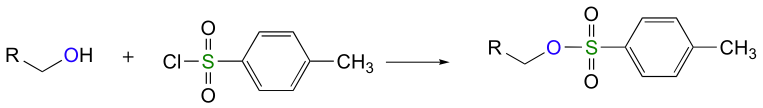
Appendix II: Review of laboratory synthesis reactions

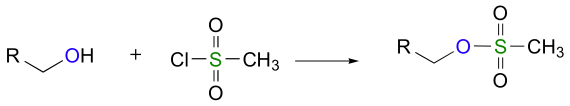
While the focus of this textbook is on organic reactions occuring in living cells, if you are a chemistry major, or are planning to take a standardized exam such as the MCAT, you will need to be familiar with a number of laboratory synthesis reactions. Here, we review the lab synthesis reactions covered in this text, which include most of the reactions typically covered in traditional organic texts. Click on the chapter/section number for direct links to the section where these reactions are introduced.

NOTE: content below redirects to an older edition of the text, which differs from the current version in some content and organization.

Section 8.5B:

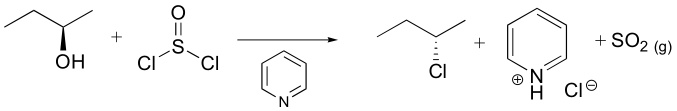


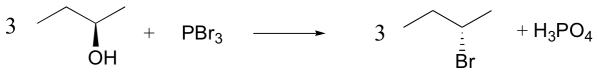
an organic tosylate (R-OTs)



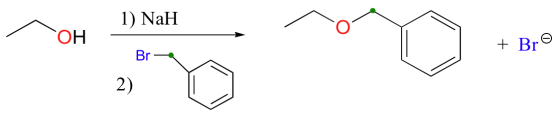
an organic mesylate (R-OMs)

alcohols converted into good leaving groups





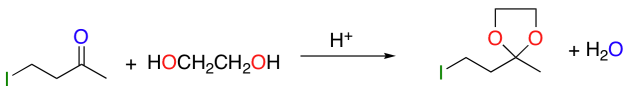
Section 9.1B:



Williamson ether synthesis

alkyl halide must be methyl or primary to avoid competing elimination

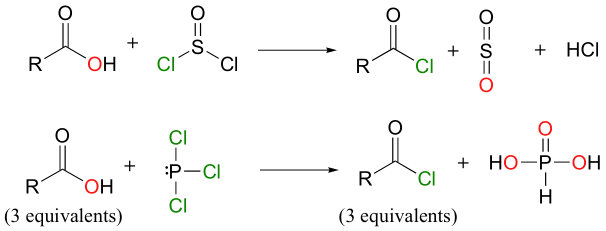
Section 11.4B:



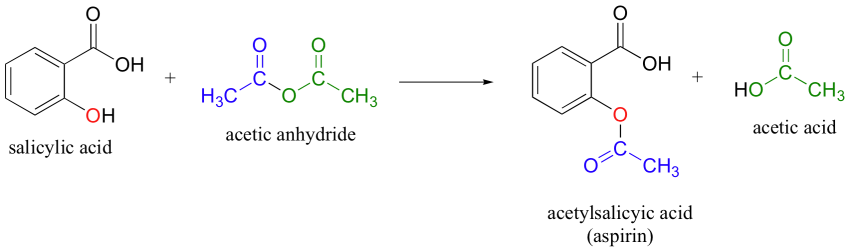
cyclic acetal 'protects' ketone/aldehyde group – stable to bases/nucleophiles

deprotect with aqueous acid

Section 12.2D:



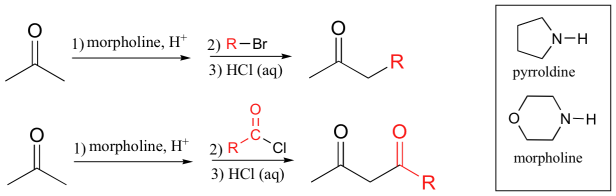
activates carboxylic acids



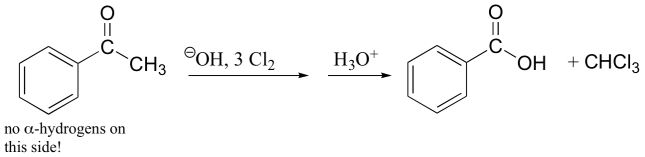
acetic anhydride is a good acetyl group donor (activated acetic acid)

adds acetyl group to acohols, amines

Section 13.6A

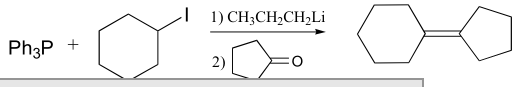


goes through enamine intermediate



haloform reaction – also works with Br_2, I_2

Section 13.6B



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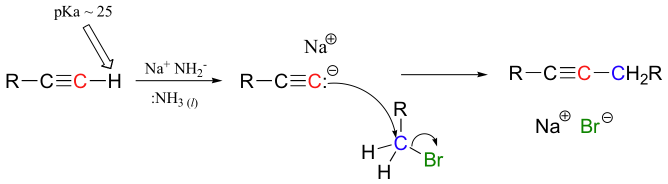
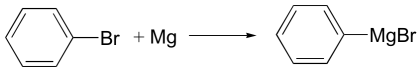
Wittig reaction

Section 13.6C



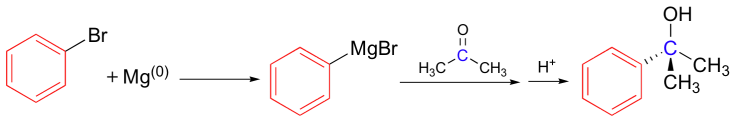
Section 13.6D

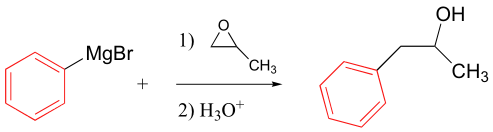


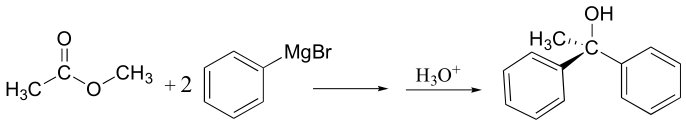
Grignard reagent – carbon nucleophile

No acidic protons can be present (it's a strong base)

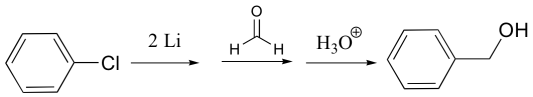
Can also use R-Cl



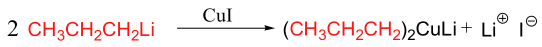




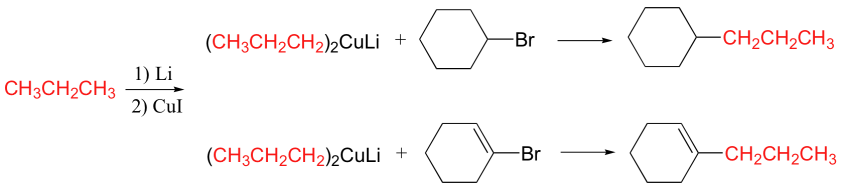
Grignards add to esters, acid chlorides ***twice***



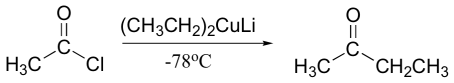
organolithium – similar to Grignard



Gilman reagent

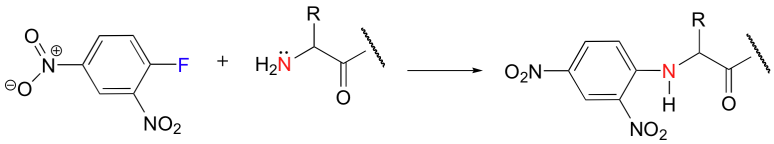


Gilman reagent will react with alkyl, vinyl halides as well as carbonyls



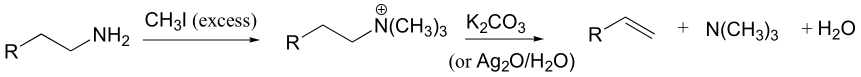
*Gilman reagent will add **once** to acid chlorides to make a ketone*

Section 14.2B

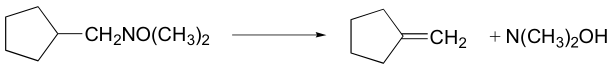


nucleophilic aromatic substitution

Section 14.3A

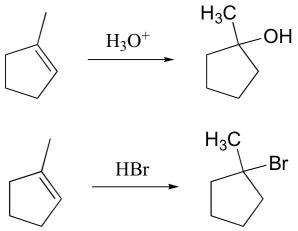


Hoffman elimination - least substituted alkene produced

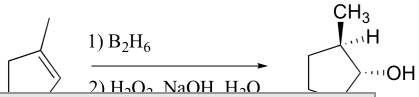


Cope elimination

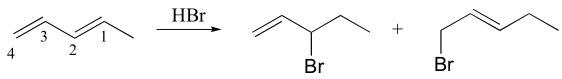
Section 15.2B



Section 15.2D

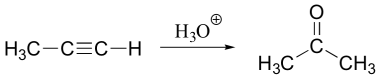


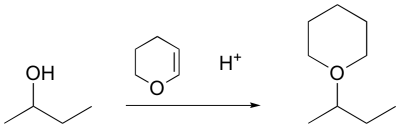
anti-Markovnikov addition of water to alkene. Notice syn addition!



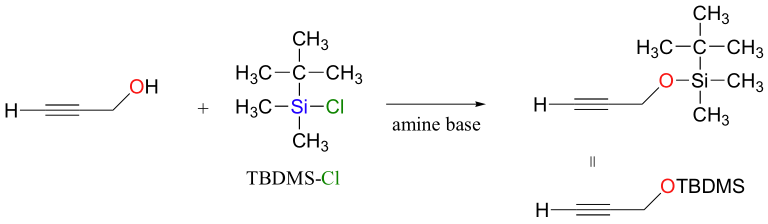
1,2 addition product

1,4 addition product



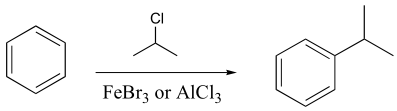


method to protect alcohol – remove with H_3O^+

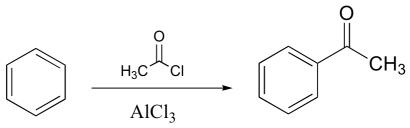


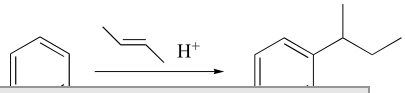
another alcohol protecting group: remove with F^- ion

Section 15.6A:

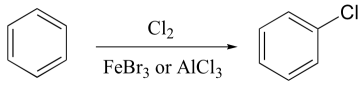


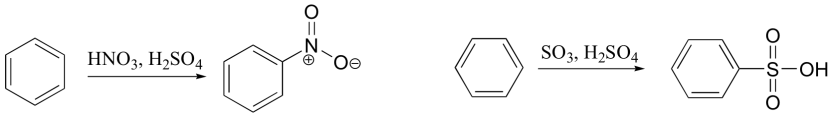
watch out for the possibility of carbocation rearrangements!





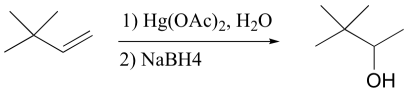
watch out for the possibility of carbocation rearrangements!





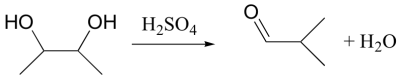
ortho-para directing vs. meta-directing groups

Section 15.7A:

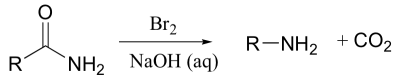


Markovnikov addition of water without possibility of carbocation shifting

Section 15.7C:

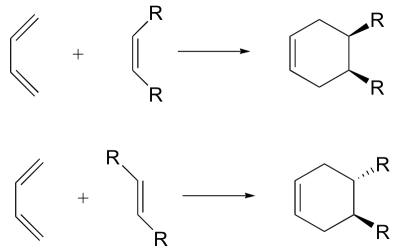


pinacol rearrangement

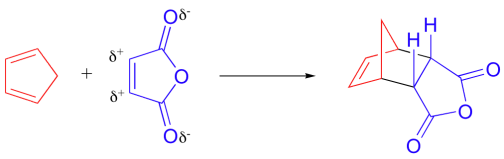


Hoffman rearrangement

Section 15.10:



Diels-Alder: cis/trans stereoselectivity



bicyclic Diels-Alder product - no stereoselectivity

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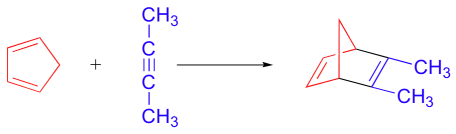
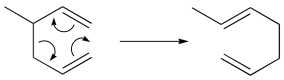
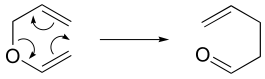


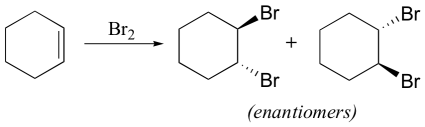


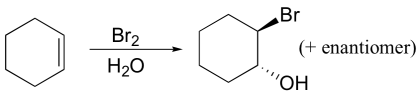
Cope rearrangement

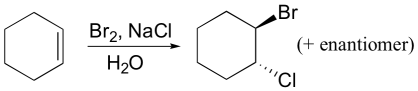


Claisen rearrangement

Section 16.11B:







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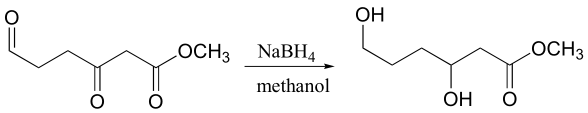
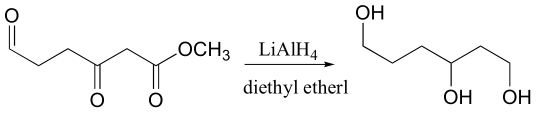
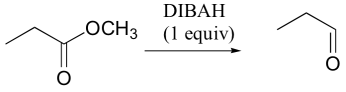


reduces aldehydes/ketones, but not carboxylic acid derivatives

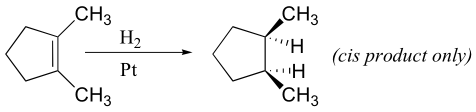


reduces aldehydes, ketones, carboxylic acid derivatives

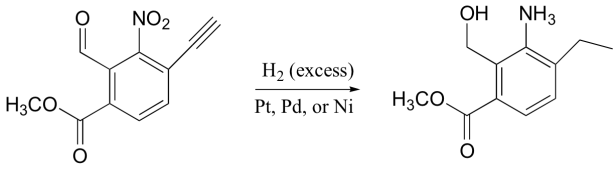


can reduce ester/amide to aldehyde ($LiAlH_4$ can't do this)

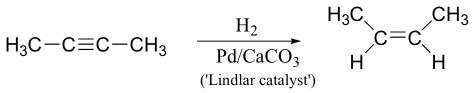
Section 16.13B:



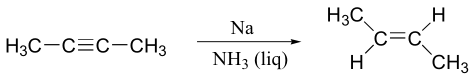
(cis product only)



alkynes, aldehyde, ketones, nitro groups also reduced by H_2/Pt (but not acid derivatives!)

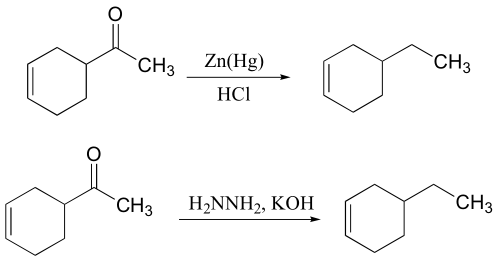


alkyne to cis-alkene



alkyne to trans-alkene

Section 16.13C:



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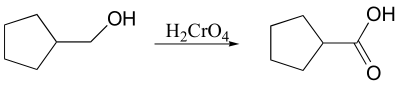
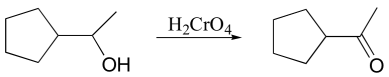
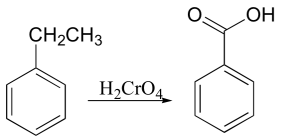


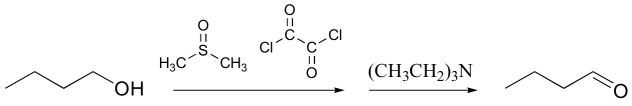
primary alcohol to acid



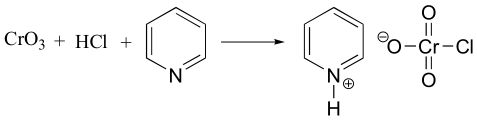
secondary alcohol to ketone



oxidation at the benzylic position

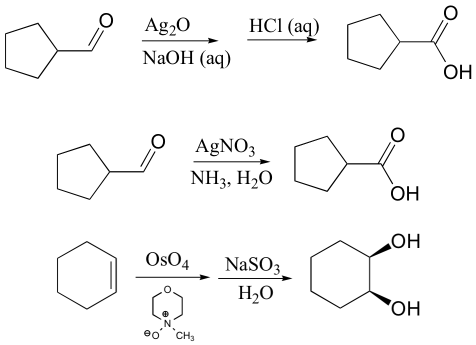


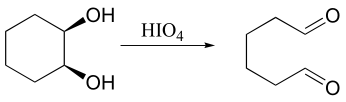
Swern oxidation



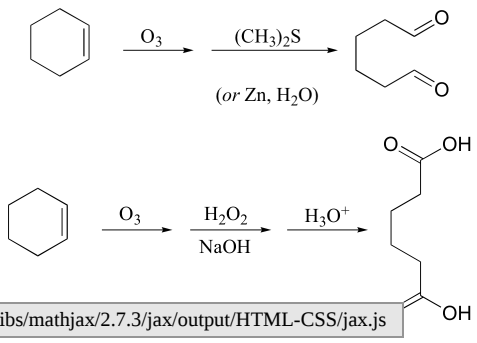
pyridinium chlorochromate
(oxidized alcohols to aldehydes/ketones)

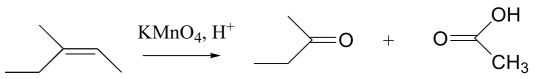
abbreviated PCC



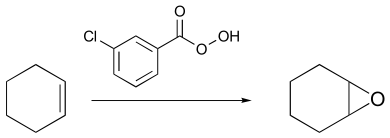


cis diols cleaved, not trans

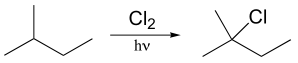




$KMnO_4$ also oxidizes primary alcohols and aldehydes to acids

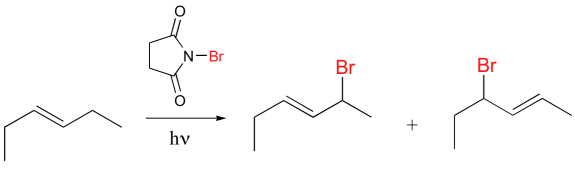


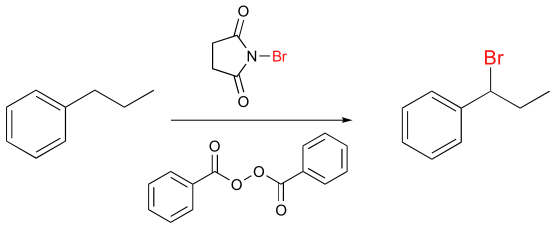
Section 17.2B:



major product

radical halogenation is regiospecific – depends on stablity of radical intermediate





NBS can be source of Br in radical halogenation reactions

regiospecificity: benzylic / allylic

Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
