

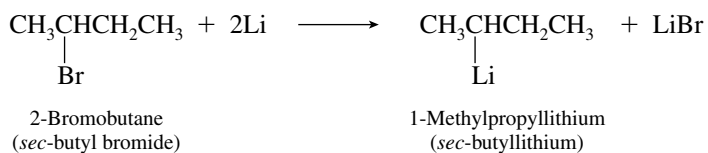
CHAPTER 14

ORGANOMETALLIC COMPOUNDS

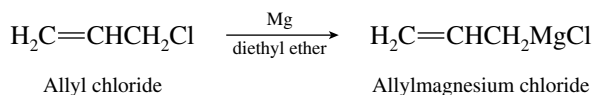
SOLUTIONS TO TEXT PROBLEMS

14.1 (b) Magnesium bears a cyclohexyl substituent and a chlorine. Chlorine is named as an anion. The compound is cyclohexylmagnesium chloride.

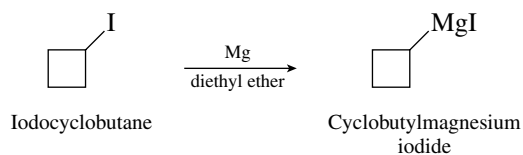
14.2 (b) The alkyl bromide precursor to *sec*-butyllithium must be *sec*-butyl bromide.



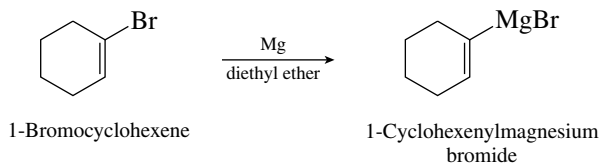
14.3 (b) Allyl chloride is converted to allylmagnesium chloride on reaction with magnesium.



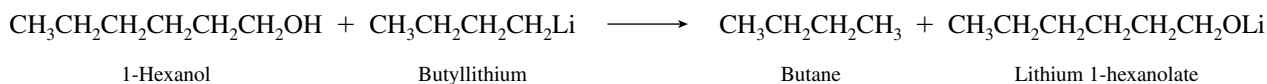
(c) The carbon–iodine bond of iodocyclobutane is replaced by a carbon–magnesium bond in the Grignard reagent.



- (d) Bromine is attached to an sp^2 -hybridized carbon in 1-bromocyclohexene. The product of its reaction with magnesium has a carbon–magnesium bond in place of the carbon–bromine bond.



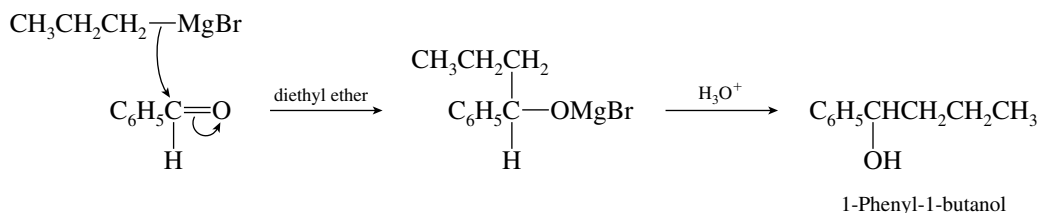
- 14.4 (b) 1-Hexanol will protonate butyllithium because its hydroxyl group is a proton donor only slightly less acidic than water. This proton-transfer reaction could be used to prepare lithium 1-hexanolate.



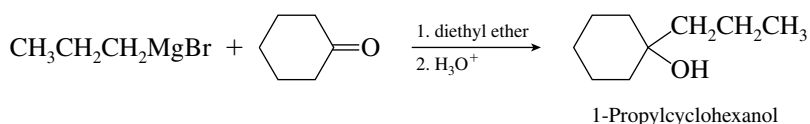
- (c) The proton donor here is benzenethiol.



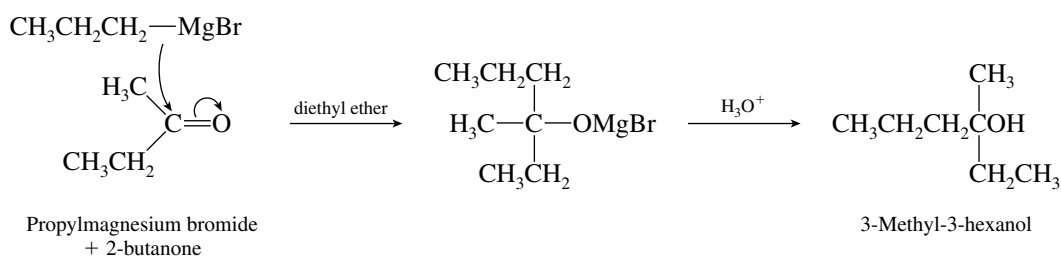
- 14.5 (b) Propylmagnesium bromide reacts with benzaldehyde by addition to the carbonyl group.



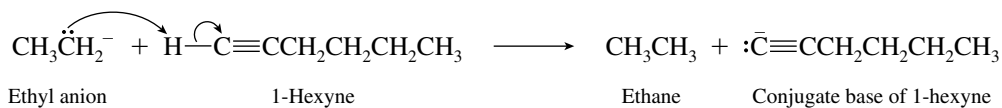
- (c) Tertiary alcohols result from the reaction of Grignard reagents and ketones.



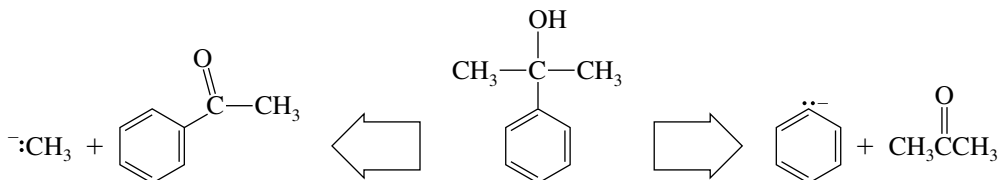
- (d) The starting material is a ketone and so reacts with a Grignard reagent to give a tertiary alcohol.



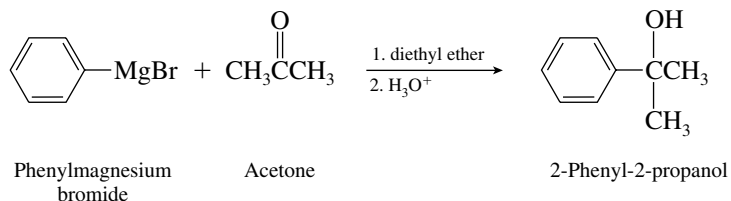
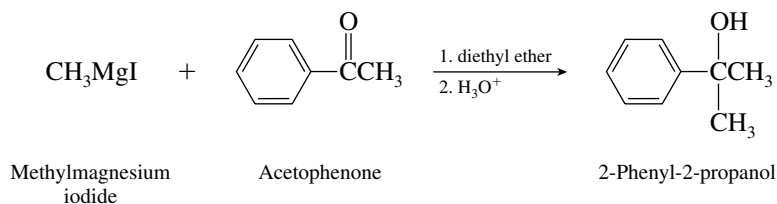
- 14.6 Ethyl anion reacts as a Brønsted base to remove a proton from the alkyne. The proton at C-1 is removed because it is the most acidic, having a pK_a of approximately 25.



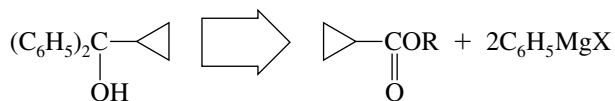
- 14.7 (b) The target alcohol is tertiary and so is prepared by addition of a Grignard reagent to a ketone. The retrosynthetic transformations are:



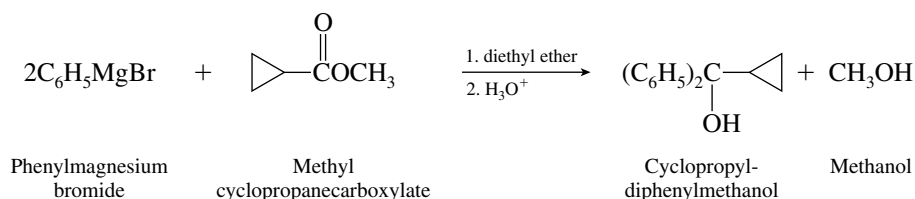
Because two of the alkyl groups on the hydroxyl-bearing carbon are the same (methyl), only two, not three, different ketones are possible starting materials:



- 14.8 (b) Recall that the two identical groups bonded to the hydroxyl-bearing carbon of the alcohol arose from the Grignard reagent. That leads to the following retrosynthetic analysis:

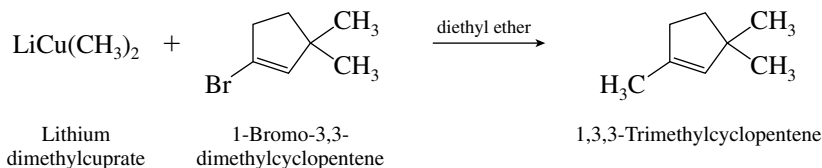


Thus, the two phenyl substituents arise by addition of a phenyl Grignard reagent to an ester of cyclopropanecarboxylic acid.

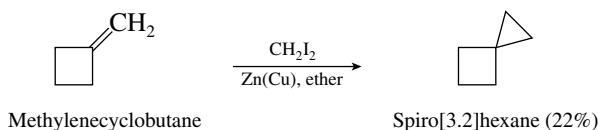


- 14.9 (b) Of the three methyl groups of 1,3,3-trimethylcyclopentene, only the one connected to the double bond can be attached by way of an organocuprate reagent. Attachment of either of

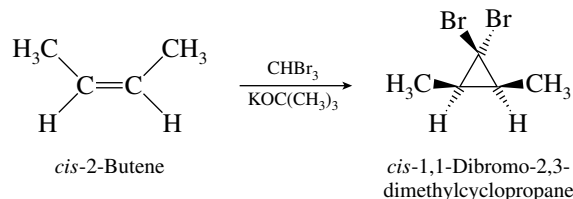
the other methyls would involve a tertiary carbon, a process that does not occur very efficiently.



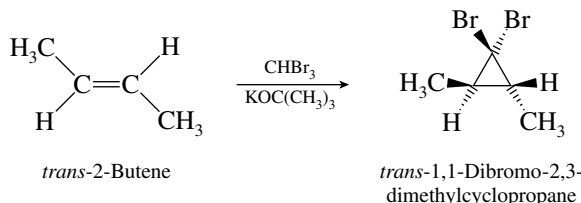
- 14.10 (b) Methyleneecyclobutane is the appropriate precursor to the spirohexane shown.



- 14.11 Syn addition of dibromocarbene to *cis*-2-butene yields a cyclopropane derivative in which the methyl groups are *cis*.



Conversely, the methyl groups in the cyclopropane derivative of *trans*-2-butene are *trans* to one another.



- 14.12 Iron has an atomic number of 26 and an electron configuration of $[\text{Ar}]4s^23d^6$. Thus, it has 8 valence electrons and requires 10 more to satisfy the 18-electron rule. Five CO ligands, each providing two electrons, are therefore needed. The compound is $\text{Fe}(\text{CO})_5$.

- 14.13 (a) Cyclopentyllithium is

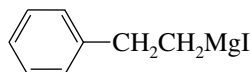


It has a carbon–lithium bond. It satisfies the requirement for classification as an organometallic compound.

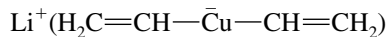
- (b) Ethoxymagnesium chloride does not have a carbon–metal bond. It is not an organometallic compound.



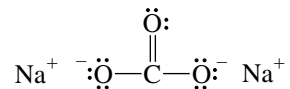
- (c) 2-Phenylethylmagnesium iodide is an example of a Grignard reagent. It is an organometallic compound.



- (d) Lithium divinylcuprate has two vinyl groups bonded to copper. It is an organometallic compound.

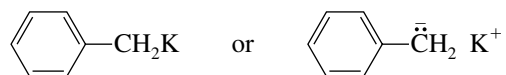


- (e) Sodium carbonate, Na_2CO_3 can be represented by the Lewis structure.



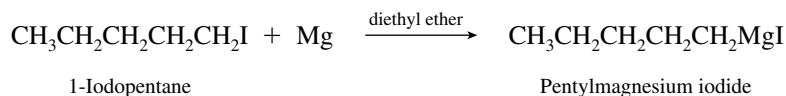
There is no carbon–metal bond, and sodium carbonate is not an organometallic compound.

- (f) Benzylpotassium is represented as

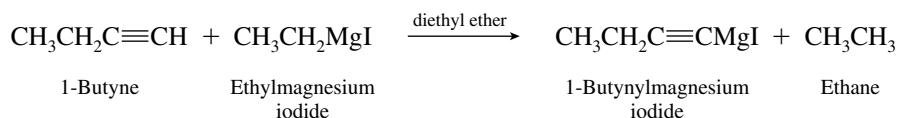


It has a carbon–potassium bond and thus is an organometallic compound.

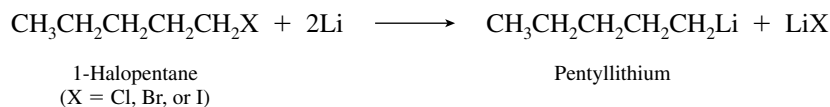
- 14.14** The two alkyl groups attached to aluminum in $[(\text{CH}_3)_2\text{CHCH}_2]_2\text{AlH}$ are isobutyl groups. The hydrogen bonded to aluminum is named in a separate word as hydride. Thus, “dibal” is a shortened form of the systematic name **diisobutylaluminum hydride**.
- 14.15** (a) Grignard reagents such as pentylmagnesium iodide are prepared by reaction of magnesium with the corresponding alkyl halide.



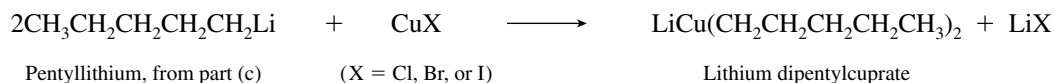
- (b) Acetylenic Grignard reagents are normally prepared by reaction of a terminal alkyne with a readily available Grignard reagent such as an ethylmagnesium halide. The reaction that takes place is an acid–base reaction in which the terminal alkyne acts as a proton donor.



- (c) Alkylolithiums are formed by reaction of lithium with an alkyl halide.

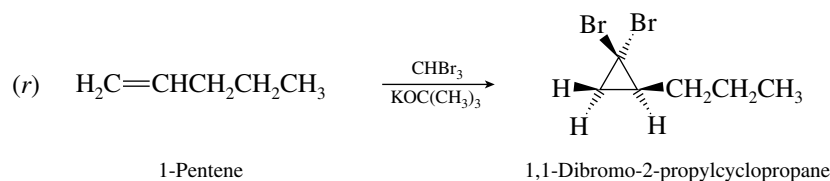
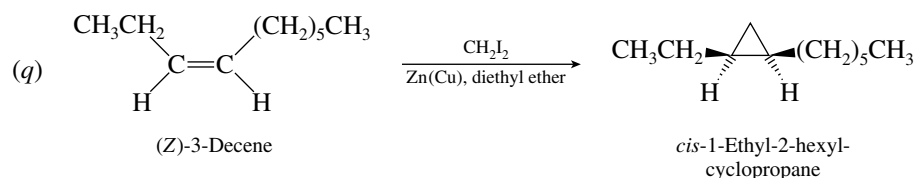
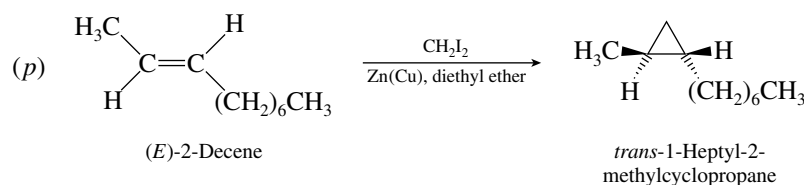
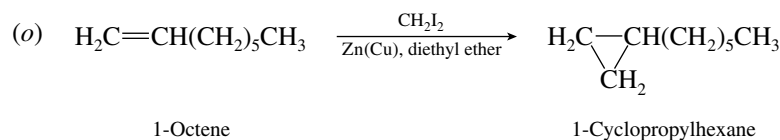
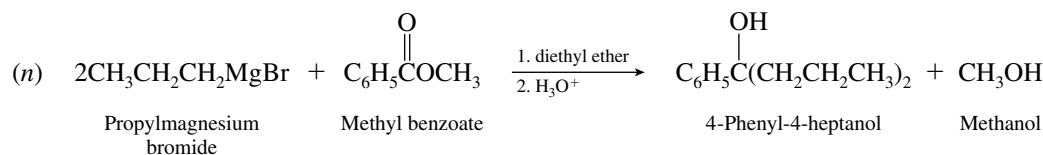
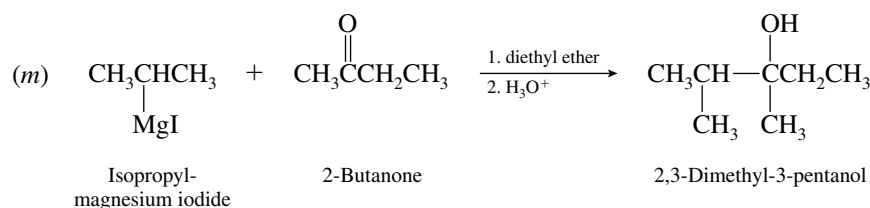
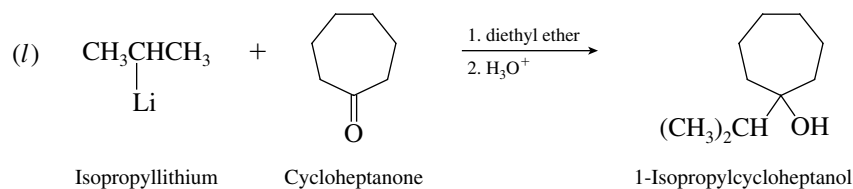
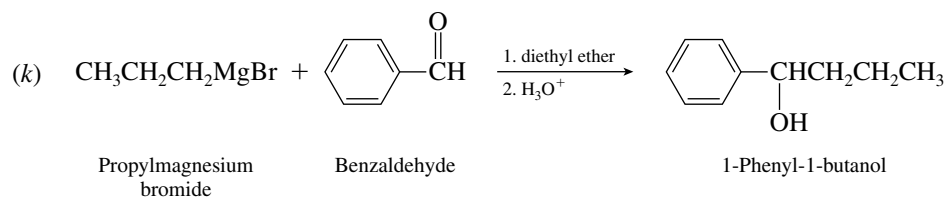


- (d) Lithium dialkylcuprates arise by the reaction of an alkylolithium with a Cu(I) salt.



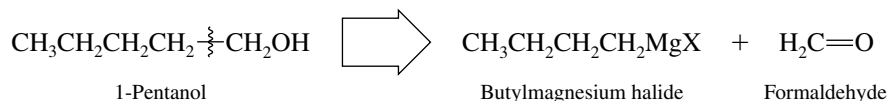
- 14.16** The polarity of a covalent bond increases with an increase in the electronegativity difference between the connected atoms. Carbon has an electronegativity of 2.5 (Table 14.1). Metals are less electronegative than carbon. When comparing two metals, the less electronegative one therefore has the more polar bond to carbon.

- (a) Table 14.1 gives the electronegativity of lithium as 1.0, whereas that for aluminum is 1.5. The carbon–lithium bond in $\text{CH}_3\text{CH}_2\text{Li}$ is more polar than the carbon–aluminum bond in $(\text{CH}_3\text{CH}_2)_3\text{Al}$.

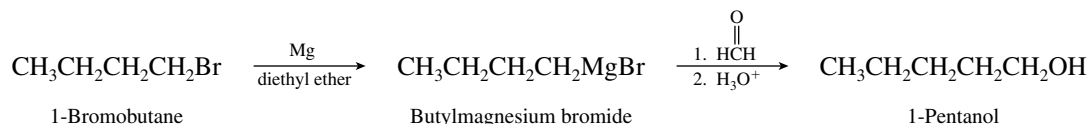


14.18 In the solutions to this problem, the Grignard reagent butylmagnesium bromide is used. In each case the use of butyllithium would be equally satisfactory.

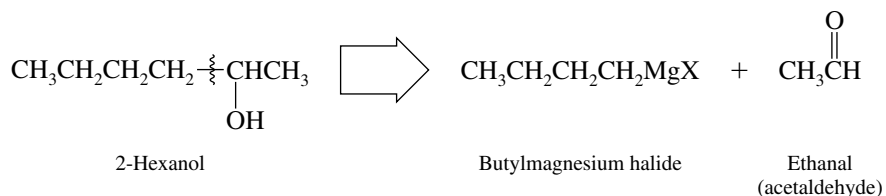
- (a) 1-Pentanol is a primary alcohol having one more carbon atom than 1-bromobutane. Retrosynthetic analysis suggests the reaction of a Grignard reagent with formaldehyde.



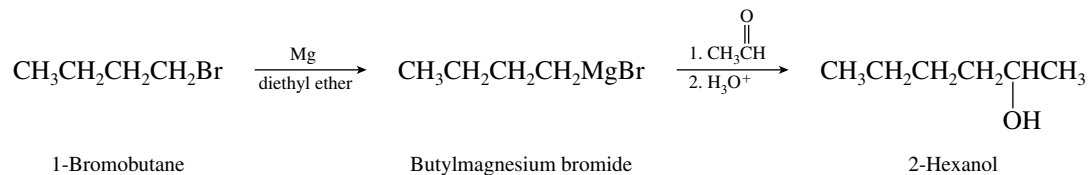
An appropriate synthetic scheme is



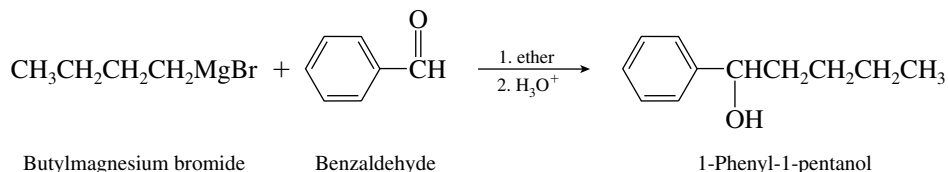
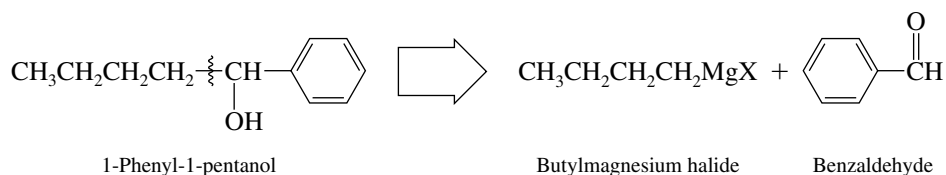
- (b) 2-Hexanol is a secondary alcohol having two more carbon atoms than 1-bromobutane. As revealed by retrosynthetic analysis, it may be prepared by reaction of ethanal (acetaldehyde) with butylmagnesium bromide.



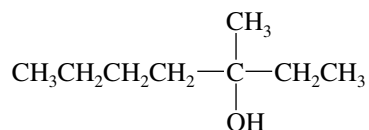
The correct reaction sequence is



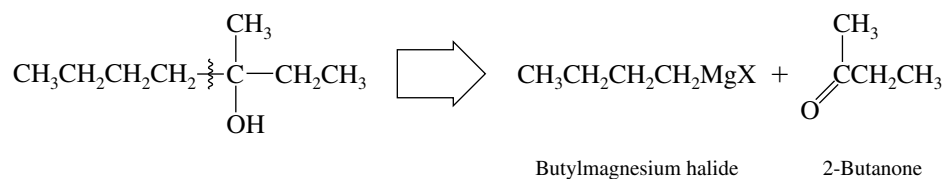
- (c) 1-Phenyl-1-pentanol is a secondary alcohol. Disconnection suggests that it can be prepared from butylmagnesium bromide and an aldehyde; benzaldehyde is the appropriate aldehyde.



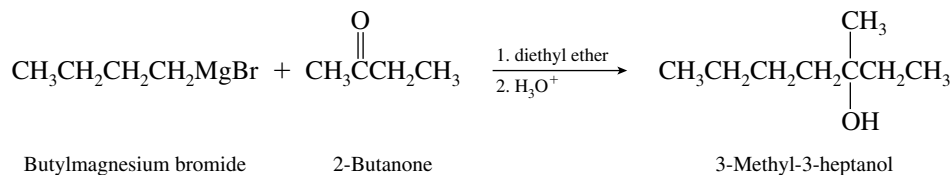
- (d) The target molecule 3-methyl-3-heptanol has the structure



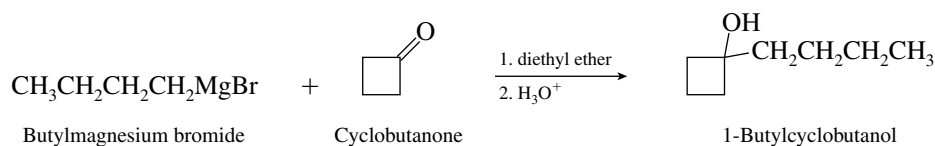
By retrosynthetically disconnecting the butyl group from the carbon that bears the hydroxyl substituent, we see that the appropriate starting ketone is 2-butanone.



Therefore

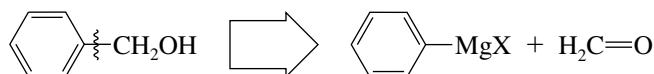


(e) 1-Butylcyclobutanol is a tertiary alcohol. The appropriate ketone is cyclobutanone.

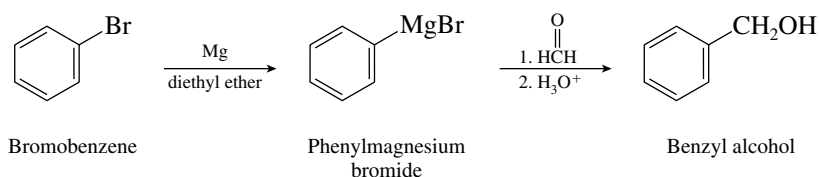


14.19 In each part of this problem in which there is a change in the carbon skeleton, disconnect the phenyl group of the product to reveal the aldehyde or ketone precursor that reacts with the Grignard reagent derived from bromobenzene. Recall that reaction of a Grignard reagent with formaldehyde ($\text{H}_2\text{C}=\text{O}$) yields a primary alcohol, reaction with an aldehyde (other than formaldehyde) yields a secondary alcohol, and reaction with a ketone yields a tertiary alcohol.

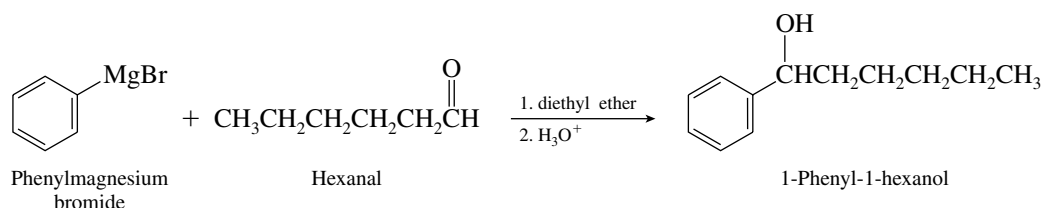
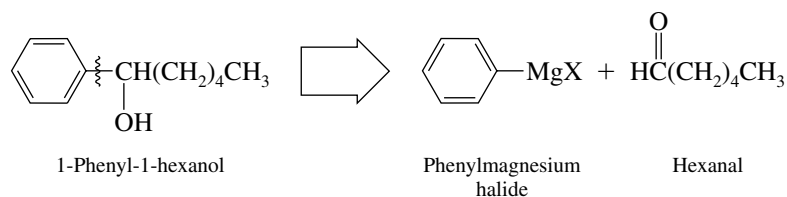
(a) Conversion of bromobenzene to benzyl alcohol requires formation of the corresponding Grignard reagent and its reaction with formaldehyde. Retrosynthetically, this can be seen as



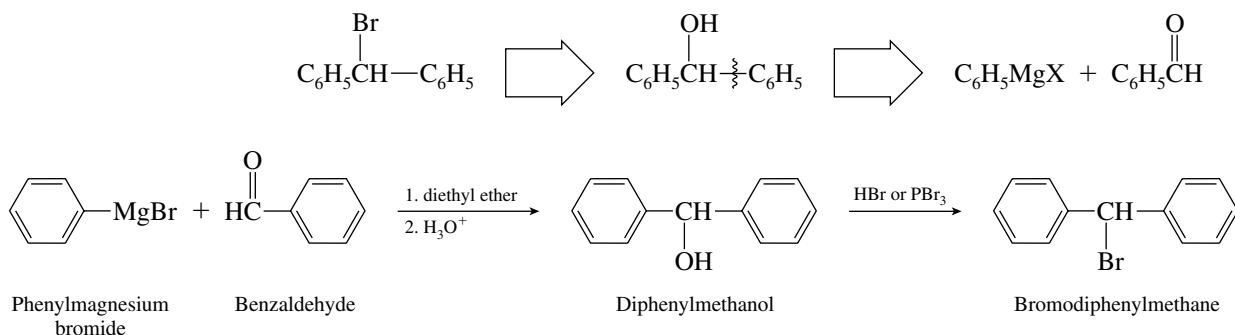
Therefore,



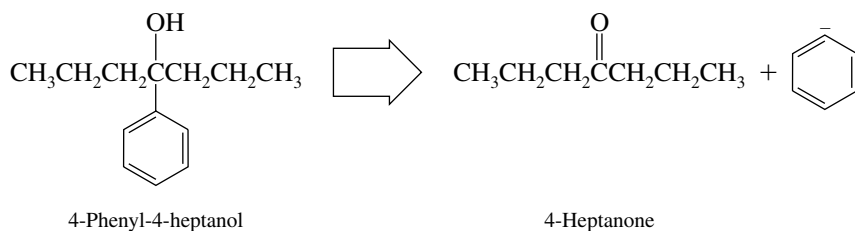
(b) The product is a secondary alcohol and is formed by reaction of phenylmagnesium bromide with hexanal.



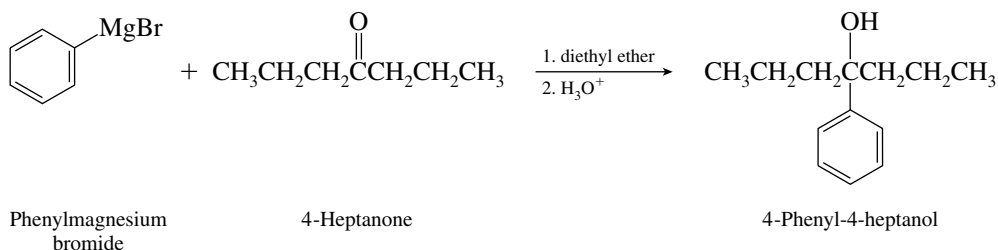
- (c) The desired product is a secondary alkyl **bromide**. A reasonable synthesis would be to first prepare the analogous secondary alcohol by reaction of phenylmagnesium bromide with benzaldehyde, followed by a conversion of the alcohol to the bromide. Retrosynthetically this can be seen as



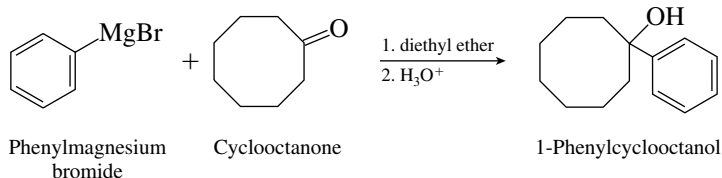
- (d) The target molecule is a tertiary alcohol, which requires that phenylmagnesium bromide react with a ketone. By mentally disconnecting the phenyl group from the carbon that bears the hydroxyl group, we see that the appropriate ketone is 4-heptanone.



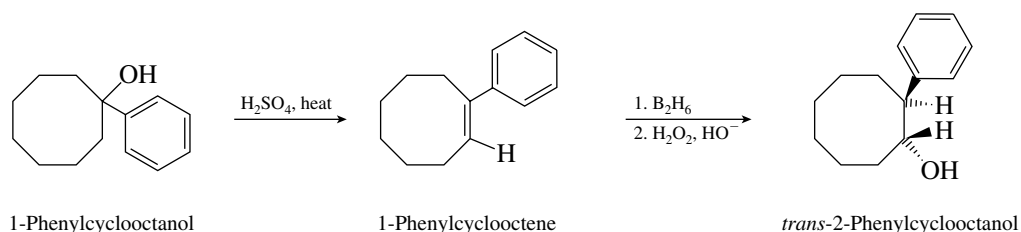
The synthesis is therefore



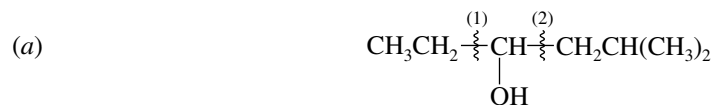
- (e) Reaction of phenylmagnesium bromide with cyclooctanone will give the desired tertiary alcohol.



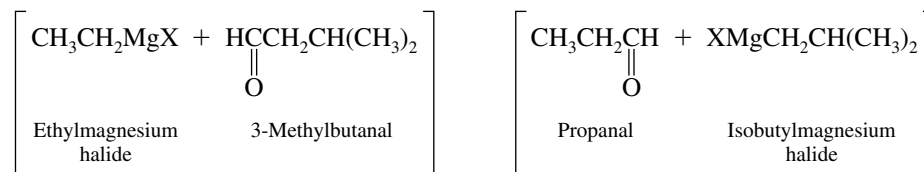
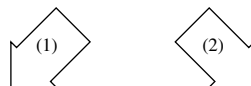
- (f) The 1-phenylcyclooctanol prepared in part (e) of this problem can be subjected to acid-catalyzed dehydration to give 1-phenylcyclooctene. Hydroboration-oxidation of 1-phenylcyclooctene gives *trans*-2-phenylcyclooctanol.



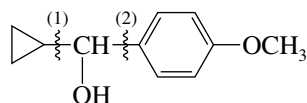
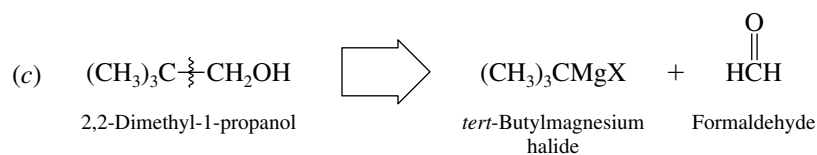
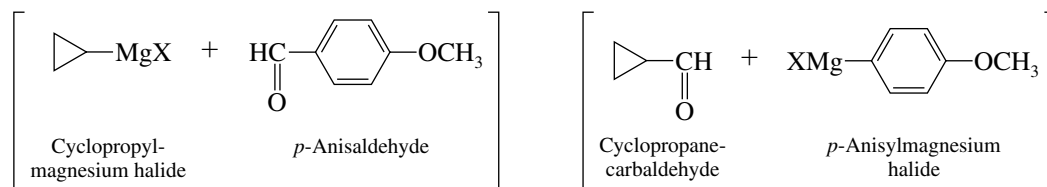
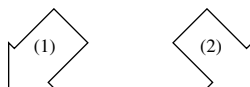
- 14.20 In these problems the principles of retrosynthetic analysis are applied. The alkyl groups attached to the carbon that bears the hydroxyl group are mentally disconnected to reveal the Grignard reagent and carbonyl compound.



5-Methyl-3-hexanol



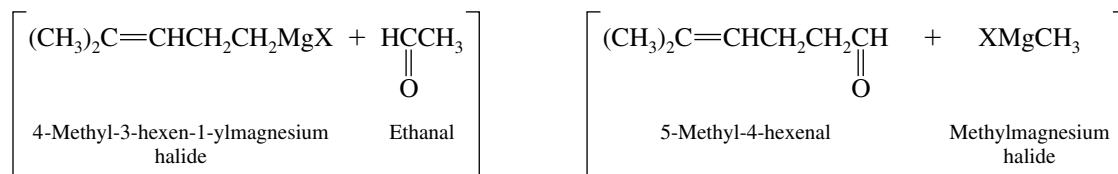
(b)

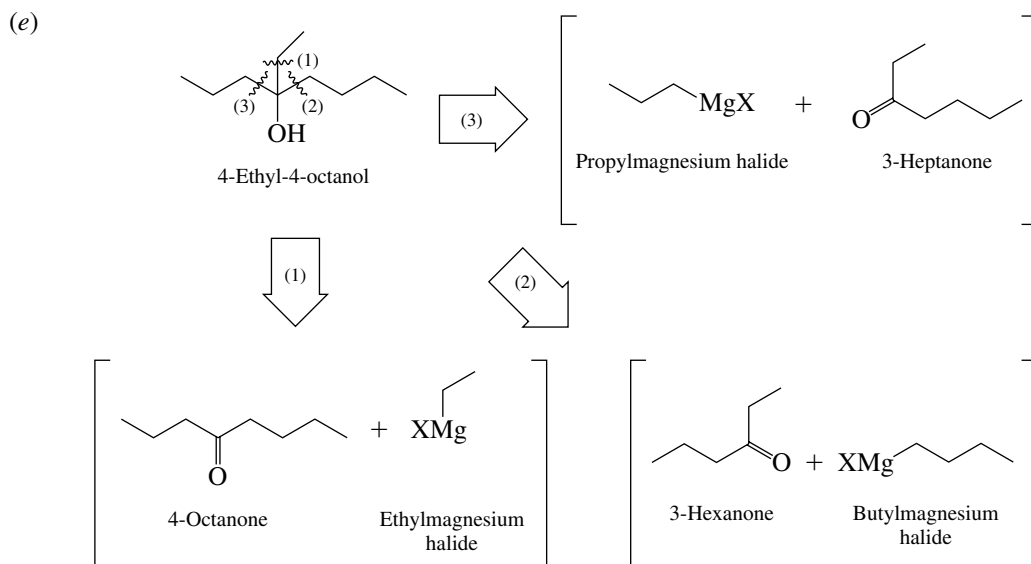
1-Cyclopropyl-1-(*p*-anisyl)methanol

(d)

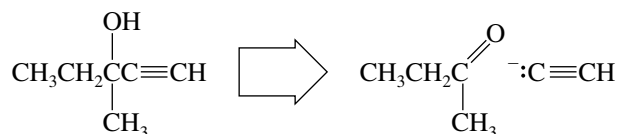


6-Methyl-5-hepten-2-ol

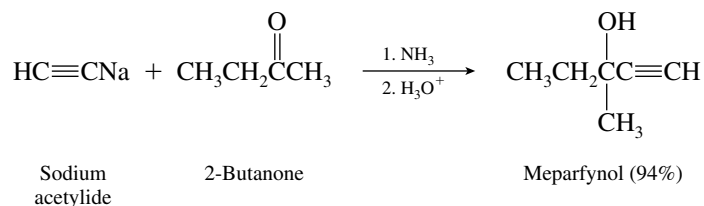




- 14.21 (a) Meparfynol is a tertiary alcohol and so can be prepared by addition of a carbanionic species to a ketone. Use the same reasoning that applies to the synthesis of alcohols from Grignard reagents. On mentally disconnecting one of the bonds to the carbon bearing the hydroxyl group

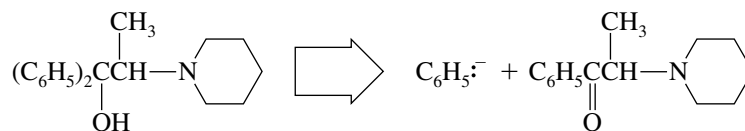


we see that the addition of acetylide ion to 2-butanone will provide the target molecule.

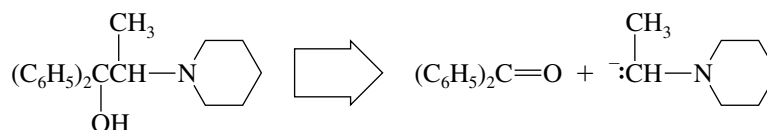


The alternative, reaction of a Grignard reagent with an alkynyl ketone, is not acceptable in this case. The acidic terminal alkyne C—H would transfer a proton to the Grignard reagent.

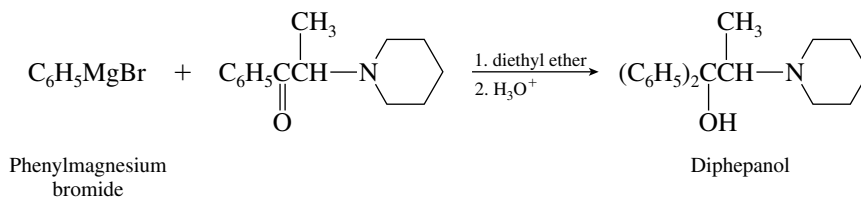
- (b) Diphepanol is a tertiary alcohol and so may be prepared by reaction of a Grignard or organolithium reagent with a ketone. Retrosynthetically, two possibilities seem reasonable:



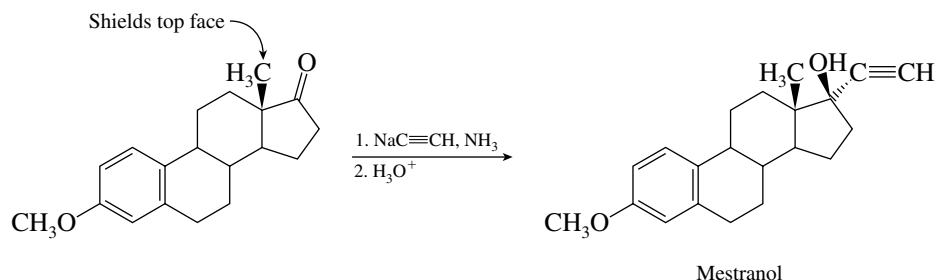
and



In principle either strategy is acceptable; in practice the one involving phenylmagnesium bromide is used.

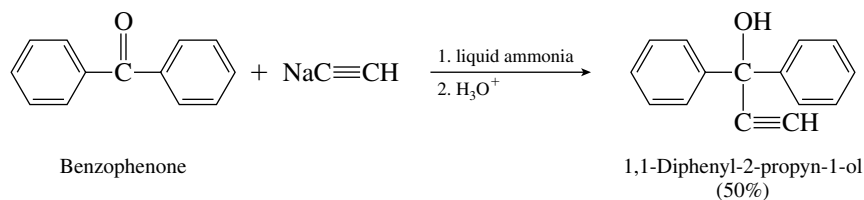


- (c) A reasonable last step in the synthesis of mestranol is the addition of sodium acetylide to the ketone shown.

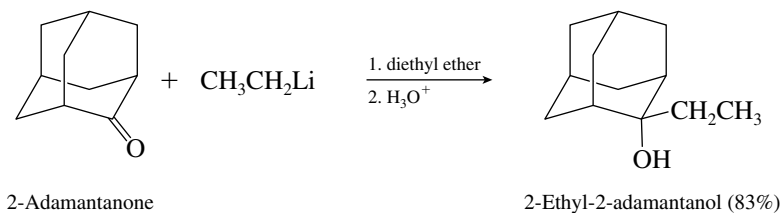


Acetylide anion adds to the carbonyl from the less sterically hindered side. The methyl group shields the top face of the carbonyl, and so acetylide adds from the bottom.

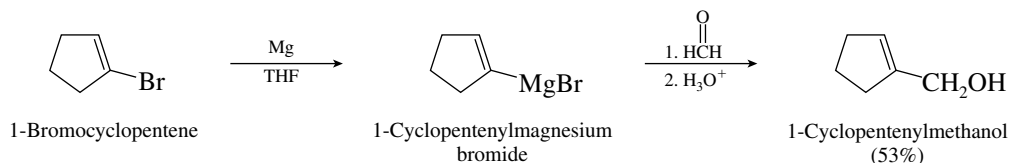
- 14.22 (a) Sodium acetylide adds to ketones to give tertiary alcohols.



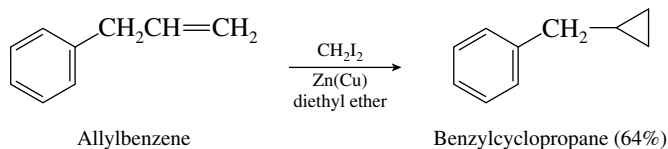
- (b) The substrate is a ketone, which reacts with ethyllithium to yield a tertiary alcohol.



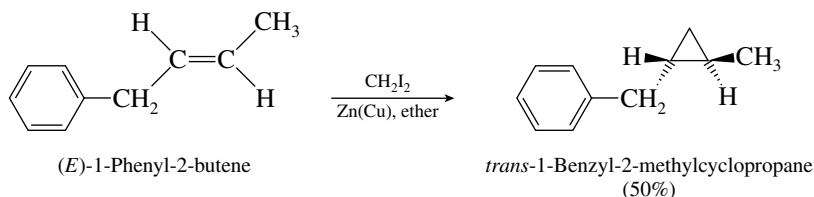
- (c) The first step is conversion of bromocyclopentene to the corresponding Grignard reagent, which then reacts with formaldehyde to give a primary alcohol.



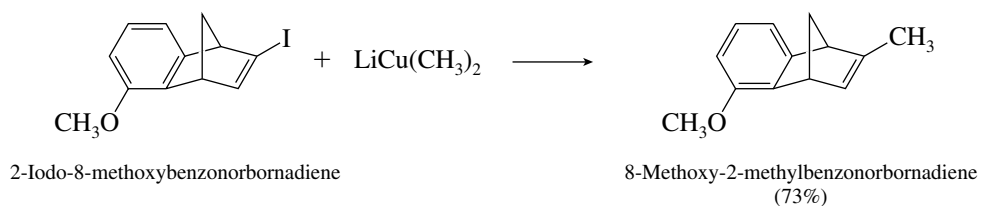
- (d) The reaction is one in which an alkene is converted to a cyclopropane through use of the Simmons–Smith reagent, iodomethylzinc iodide.



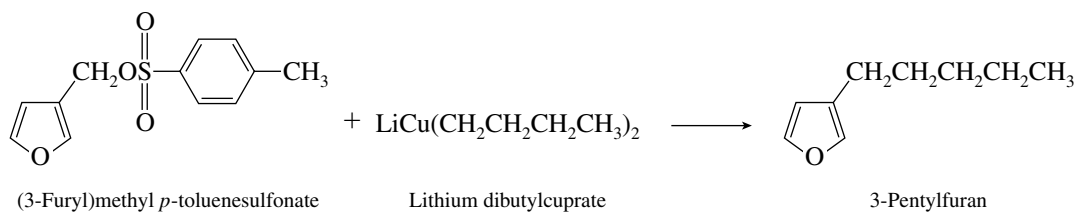
- (e) Methylene transfer using the Simmons–Smith reagent is stereospecific. The trans arrangement of substituents in the alkene is carried over to the cyclopropane product.



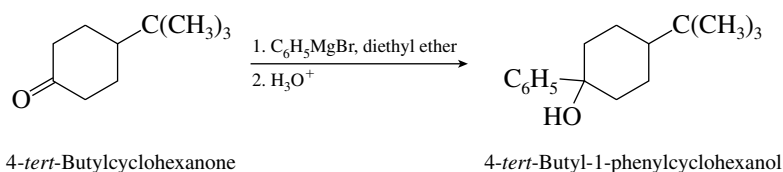
- (f) Lithium dimethylcuprate transfers a methyl group, which substitutes for iodine on the iodoalkene. Even halogens on sp^2 -hybridized carbon are reactive in substitution reactions with lithium dialkylcuprates.



- (g) The starting material is a *p*-toluenesulfonate ester. *p*-Toluenesulfonates are similar to alkyl halides in their reactivity. Substitution occurs; a butyl group from lithium dibutylcuprate replaces *p*-toluenesulfonate.

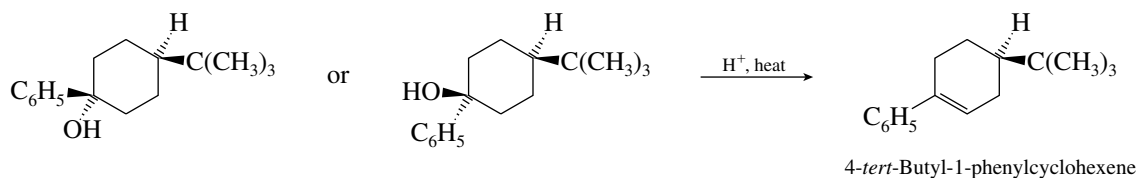


14.23 Phenylmagnesium bromide reacts with 4-*tert*-butylcyclohexanone as shown.

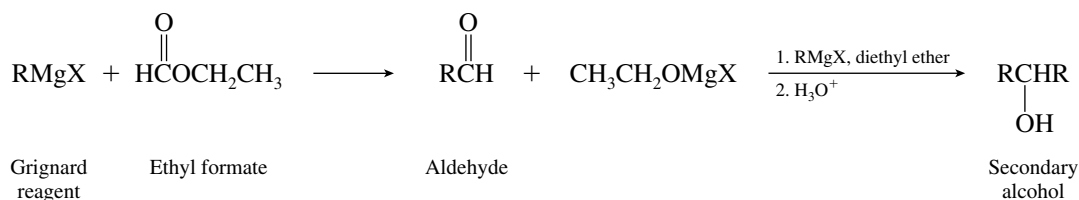


The phenyl substituent can be introduced either *cis* or *trans* to the *tert*-butyl group. The two alcohols are therefore stereoisomers (diastereomers).

Dehydration of either alcohol yields 4-*tert*-butyl-1-phenylcyclohexene.

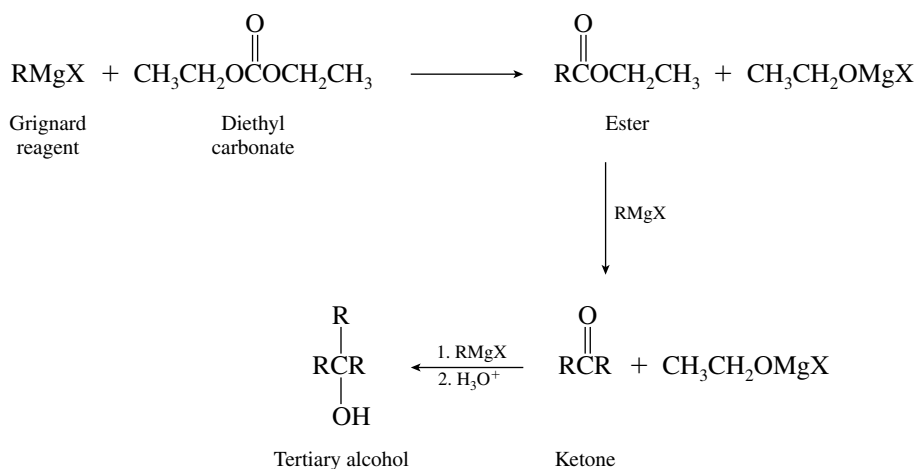


- 14.24 (a) By working through the sequence of reactions that occur when ethyl formate reacts with a Grignard reagent, we can see that this combination leads to **secondary alcohols**.



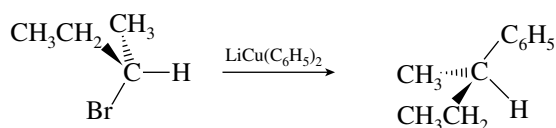
This is simply because the substituent on the carbonyl carbon of the ester, in this case a hydrogen, is carried through and becomes a substituent on the hydroxyl-bearing carbon of the alcohol.

- (b) Diethyl carbonate has the potential to react with 3 moles of a Grignard reagent.



The tertiary alcohols that are formed by the reaction of diethyl carbonate with Grignard reagents have three identical R groups attached to the carbon that bears the hydroxyl substituent.

- 14.25 If we use the 2-bromobutane given, along with the information that the reaction occurs with net inversion of configuration, the stereochemical course of the reaction may be written as

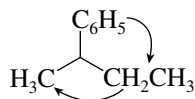


The phenyl group becomes bonded to carbon from the opposite side of the leaving group.

Applying the Cahn–Ingold–Prelog notational system described in Section 7.6 to the product, the order of decreasing precedence is

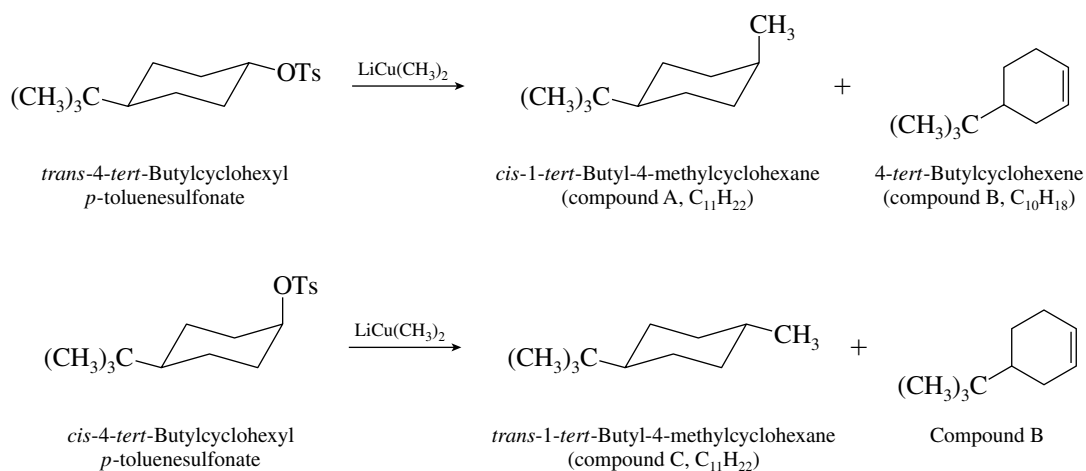


Orienting the molecule so that the lowest ranked substituent (H) is away from us, we see that the order of decreasing precedence is clockwise.



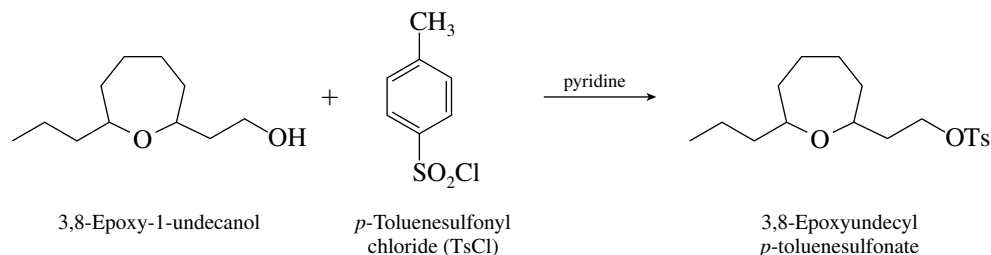
The absolute configuration is *R*.

- 14.26** The substrates are secondary alkyl *p*-toluenesulfonates, and so we expect elimination to compete with substitution. Compound B is formed in both reactions and has the molecular formula of 4-*tert*-butylcyclohexene. Because the two *p*-toluenesulfonates are diastereomers, it is likely that compounds A and C, especially since they have the same molecular formula, are also diastereomers. Assuming that the substitution reactions proceed with inversion of configuration, we conclude that the products are as shown.

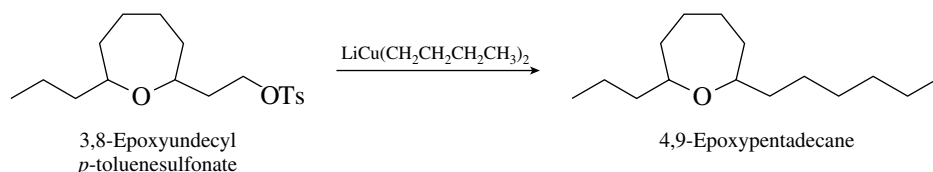


Inversion of configuration is borne out by the fact given in the problem that compound C is more stable than compound A. Both substituents are equatorial in C; the methyl group is axial in A.

- 14.27** We are told in the statement of the problem that the first step is conversion of the alcohol to the corresponding *p*-toluenesulfonate. This step is carried out as follows:

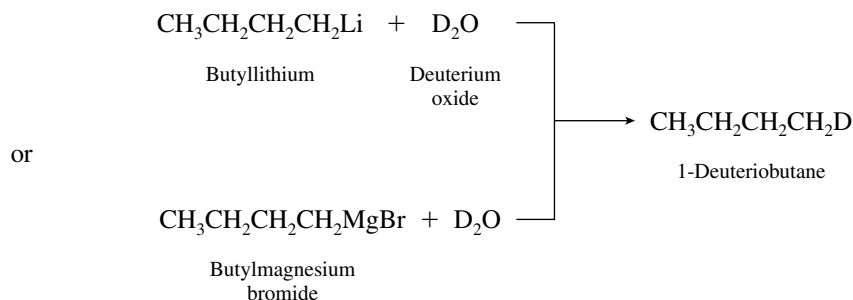


Alkyl *p*-toluenesulfonates react with lithium dialkylcuprates in the same way that alkyl halides do. Treatment of the preceding *p*-toluenesulfonate with lithium dibutylcuprate gives the desired compound.

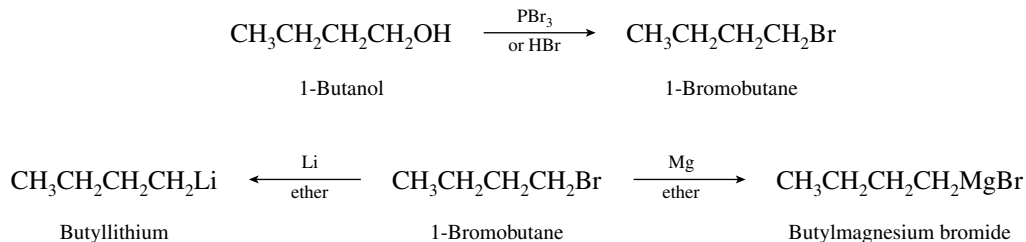


As actually performed, a 91% yield of the desired product was obtained in the reaction of the *p*-toluenesulfonate with lithium dibutylcuprate.

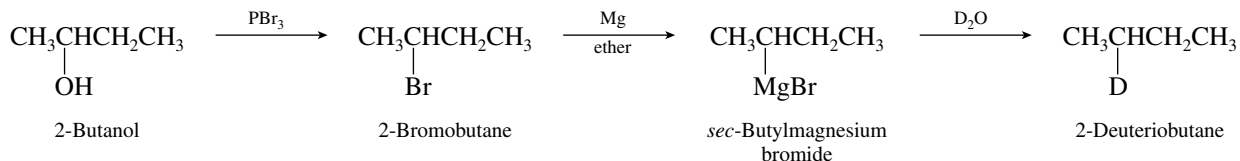
- 14.28 (a) The desired 1-deuteriobutane can be obtained by reaction of D_2O with butyllithium or butylmagnesium bromide.



Preparation of the organometallic compounds requires an alkyl bromide, which is synthesized from the corresponding alcohol.

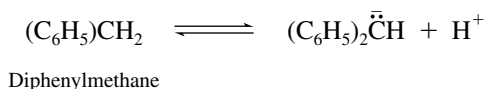


- (b) In a sequence identical to that of part (a) in design but using 2-butanol as the starting material, 2-deuteriobutane may be prepared.

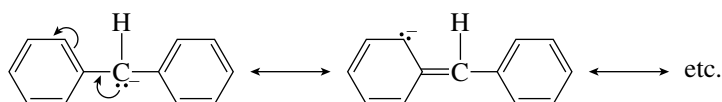


An analogous procedure involving *sec*-butyllithium in place of the Grignard reagent can be used.

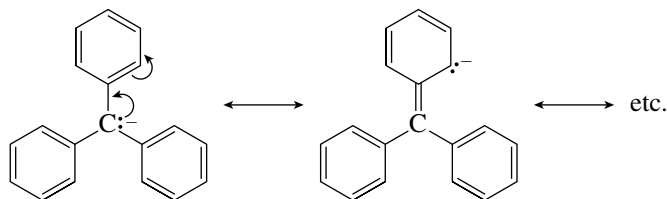
- 14.29 All the protons in benzene are equivalent. In diphenylmethane and in triphenylmethane, protons are attached either to the sp^2 -hybridized carbons of the ring or to the sp^3 -hybridized carbon between the rings. The large difference in acidity between diphenylmethane and benzene suggests that it is not a ring proton that is lost on ionization in diphenylmethane but rather a proton from the methylene group.



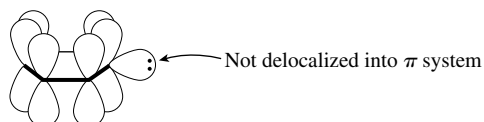
The anion produced is stabilized by resonance. It is a **benzylic** carbanion.



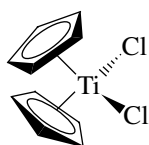
Both rings are involved in delocalizing the negative charge. The anion from triphenylmethane is stabilized by resonance involving all three rings.



Delocalization of the negative charge by resonance is not possible in the anion of benzene. The pair of unshared electrons in phenyl anion is in an sp^2 hybrid orbital that does not interact with the π system.

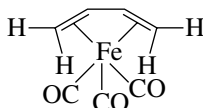


- 14.30** The titanium-containing compound is a metallocene. (It has cyclopentadienyl rings as ligands.) With an atomic number of 22, titanium has an electron configuration of $[\text{Ar}]4s^23d^2$. As the following accounting shows, this titanium complex is 2 electrons short of satisfying the 18-electron rule.



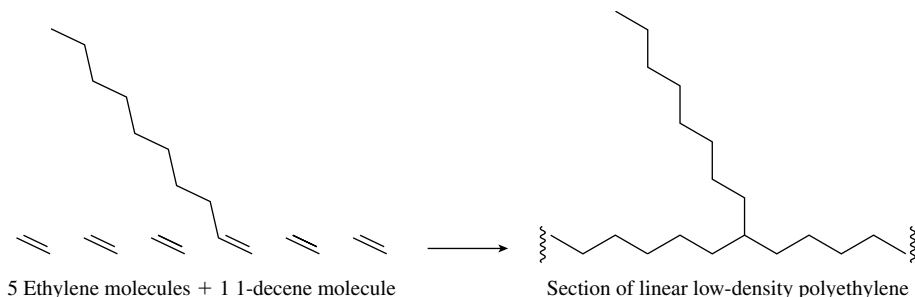
Ti:	4 electrons
Two cyclopentadienyl rings:	10 electrons
Two chlorine atoms:	2 electrons
Total:	16 electrons

1,3-Butadiene(tricarbonyl)iron satisfies the 18-electron rule. The electron configuration of iron is $[\text{Ar}]4s^23d^6$.



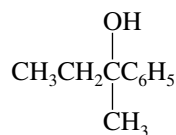
Fe:	8 electrons
1,3-Butadiene ligand:	4 electrons
Three CO ligands:	6 electrons
Total:	18 electrons

- 14.31** Using 1-decene as an example, we can see from the following schematic that the growing polymer will incorporate a C_8 side chain at every point where 1-decene replaces ethylene.

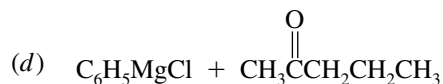
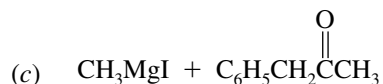
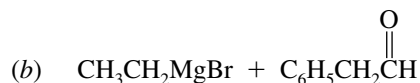
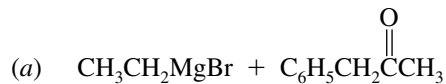


- 14.32–14.36** Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual*. You should use *Learning By Modeling* for these exercises.

- B-5.** Which, if any, of the following pairs of reagents could be used to prepare 2-phenyl-2-butanol?

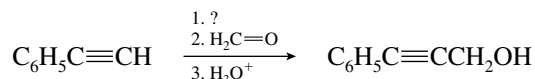


2-Phenyl-2-butanol



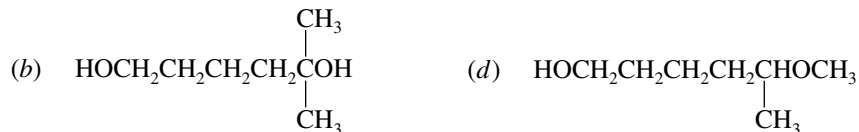
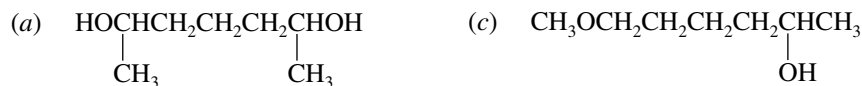
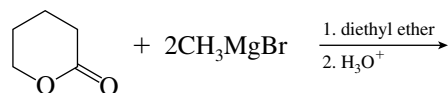
- (e) None of these combinations would be effective.

- B-6.** Which of the following reagents would be effective for the following reaction sequence?

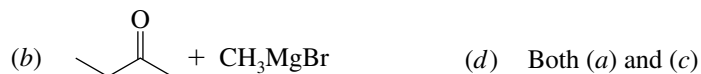
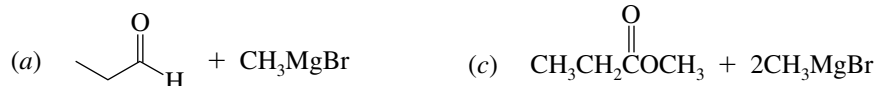


- (a) Sodium ethoxide
(b) Magnesium in diethyl ether
- (c) Butyllithium
(d) Potassium hydroxide

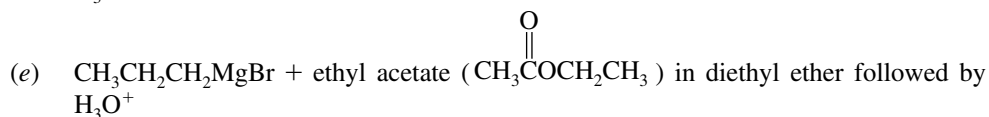
- B-7.** What is the product of the following reaction?



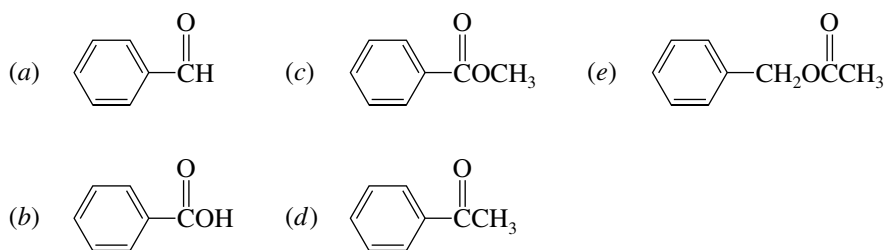
- B-8.** Which of the following combinations of reagents will yield a chiral product after hydrolysis in aqueous acid?



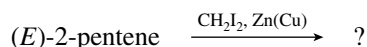
- B-9.** Which sequence of steps describes the best synthesis of 2-phenylpropene?
- Benzene + 2-chloropropene, AlCl_3
 - Benzene + propene, H_2SO_4
 1. Benzaldehyde ($\text{C}_6\text{H}_5\text{CH}=\text{O}$) + $\text{CH}_3\text{CH}_2\text{MgBr}$, diethyl ether
2. H_3O^+
3. H_2SO_4 , heat
 1. Bromobenzene + Mg, diethyl ether
2. Propanal ($\text{CH}_3\text{CH}_2\text{CH}=\text{O}$)
3. H_3O^+
4. H_2SO_4 , heat
 1. Bromobenzene + Mg, diethyl ether
2. Acetone [$(\text{CH}_3)_2\text{C}=\text{O}$]
3. H_3O^+
4. H_2SO_4 , heat
- B-10.** What sequence of steps represents the best synthesis of 4-heptanol ($\text{CH}_3\text{CH}_2\text{CH}_2$)₂CHOH?
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}$ (2 mol) + formaldehyde ($\text{CH}_2=\text{O}$) in diethyl ether followed by H_3O^+
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}$ + butanal ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{O}$) in diethyl ether followed by H_3O^+
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{MgBr}$ + acetone [$(\text{CH}_3)_2\text{C}=\text{O}$] in diethyl ether followed by H_3O^+
 - $(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{CHMgBr}$ + formaldehyde ($\text{CH}_2=\text{O}$) in diethyl ether followed by H_3O^+



- B-11.** All of the following compounds react with ethylmagnesium bromide. Alcohols are formed from four of the compounds. Which one does *not* give an alcohol?



- B-12.** Give the major product of the following reaction:



- cis*-1-Ethyl-2-methylcyclopropane
- trans*-1-Ethyl-2-methylcyclopropane
- 1-Ethyl-1-methylcyclopropane
- An equimolar mixture of products (a) and (b)