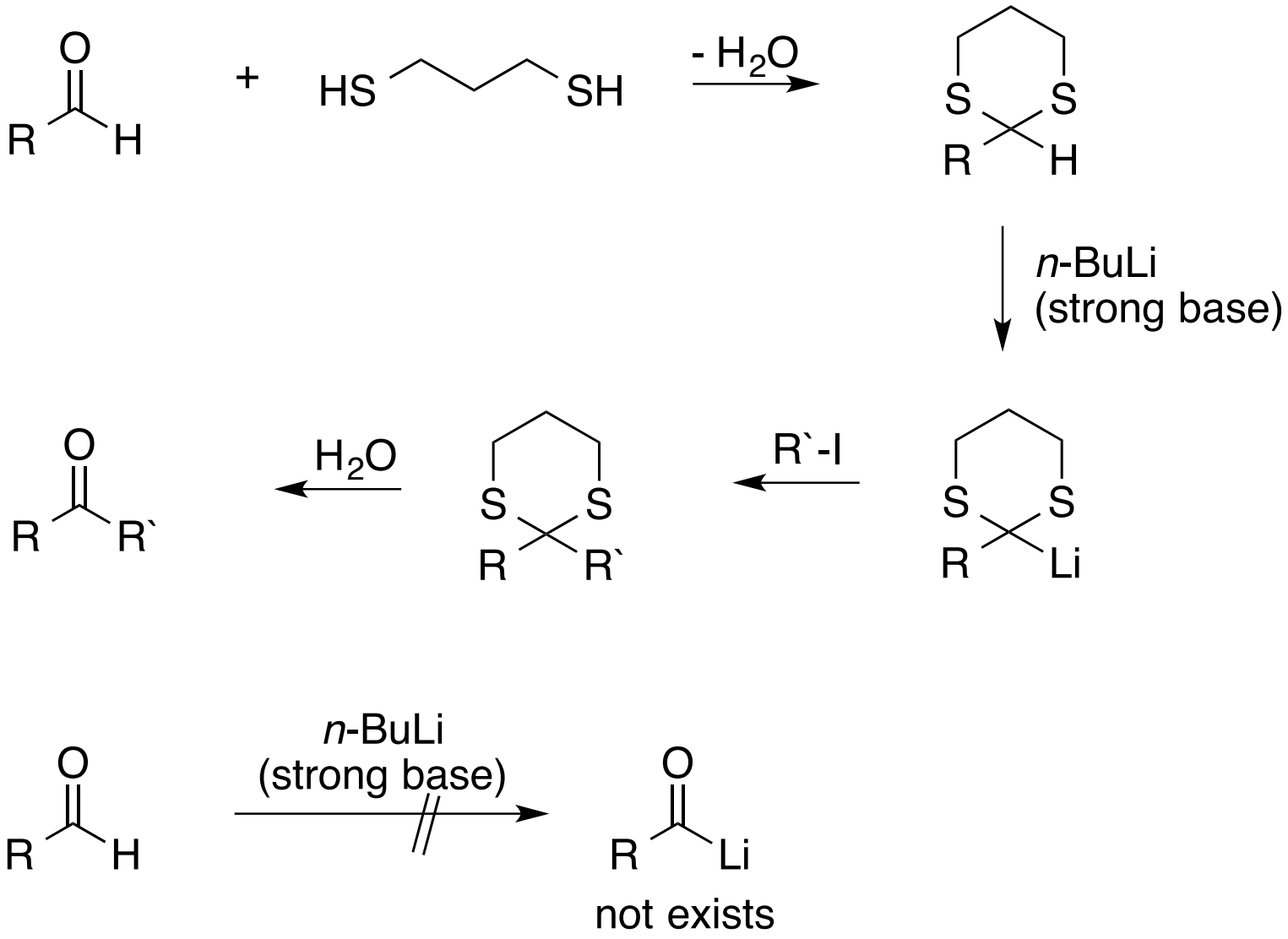
Elimination (Hofmann analogue)



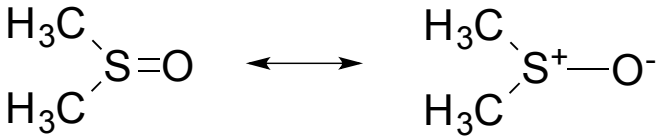
Oxidation



Synthetic use of thioacetates

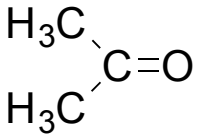


Sulfoxides



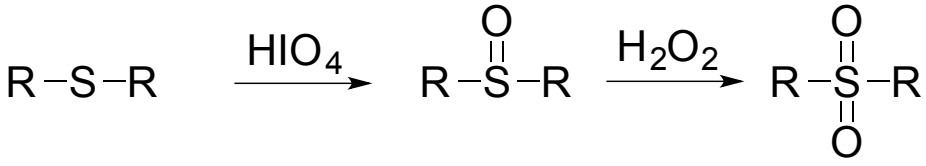
dimethyl sulfoxide

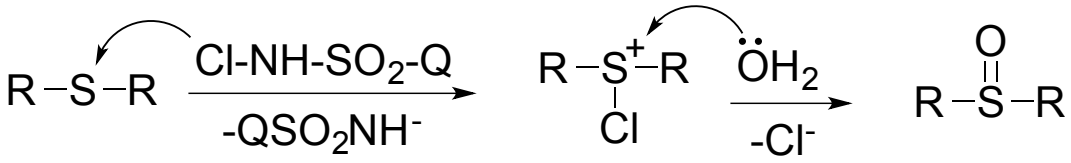
mp 18 °C, bp 189 °C

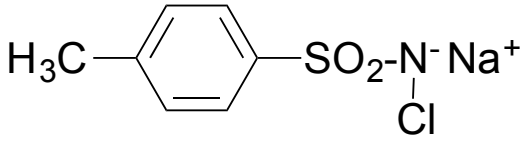


acetone (bp 56 °C)

Synthesis, oxidation

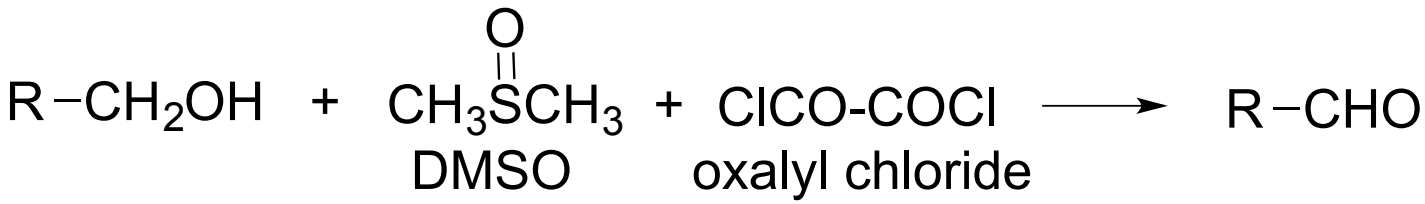




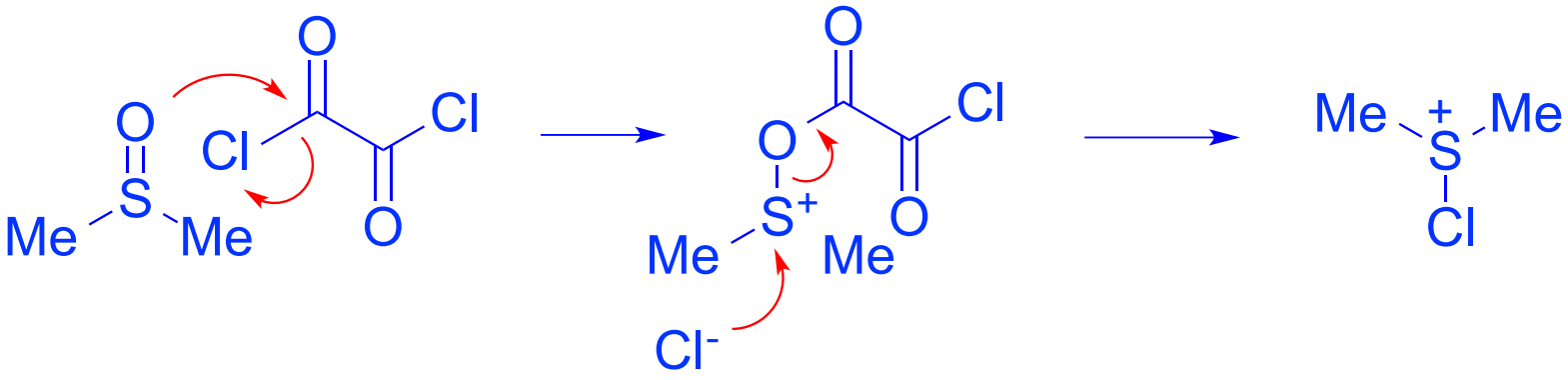


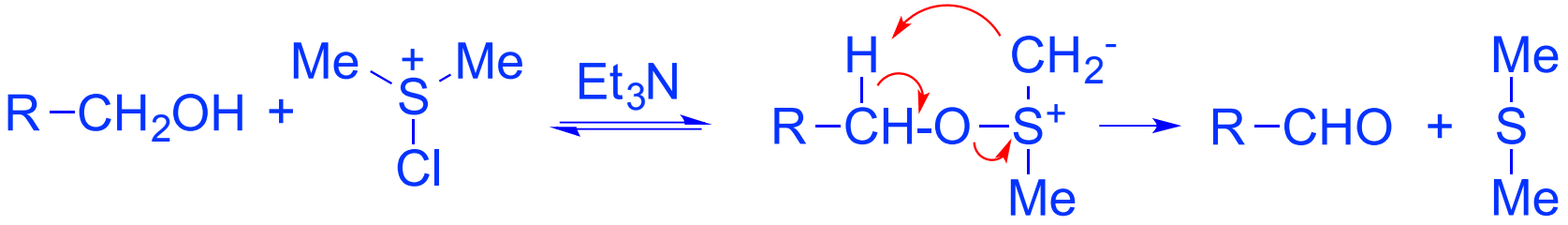
chloramine-T

Swern oxidation

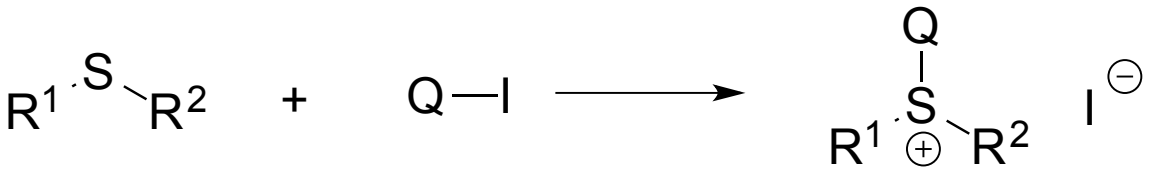


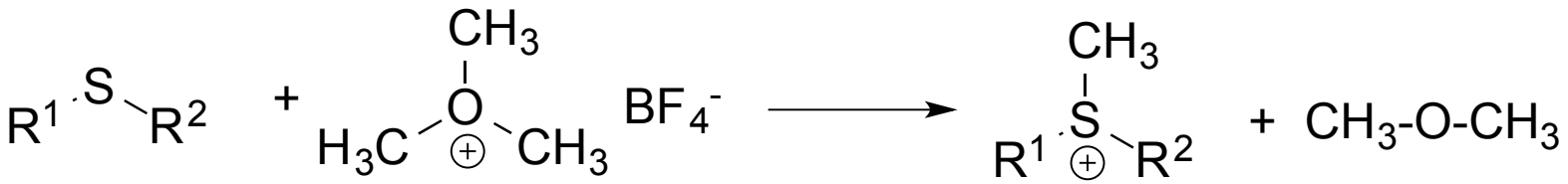
mechanism



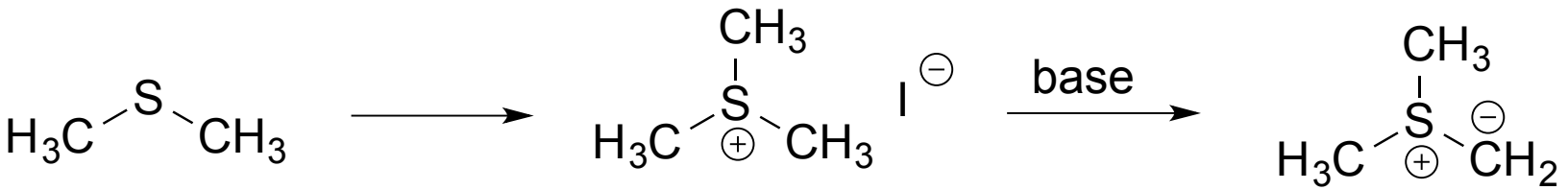


Sulfonium salts and sulfur ylides





Meerwein salt

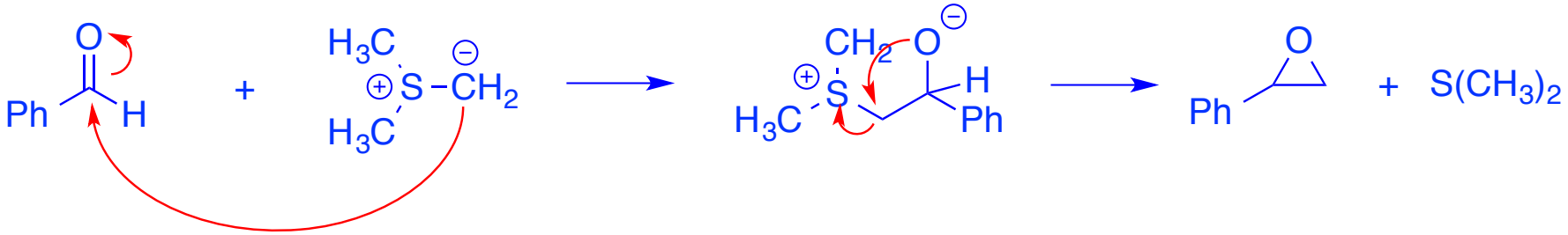


sulfur ylide

Ylide: a neutral dipolar molecule containing a formally negatively charged atom (usually a carbanion) directly attached to a heteroatom (usually N, P, O), with a formal positive charge and in which both atoms have full octet of electrons.

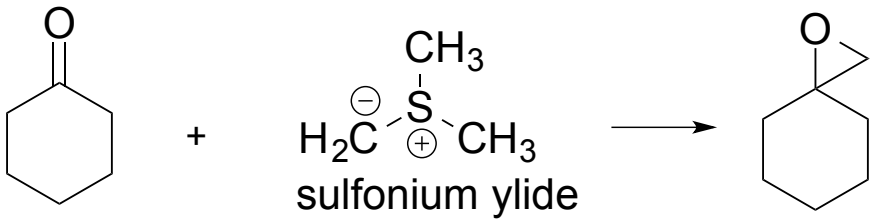
Corey-Chaykovsky Reaction

mechanism

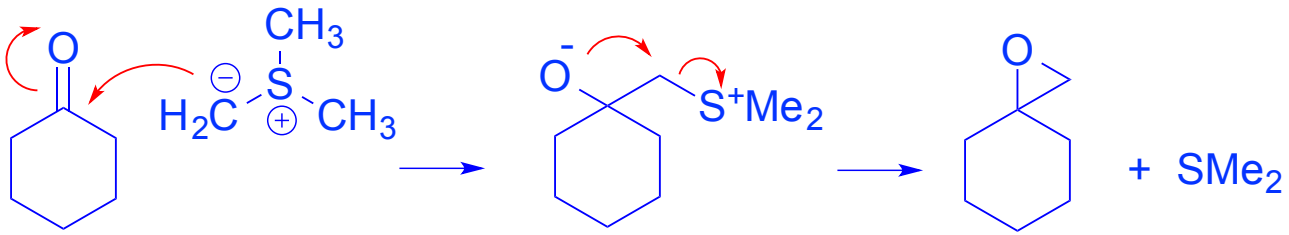


Corey-Chaykovsky Aziridation

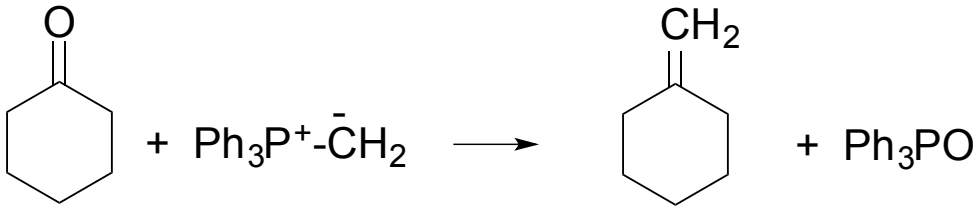
Example



mechanism



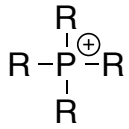
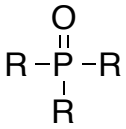
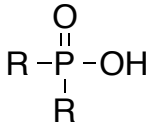
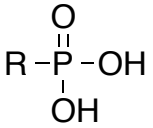
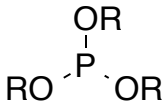
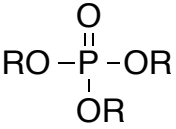
Reaction of phosphonium ylides (see also Wittig reaction)



$Ph_3P{=}O$ 529 kJ/mol

$Ph_2S{=}O$ 367 kJ/mol

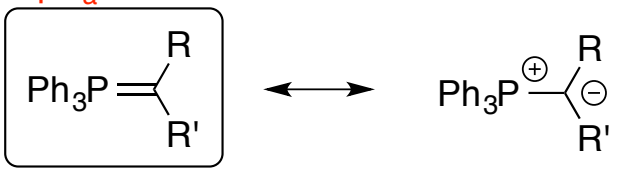
Phosphorus-containing compounds

oxidation state	compound		
-3	PH_3 phosphine	PR_3 trialkyl phosphines	 trialkylphosphonium ion
-1	 phosphine oxides		
+1	 phosphenic acides		
+3	 phosphonic acides	 phosphite esters	
+5	P_2O_5	 phosphate esters	

Phosphorus ylides

Unstabilized phosphorus ylides

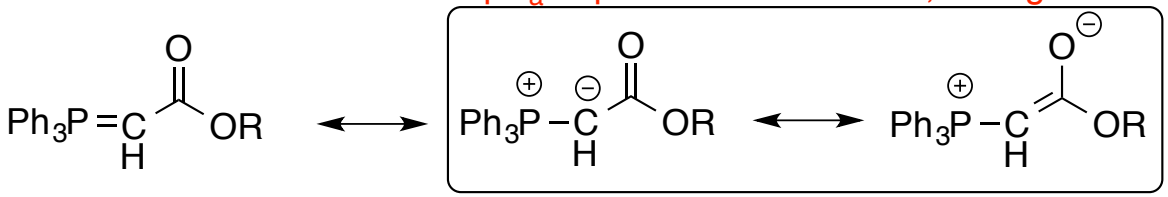
pK_a 18-20



principal form
R, R' = H or alkyl

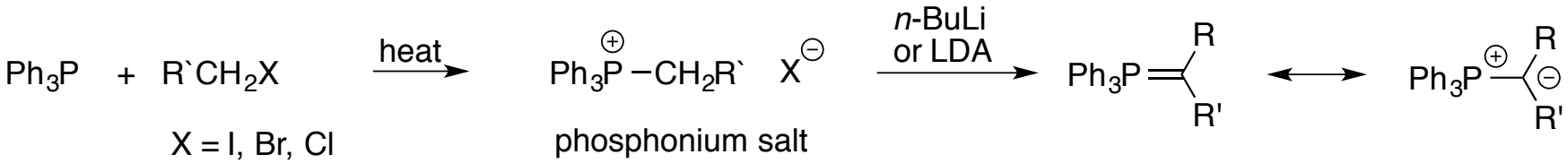
Stabilized phosphorus ylides

pK_a depends on substitutent, stronger acid

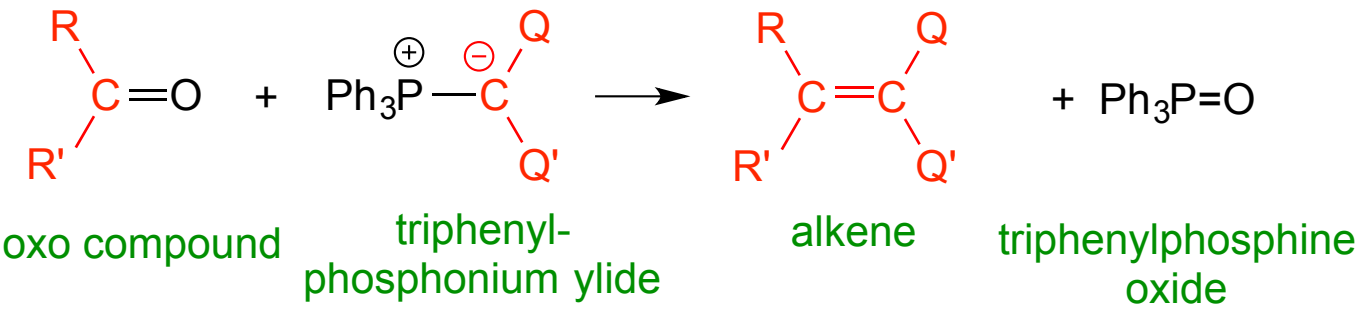


resonance stabilized ylide (predomonates)

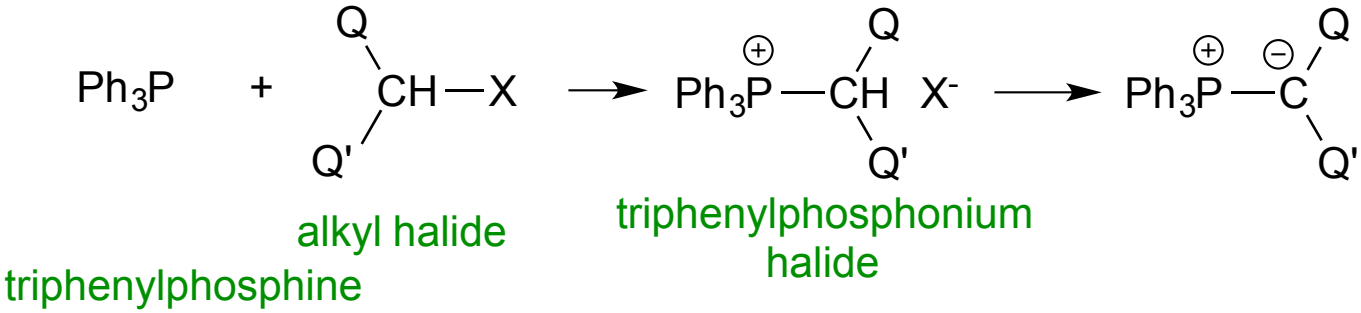
Prepatation



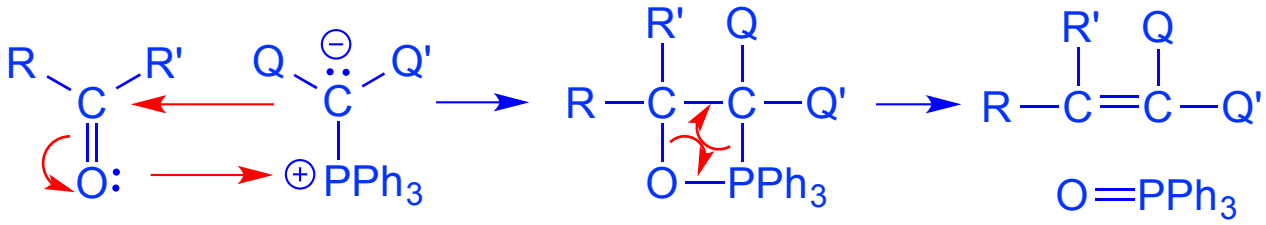
Wittig reaction (synthesis of alkenes)



Synthesis of triphenylphosphonium ylide

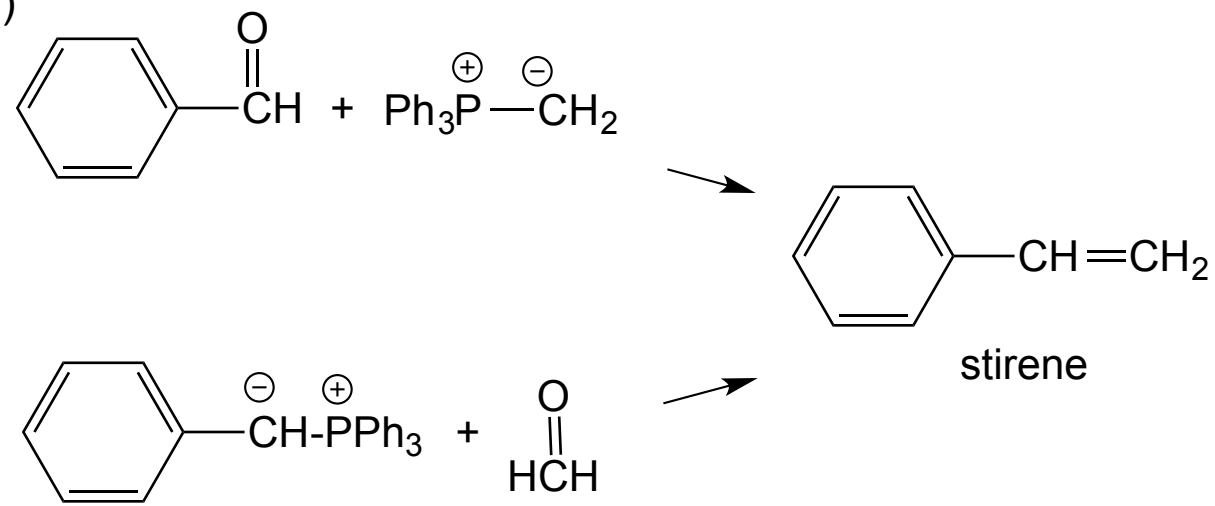


Mechanism

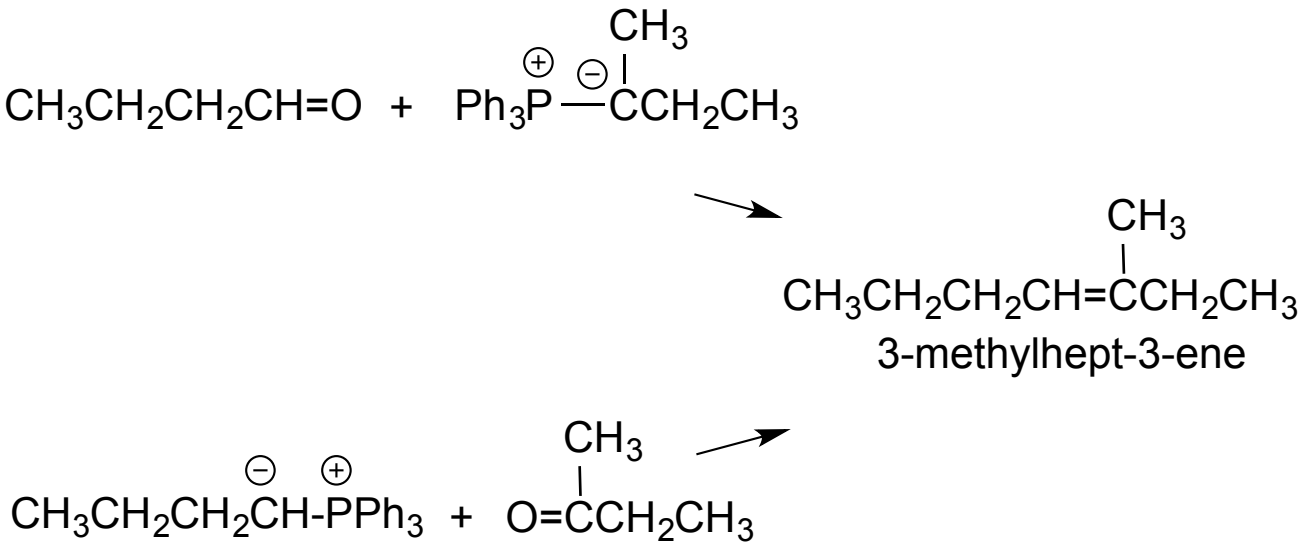


Examples

a)

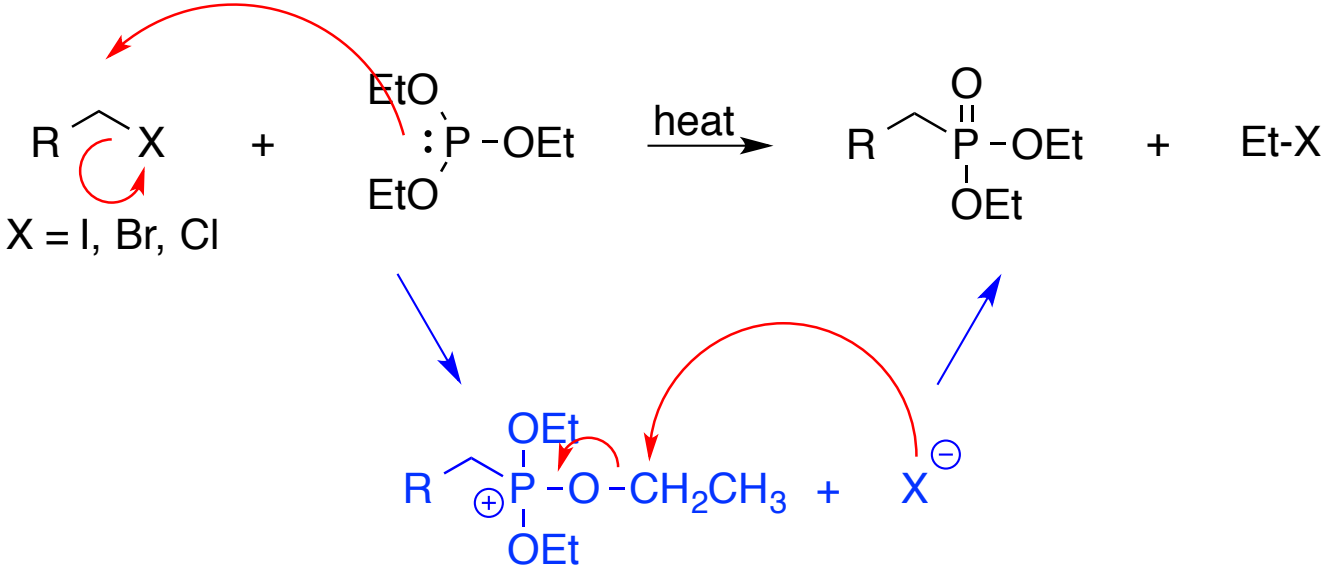

O
CH
+
Ph3P
CH2
CH=CH2
stirene
CH-PPh3
+
O
HCH

b)


CH3
CH3CH2CH2CH=O
+
Ph3P
CCH2CH3
CH3
CH3CH2CH2CH=CCH2CH3
3-methylhept-3-ene
CH3CH2CH2CH-PPh3
+
O=CCH2CH3

Horner-Wadsworth-Emmons reaction (uses phosphonate esters as intermediates)

Preparation of alkylphosphonates (Arbuzov reaction)



Horner-Wadsworth-Emmons reaction