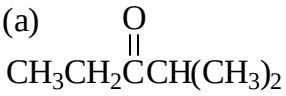
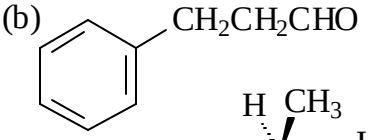
Chem 226 — Problem Set #9 —
"Fundamentals of Organic Chemistry," 4th edition, John McMurry.

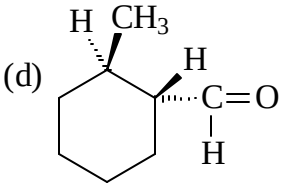
Chapter 9

2. Name the following aldehydes and ketones.

(a) 

(b) 

(c) 

(d) 

(a) 2-methyl-3-pentanone, (b) 3-phenylpropanal, (c) 2,6-octanedione,
(d) (1R,2R)-2-methylcyclohexanecarbaldehyde

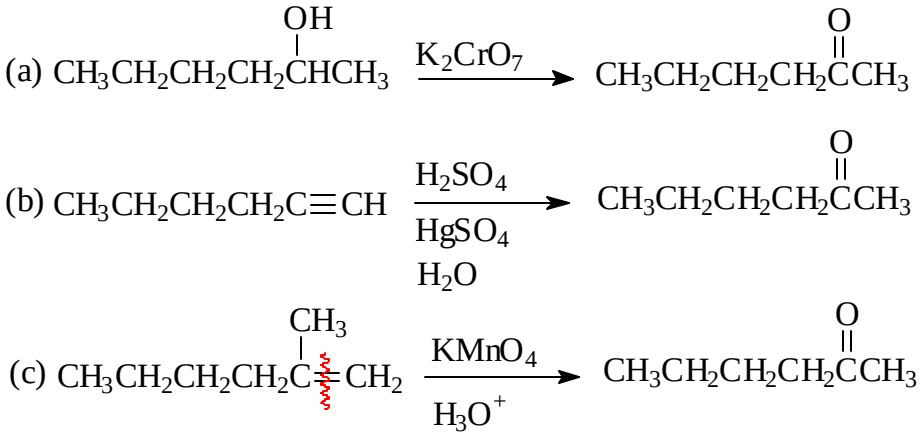
4. How could you prepare pentanal from the following starting materials?
(a) 1-pentanol, (b) $CH_3CH_2CH_2CH_2COOH$, (c) 5-decene

(a) $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2CH_2CHO$

(b)
$CH_3CH_2CH_2CH_2C(=O)-OH \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} CH_3CH_2CH_2CH_2CH_2OH$
$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2CH_2CHO$

(c)
$CH_3CH_2CH_2CH_2CH=CHCH_2CH_2CH_2CH_3 \xrightarrow[H_3O^+]{KMnO_4}$
$CH_3CH_2CH_2CH_2C(=O)-OH \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} CH_3CH_2CH_2CH_2CH_2OH$
$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2CH_2CH_2CHO$

5. How could you prepare 2-hexanone from the following starting materials?
(a) 2-hexanol, (b) 1-hexyne, (c) 2-methyl-1-hexene



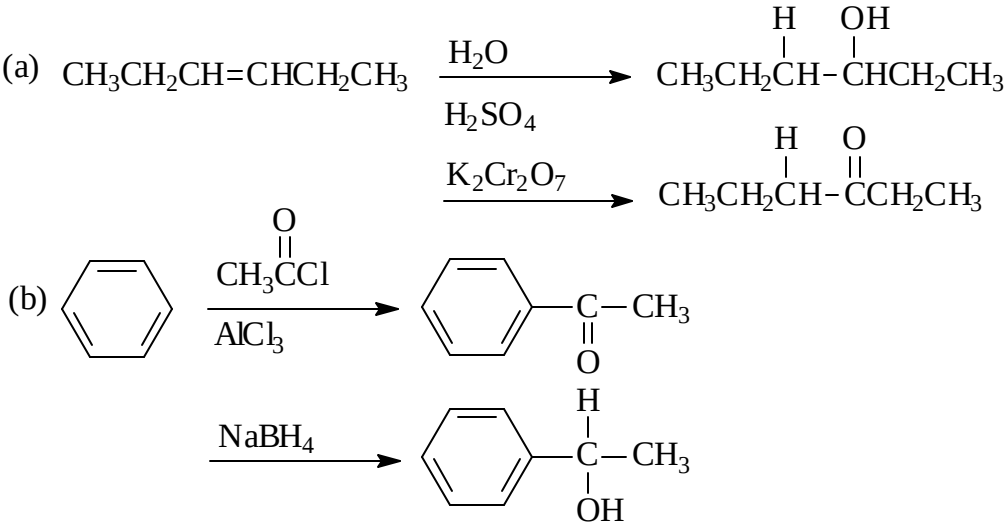
(b) The enol that initially forms here undergoes keto-enol tautomerism. Terminal alkynes give methyl ketones; they follow Markovnikov's rule.

(c) Potassium permanganate under basic conditions would hydroxylate the alkene to form a vicinal diol, but under acidic conditions it completely cleaves the double bond. The $=CH_2$ group would become carbon dioxide.

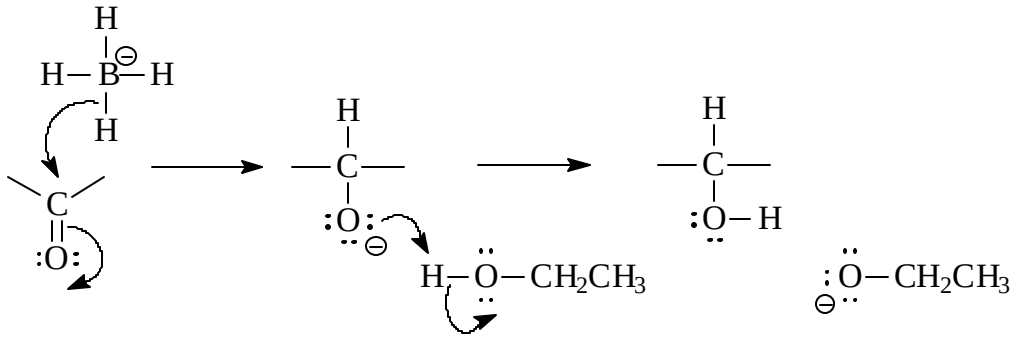
6. How would you carry out the following transformations? More than one step may be required.

(a) 3-hexene ⟶ 3-hexanone

(b) benzene ⟶ 1-phenylethanol



9. The reduction of a ketone to a secondary alcohol on treatment with $NaBH_4$ is a nucleophilic addition reaction in which the nucleophile hydride ion ($:H^-$) adds to the carbonyl group, and the alkoxide ion intermediate is then protonated. Show the mechanism of this reduction.

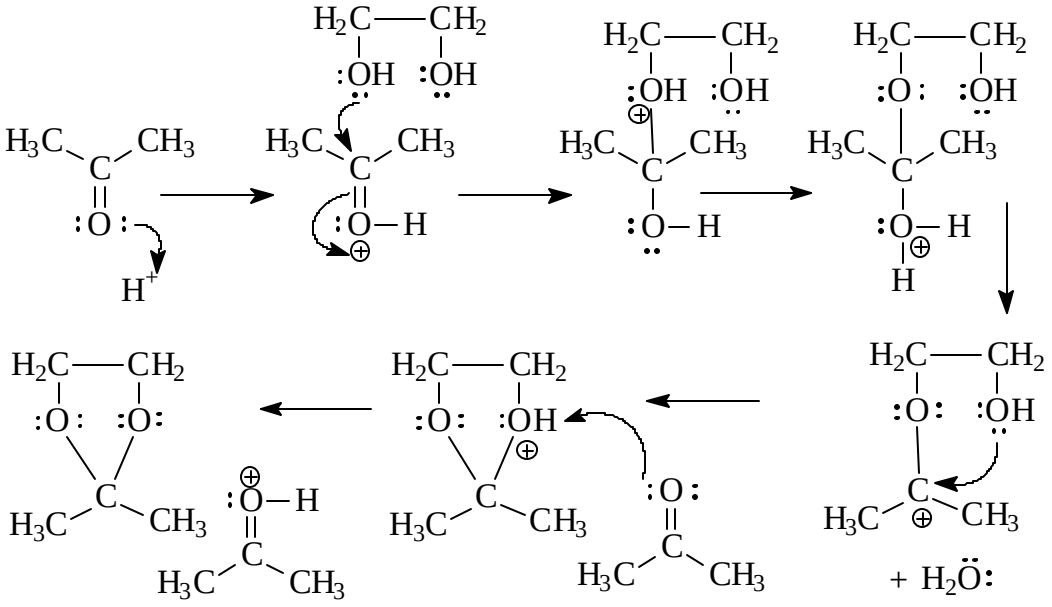


Ethanol is frequently used as a solvent in these reactions. In any event a proton must be supplied by something in the solution.

11. When dissolved in water, trichloroacetaldehyde (chloral, CCl_3CHO) exists primarily as the gem diol, chloral hydrate. Show the structure of chloral hydrate.

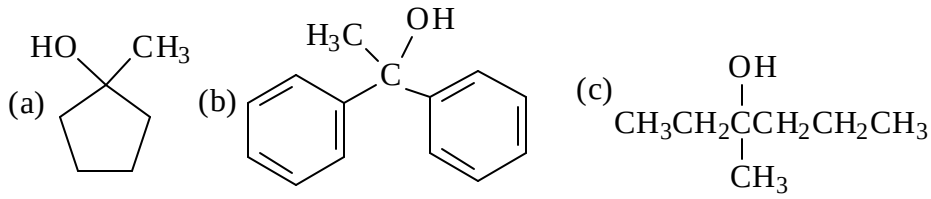
$CCl_3CH(OH)_2$

14. Show the mechanism of the acid-catalyzed formation of a *cyclic* acetal from ethylene glycol and acetone.



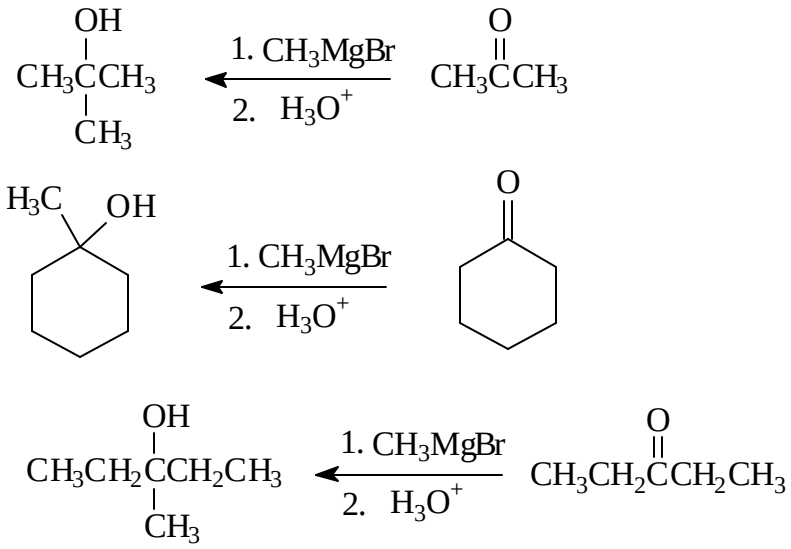
17. Show the products obtained from addition of CH_3MgBr to the following compounds.
(a) cyclopentanone, (b) benzophenone, (c) 3-hexanone

One assumes that McMurry means the alcohol one would get upon acidification after adding the Grignard reagent to the ketone.

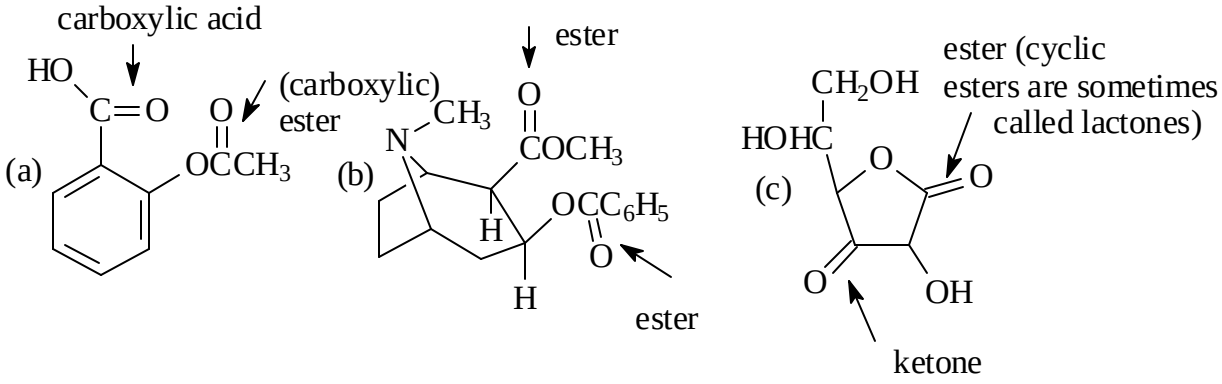


18. How might you use a Grignard addition reaction to prepare the following alcohols?
(a) 2-methyl-2-propanol, (b) 1-methylcyclohexanol, (c) 3-methyl-3-pentanol

To make a tertiary alcohol, we can react a ketone with the Grignard reagent.
To make a secondary alcohol we can react an aldehyde with the Grignard reagent.
To make a primary alcohol we can react formaldehyde with the Grignard reagent.

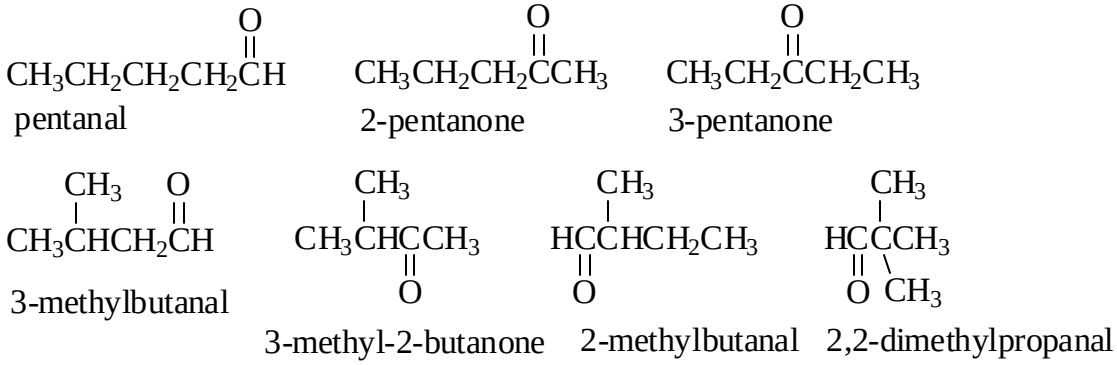


19. Identify the different kinds of carbonyl groups in the following molecules.



We usually call the esters of carboxylic acids just esters since this type of ester is so common. However, other acids – sulfonic acids, for example – can also form esters.

22. Draw and name the seven aldehydes and ketones with the formula $C_5H_{10}O$.



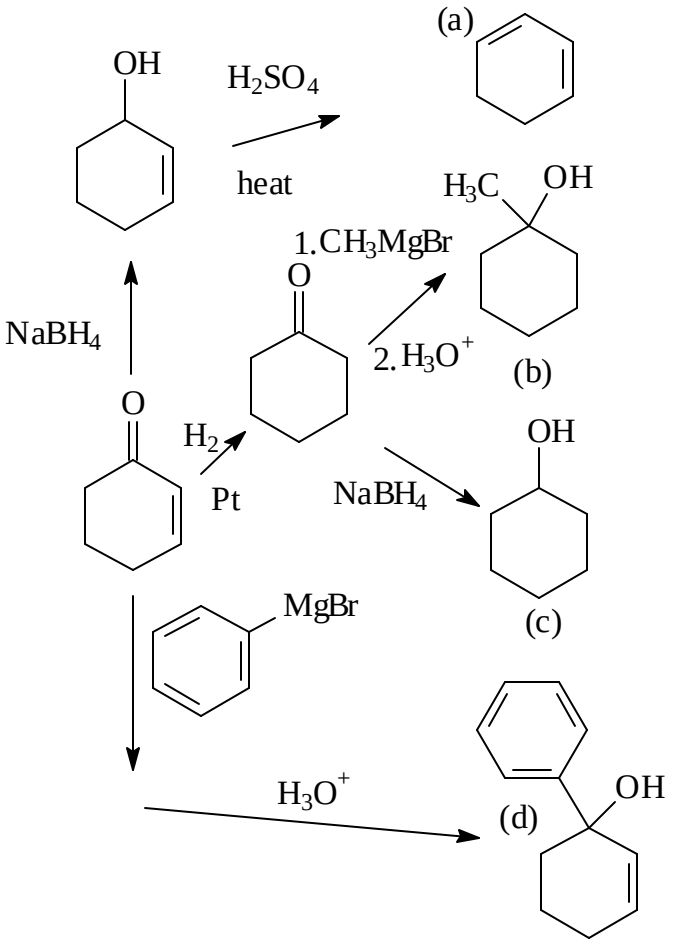
23. Which of the compounds you identified in question 22 are chiral?

Our approach here will be to look for stereocenters. If a molecule has one, and only one stereocenter, it will be chiral. If a molecule does not have any stereocenters it is unlikely to be chiral. [In this course it is very unlikely we will see chiral molecules that do not have stereocenters.] If a molecule has two or more stereocenters it will be chiral unless it is a meso structure.

2-Methylbutanal is the only molecule above that has has a stereocenter, and it has just one (C-2). It is chiral.

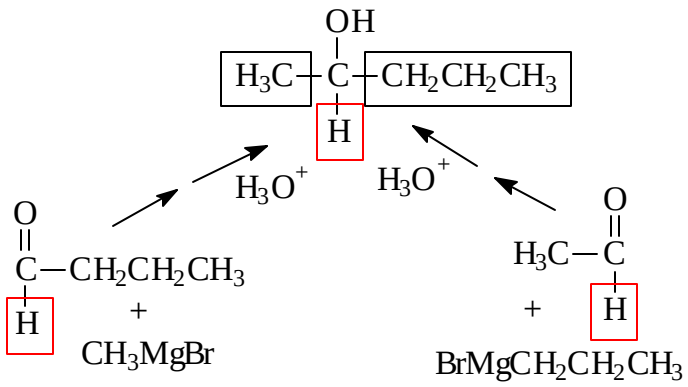
32. Starting from 2-cyclohexenone and any other reagents needed, how would you prepare the following substances? (More than one step may be required.)

(a) 1,3-cyclohexadiene, (b) 1-methylcyclohexanol, (c) cyclohexanol,
(d) 1-phenyl-2-cyclohexen-1-ol

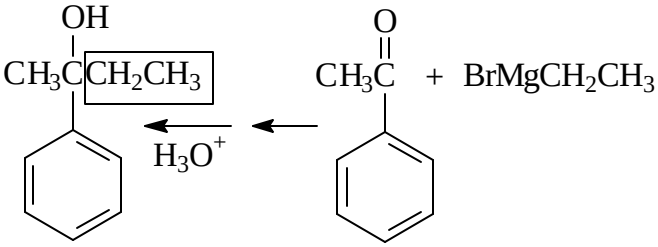


34. Use a Grignard reaction on an aldehyde or ketone to synthesize the following compounds.
(a) 2-pentanol, (b) 2-phenyl-2-butanol, (c) 1-ethylcyclohexanol, (d) diphenylmethanol

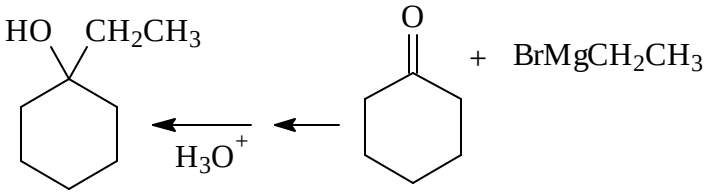
When undertaking a Grignard synthesis of an alcohol keep in mind that two of the groups (including all hydrogens) attached to the carbon bearing the OH group will come from the carbonyl compound and one of them (not a hydrogen) will come from the Grignard reagent.



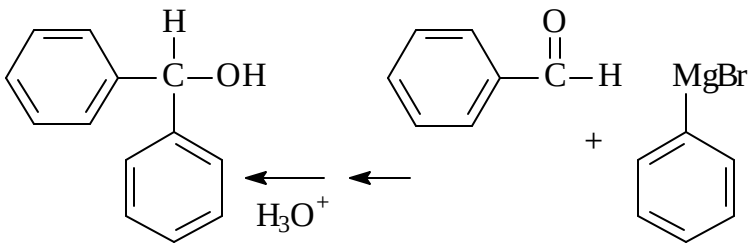
(a) Viewed one way, we are trying to make a secondary alcohol, so we employ an aldehyde and a Grignard reagent. The Grignard reagent can provide either of the boxed alkyl groups, while the aldehyde will provide the other. The hydrogen must be provided by the aldehyde – there is no HMgX that can react with a ketone to give a secondary alcohol.



(b) Since we are trying to make a tertiary alcohol, we will employ a ketone and a Grignard reagent. The ketone will provide two of the groups attached to the carbon holding the OH (as well as that carbon itself) and the Grignard reagent will provide the third group. In this case I have arranged for the Grignard to provide the boxed ethyl group and the acetophenone will provide the methyl and phenyl groups. Two other combinations could have been used. What are they?



(c) We are, again, trying to make a tertiary alcohol, so we will use a ketone and the Grignard. The carbon holding the OH and two of the groups attached to it must come from the ketone and the third group must come from the Grignard. The situation here is made a little interesting by virtue of the ring, since the ring constitutes two of the groups attached to the OH bearing carbon, but is “one piece” and cannot come from two different sources. Consequently, the only choice for the ketone is cyclohexanone and this forces the Grignard to be ethylmagnesium halide.



(d) A secondary alcohol requires an aldehyde and Grignard reagent. There is no choice here since two of the groups are phenyls. The aldehyde must be benzaldehyde and the Grignard must provide another phenyl group.