

## Chapter 10 – Organohalides

### Chapter Outline

- I. Introduction to alkyl halides (Sections 10.1 – 10.2).
  - A. Naming alkyl halides (Section 10.1).
    - 1. Rules for naming alkyl halides:
      - a. Find the longest chain and name it as the parent.  
If a double or triple bond is present, the parent chain must contain it.
      - b. Number the carbon atoms of the parent chain, beginning at the end nearer the first substituent, whether alkyl or halo.
      - c. Number each substituent.
        - i. If more than one of the same kind of substituent is present, number each, and use the prefixes *di-*, *tri-*, *tetra-* and so on.
        - ii. If different halogens are present, number all and list them in alphabetical order.
      - d. If the parent chain can be numbered from either end, start at the end nearer the substituent that has alphabetical priority.
    - 2. Some alkyl halides are named by first citing the name of the alkyl group and then citing the halogen.
  - B. Structure of alkyl halides (Section 10.2).
    - 1. Alkyl halides have approximately tetrahedral geometry.
    - 2. Bond lengths increase with increasing size of the halogen bonded to carbon.
    - 3. Bond strengths decrease with increasing size of the halogen bonded to carbon.
    - 4. Carbon–halogen bonds are polar, and halomethanes have dipole moments.
    - 5. Alkyl halides behave as electrophiles in polar reactions.
- II. Preparation of alkyl halides (Sections 10.3 – 10.6).
  - A. Radical halogenation of alkanes (Section 10.3).
    - 1. The sequence of steps: initiation, propagation, termination.
    - 2. Complications of radical halogenation.
      - a. The reaction continues on to produce di- and polysubstituted products.
      - b. If more than one type of hydrogen is present, more than one type of monosubstituted product is formed.
      - c. The reactivity order of different types of hydrogen towards chlorination is: primary < secondary < tertiary.
        - i. This reactivity order is due to the bond dissociation energies for formation of the alkyl radicals.
        - ii. The stability order of alkyl radicals: primary < secondary < tertiary.
      - d. According to the Hammond Postulate, the product with the more stable transition state (here, the more stable radical intermediate) forms faster.
      - e. Bromination is more selective than chlorination.  
The stability of the radical intermediate is even more important for bromination because radical formation is less endergonic.
  - C. Allylic bromination of alkenes (Sections 10.4 – 10.5).
    - 1. Reaction of an alkene with NBS causes bromination at the position allylic to the double bond (Section 10.4).
    - 2. This reaction occurs by a radical chain mechanism.
      - a. Br• abstracts an allylic hydrogen.
      - b. The allylic radical reacts with Br<sub>2</sub> to form an allylic bromide, plus Br•.
    - 3. Reaction occurs at the allylic position because an allylic C–H bond is weaker than most other C–H bonds, and an allylic radical is more stable.

4. Reasons for stability of an allylic radical (Section 10.5).
  - a. The carbon with the unpaired electron is  $sp^2$ -hybridized, and its  $p$  orbital can overlap with the  $p$  orbitals of the double-bond carbons.
  - b. The radical intermediate is thus stabilized by resonance.  
This stability is due to delocalization of the unpaired electron over an extended  $\pi$  network.
  - c. Reaction of the allylic radical with  $Br_2$  can occur at either end of the  $\pi$  orbital system.
    - i. A mixture of products may be formed if the alkene is unsymmetrical.
    - ii. These products aren't usually formed in equal quantities: reaction to form the more substituted double bond is favored.
  - d. Products of allylic bromination can be dehydrohalogenated to form dienes.

D. Alkyl halides from alcohols (Section 10.6).

1. Tertiary alkyl chlorides, bromides or iodides can be prepared by the reaction of a tertiary alcohol with  $HCl$ ,  $HBr$  or  $HI$ .  
Reaction of secondary or primary alcohols occurs under more drastic conditions, which may destroy other acid-sensitive functional groups.
2. Primary and secondary alkyl halides can be formed by treatment of the corresponding alcohols with  $SOCl_2$  or  $PBr_3$ .  
Reaction conditions are mild, less acidic, and are less likely to cause acid-catalyzed rearrangements.

III. Reactions of alkyl halides (Sections 10.7 – 10.8).

A. Grignard reagents (Section 10.7).

1. Organohalides react with  $Mg$  to produce organomagnesium halides,  $RMgX$ .  
These compounds are known as Grignard reagents.
2. Grignard reagents can be formed from alkyl, alkenyl and aryl halides.  
Steric hindrance is no barrier to formation of Grignard reagents.
3. The carbon bonded to  $Mg$  is negatively polarized and is nucleophilic.
4. Grignard reagents react with weak acids to form hydrocarbons.

B. Organometallic coupling reagents (Section 10.8).

1. Alkyl halides can react with  $Li$  to form alkyllithiums.
2. These alkyllithiums can combine with  $CuI$  to form lithium diorganocopper compounds ( $R_2CuLi$ ), which are known as Gilman reagents.
3.  $R_2CuLi$  compounds can react with alkyl halides (except for fluorides) to form hydrocarbon products.
4. Organometallic coupling reactions are useful for forming large molecules from small pieces.
  - a. The reaction can be carried out on alkyl, vinyl and aryl halides.
  - b. A radical mechanism is probably involved.
5. A related reaction is the palladium-catalyzed coupling of aryl or vinyl organotin reagents with organohalides.

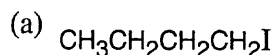
IV. Oxidation and reduction in organic chemistry (Section 10.9).

- A. In organic chemistry, an oxidation is a reaction that results in a loss in electron density by carbon.
  1. This loss may be due to two kinds of reactions:
    - a. Bond formation between carbon and a more electronegative atom (usually O, N or halogen).
    - b. Bond breaking between carbon and a less electronegative atom (usually H).
  2. Examples include chlorination of alkanes and reaction of alkenes with  $Br_2$ .
- B. A reduction is a reaction that results in a gain of electron density by carbon.
  1. This gain may be due to two kinds of reactions:
    - a. Bond formation between carbon and a less electronegative atom.
    - b. Bond breaking between carbon and a more electronegative atom.

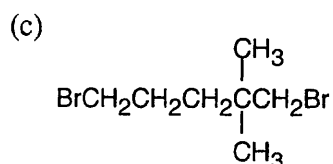
2. Examples include conversion of a Grignard reagent to an alkane, and reduction of an alkene with  $H_2$ .
- C. Alkanes are at the lowest oxidation level, and  $CO_2$  is at the highest level.
- D. A reaction that converts a compound from a lower oxidation level to a higher oxidation level is an oxidation.
- E. A reaction that converts a compound from a higher oxidation level to a lower oxidation level is a reduction.

### Solutions to Problems

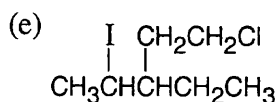
**10.1** The rules that were given for naming alkanes in Section 3.4 are used for alkyl halides. A halogen is treated as an alkyl substituent.



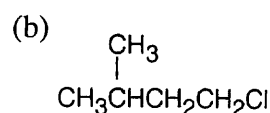
**1-Iodobutane**



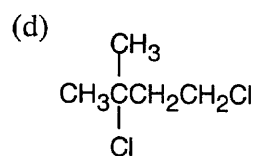
**1,5-Dibromo-2,2-dimethylpentane**



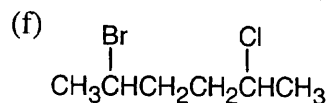
**1-Chloro-3-ethyl-4-iodopentane**



**1-Chloro-3-methylbutane**

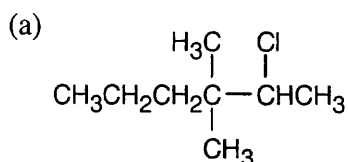


**1,3-Dichloro-3-methylbutane**

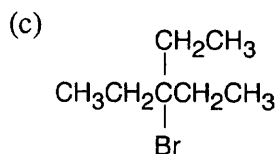


**2-Bromo-5-chlorohexane**

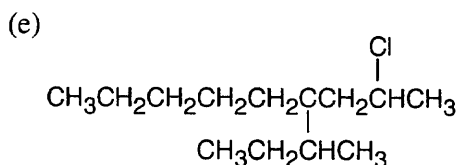
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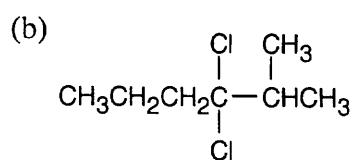
**2-Chloro-3,3-dimethylhexane**



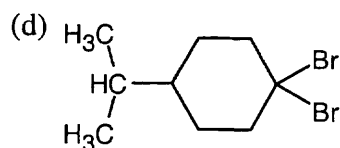
**3-Bromo-3-ethylpentane**



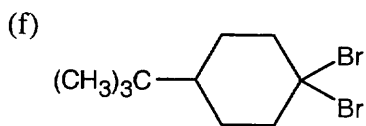
**4-sec-Butyl-2-chlorononane**



**3,3-Dichloro-2-methylhexane**

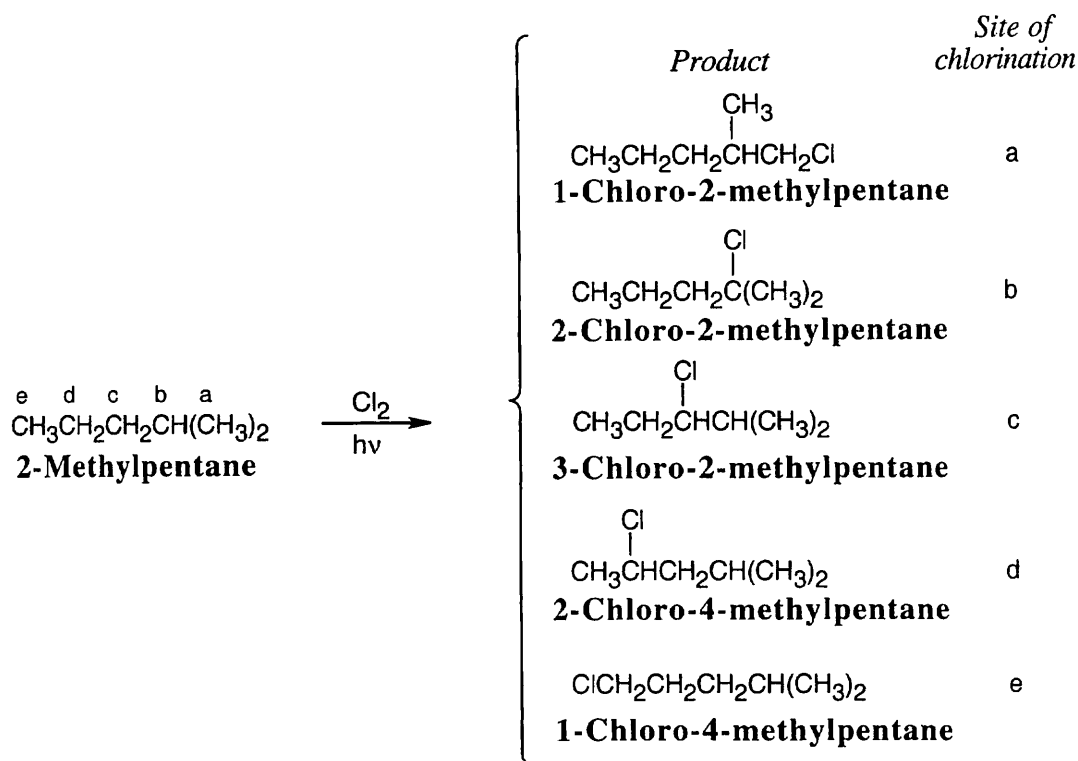


**1,1-Dibromo-4-isopropylcyclohexane**



**1,1-Dibromo-4-tert-butylcyclohexane**

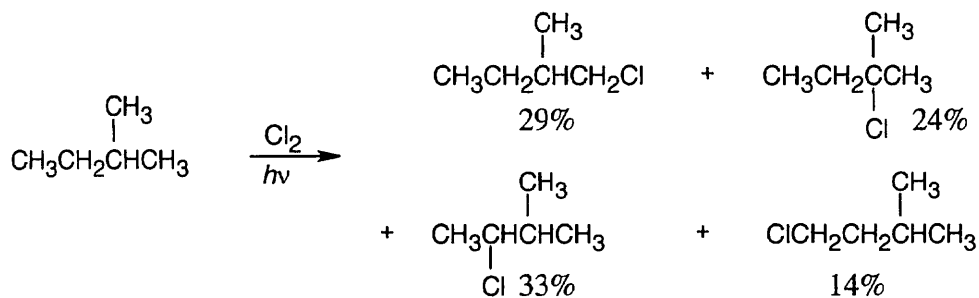
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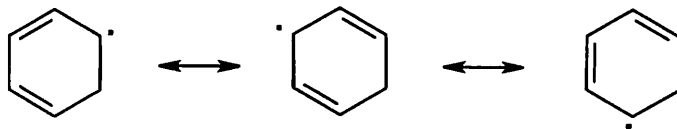
Chlorination at sites b and e yields achiral products. The products of chlorination at sites a, c and d are chiral; each product is formed as a racemic mixture of enantiomers.

## 10.4

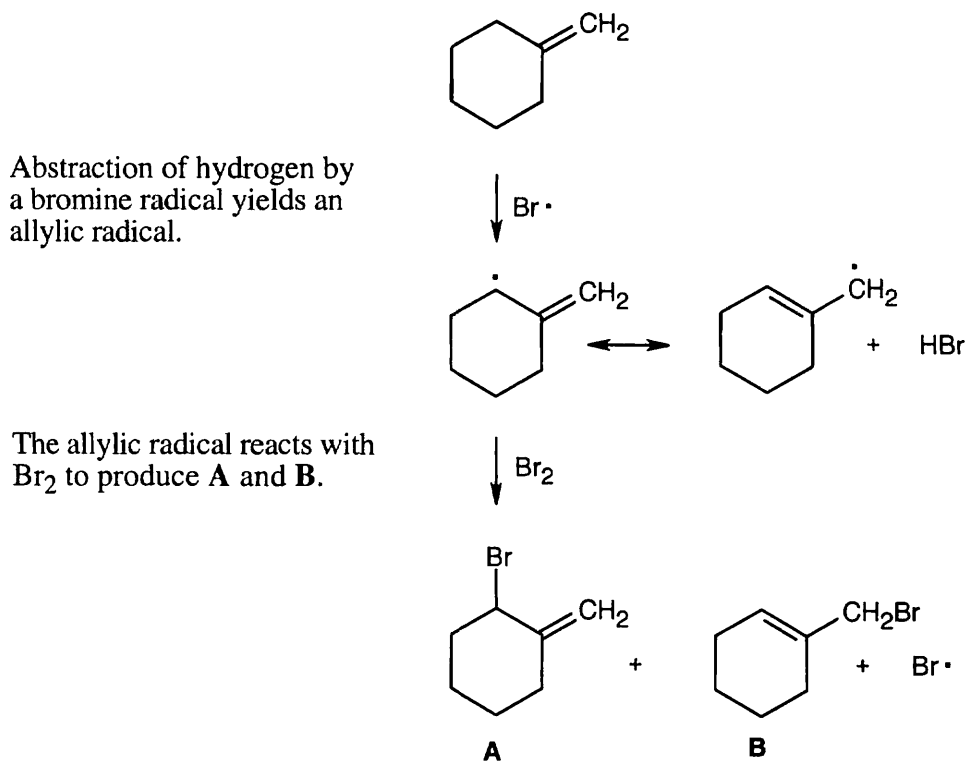
$  \begin{array}{c}  \text{a} \\    \\  \text{CH}_3 \\    \\  \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_3 \\    \quad \quad   \\  \text{d} \quad \text{c} \quad \text{H} \quad \text{a} \\    \\  \text{b} \\  \text{2-Methylbutane}  \end{array}  $	Type of -H	a	b	c	d
	Number of -H of each type	6	1	2	3
	Relative reactivity	1.0	5.0	3.5	1.0
	Number times reactivity	6.0	5.0	7.0	3.0
	Percent chlorination	29%	24%	33%	14%



## 10.5

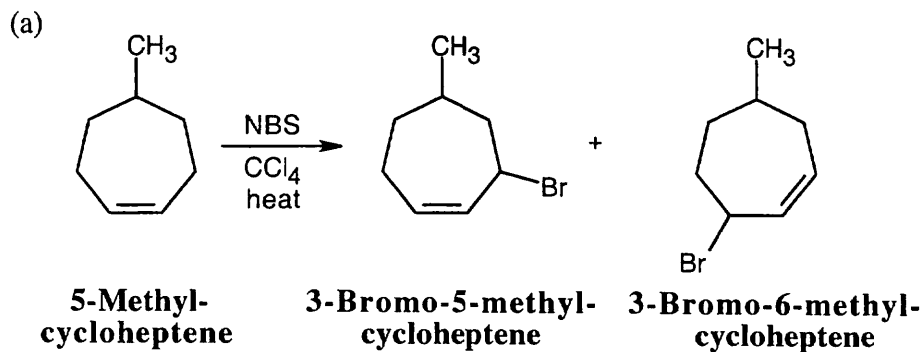


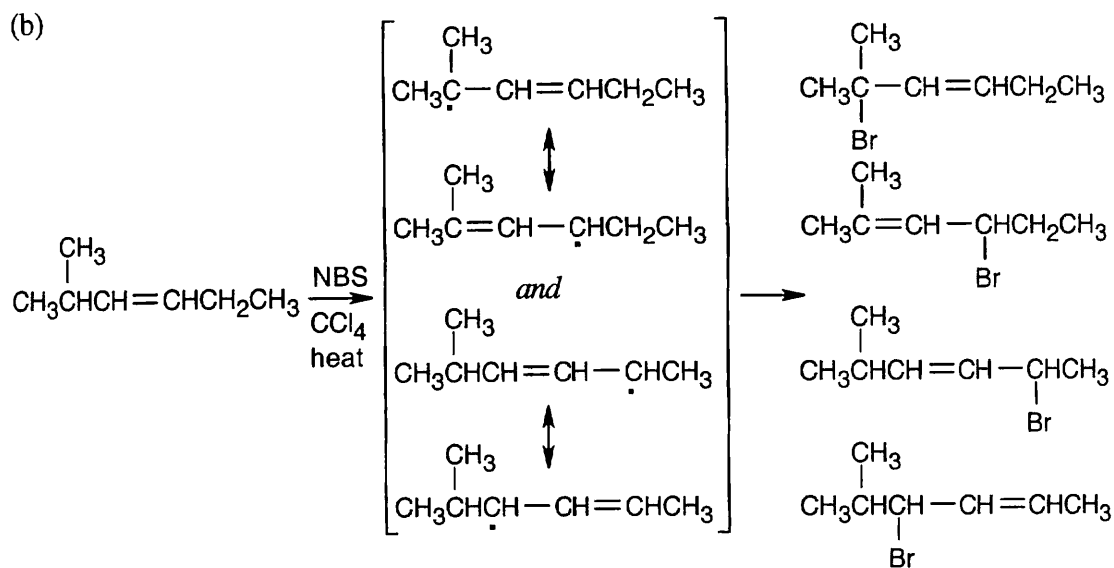
## 10.6



Product **B** is favored because reaction at the primary end of the allylic radical yields a product with a trisubstituted double bond.

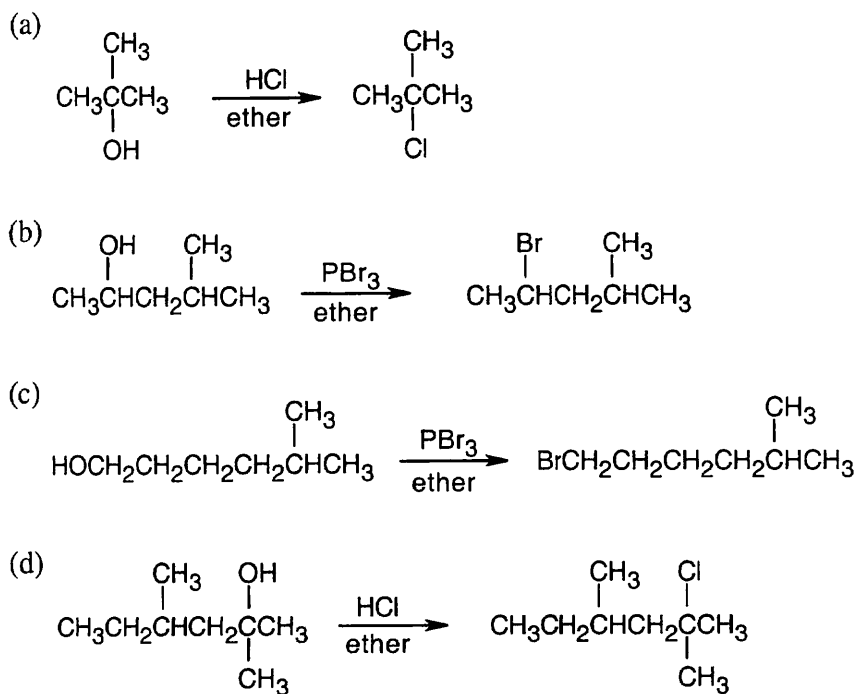
## 10.7



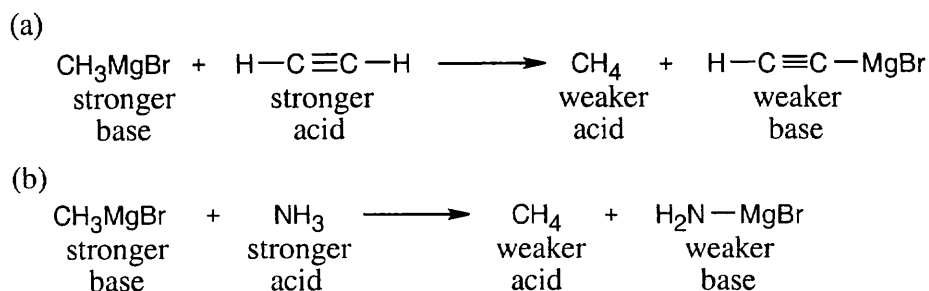


Two different allylic radicals can form, and four different bromohexenes can be produced.

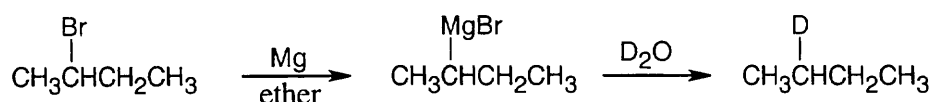
**10.8** Remember that halogen acids are used for converting tertiary alcohols to alkyl halides.  $\text{PBr}_3$  and  $\text{SOCl}_2$  are used for converting secondary and primary alcohols to alkyl halides.



- 10.9** Table 8.1 shows that the  $pK_a$  of  $\text{CH}_3\text{--H}$  is 60. Since  $\text{CH}_4$  is a very weak acid,  $^-\text{:CH}_3$  is a very strong base. Alkyl Grignard reagents are similar in base strength to  $^-\text{:CH}_3$ , but alkynyl Grignard reagents are somewhat weaker bases. Both reactions (a) and (b) occur as written.

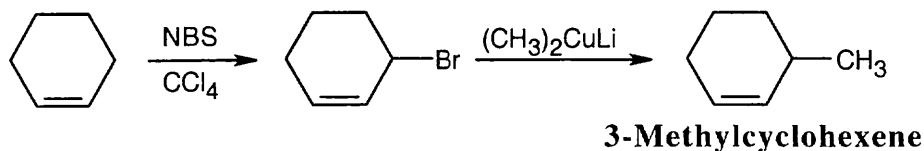


- 10.10** Just as Grignard reagents react with *proton* donors to convert  $\text{R--MgX}$  into  $\text{R--H}$ , they also react with *deuterium* donors to convert  $\text{R--MgX}$  into  $\text{R--D}$ . In this case:



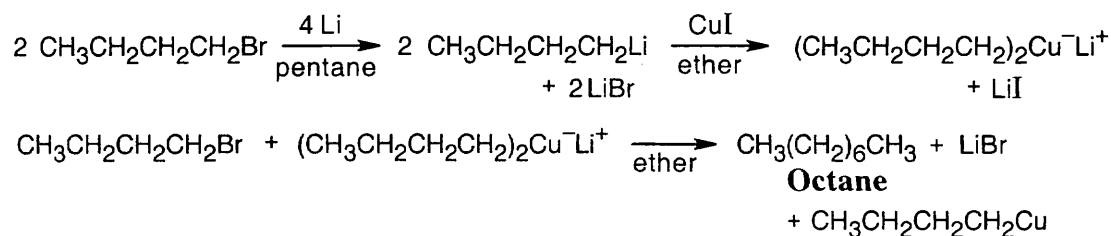
- 10.11** (a) **Strategy:** The methyl group has an allylic relationship to the double bond. Thus, an organometallic coupling reaction between 3-bromocyclohexene and lithium dimethylcopper gives the desired product. 3-Bromocyclohexene can be formed by allylic bromination of cyclohexene with NBS.

**Solution:**



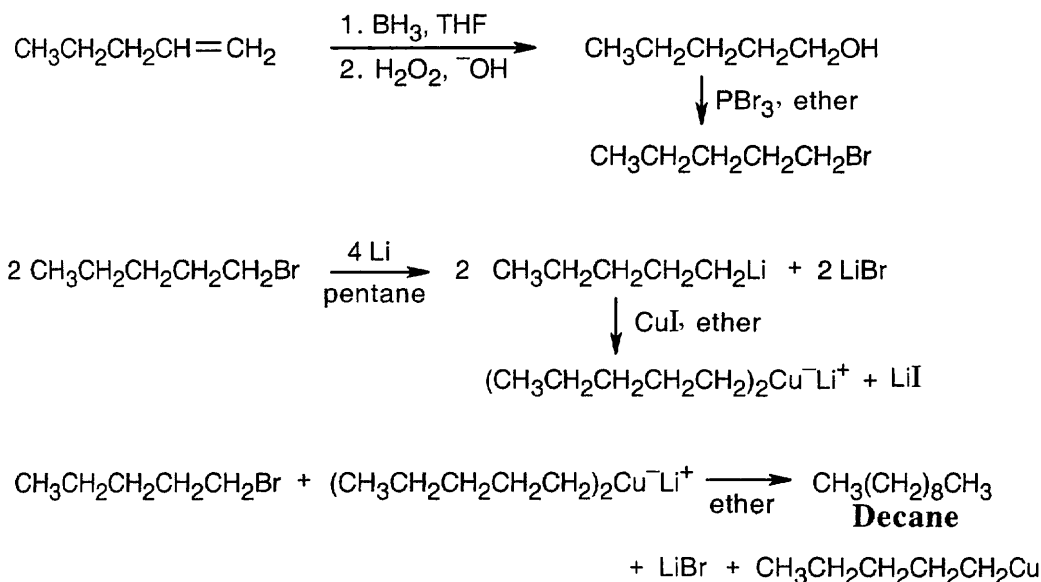
- (b) **Strategy:** We are asked to synthesize an eight-carbon product from a four-carbon starting material. Thus, an organometallic coupling reaction between 1-bromobutane and lithium dibutylcopper gives octane as the product. The Gilman reagent is formed from 1-bromobutane.

**Solution:**



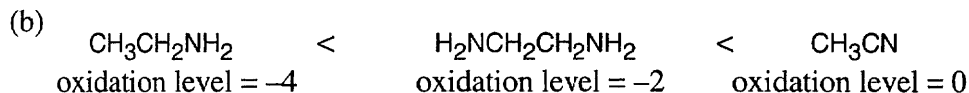
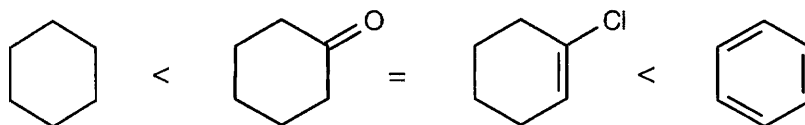
(c) **Strategy:** The synthesis in (b) suggests a route to the product. Decane can be synthesized from 1-bromopentane and lithium dipentylcopper. 1-Bromopentane is formed by hydroboration of 1-pentene, followed by treatment of the resulting alcohol with  $\text{PBr}_3$ .

**Solution:**



- 10.12 (a) Strategy:** As described in Worked Example 10.2, the oxidation level of a compound can be found by adding the number of C–O, C–N, and C–X bonds and subtracting the number of C–H bonds. Cyclohexane, the first compound shown, has 12 C–H bonds, and has an oxidation level of –12. Cyclohexanone has 2 C–O bonds (from the double bond) and 10 C–H bonds, for an oxidation level of –8. 1-Chlorocyclohexene has one C–Cl bond and 9 C–H bonds, and also has an oxidation level of –8. Benzene has 6 C–H bonds, for an oxidation level of –6.

**Solution:** In order of increasing oxidation level:

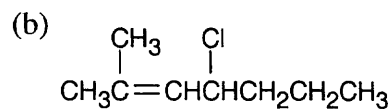


- 10.13 (a)** The aldehyde carbon of the reactant has an oxidation level of 1 (2 C–O bonds minus 1 C–H bond). The alcohol carbon of the product has an oxidation level of –1 (1 C–O bond minus 2 C–H bonds). The reaction is a reduction because the oxidation level of the product is lower than the oxidation level of the reactant.
- (b)** The oxidation level of the upper carbon of the double bond in the reactant changes from 0 to +1 in the product; the oxidation level of the lower carbon of the double bond changes from 0 to –1. The total oxidation level, however, is the same for both product and reactant, and the reaction is neither an oxidation nor a reduction.



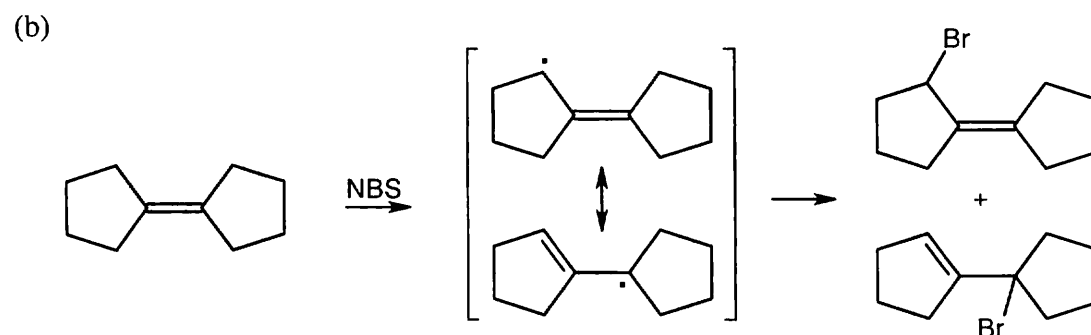
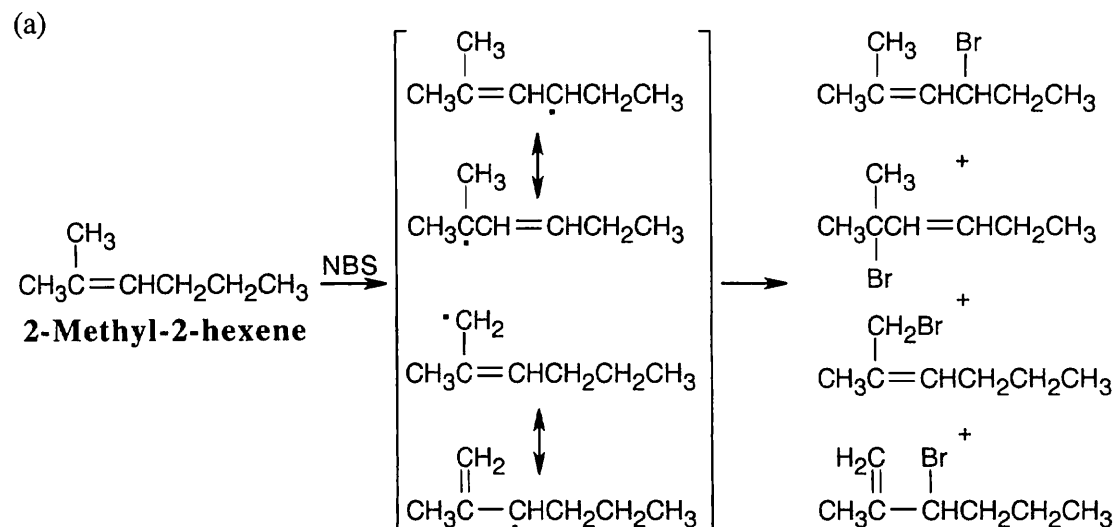
## Visualizing Chemistry

10.14

*cis*-1-Chloro-3-methylcyclohexane

4-Chloro-2-methyl-2-heptene

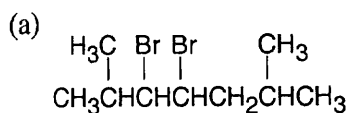
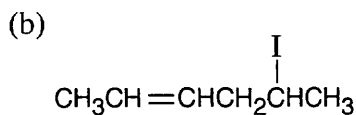
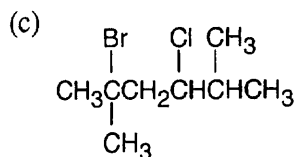
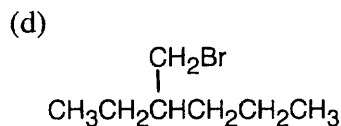
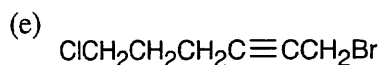
10.15



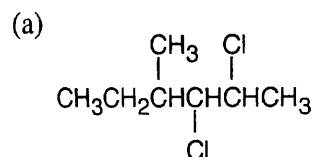
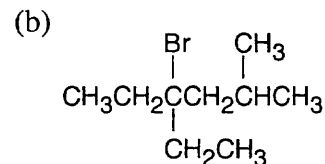
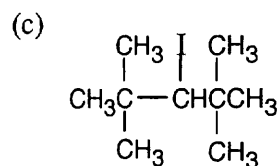
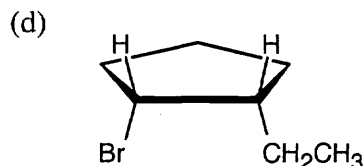
**10.16** The name of the compound is (*R*)-2-bromopentane. Reaction of (*S*)-2-pentanol with  $\text{PBr}_3$  to form (*R*)-2-bromopentane occurs with a change in stereochemistry because the configuration at the chirality center changes from *S* to *R*.

## Additional Problems

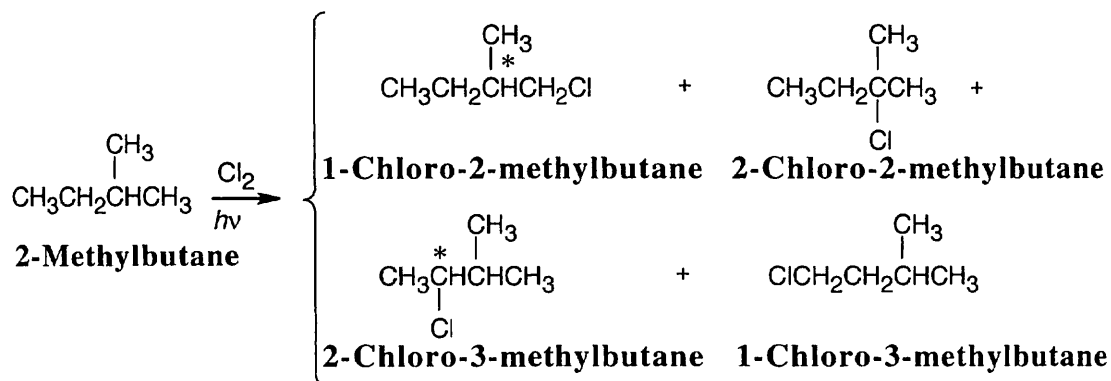
10.17

**3,4-Dibromo-2,6-dimethylheptane****5-Iodo-2-hexene****2-Bromo-4-chloro-2,5-dimethylhexane****3-(Bromomethyl)hexane****1-Bromo-6-chloro-2-hexyne**

10.18

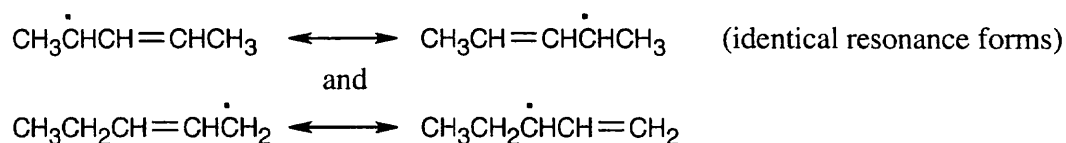
**2,3-Dichloro-4-methylhexane****4-Bromo-4-ethyl-2-methylhexane****3-Iodo-2,2,4,4-tetramethylpentane****cis-1-Bromo-2-ethylcyclopentane**

10.19

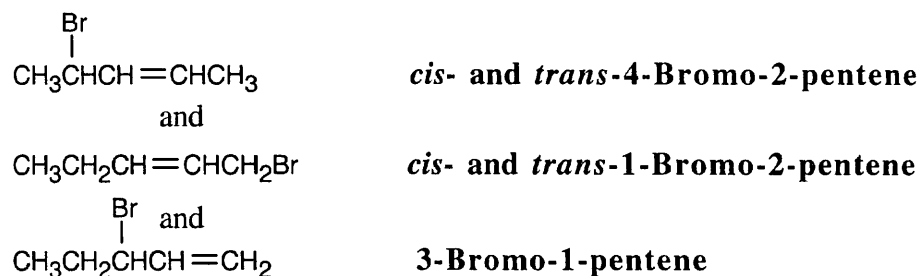


Two of the above products are chiral (chirality centers are starred). None of the products are optically active; each chiral product is a racemic mixture.

**10.20** Abstraction of hydrogen by  $\text{Br}\cdot$  can produce either of two allylic radicals. The first radical, resulting from abstraction of a secondary hydrogen, is more likely to be formed.

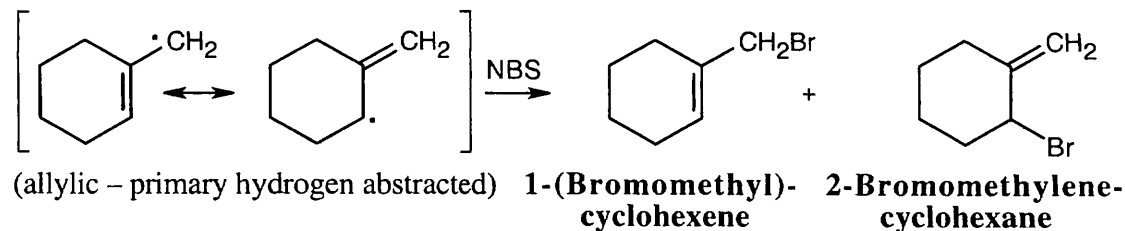
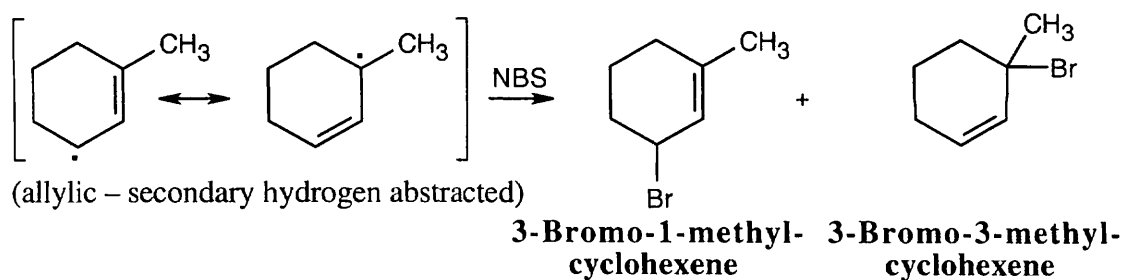
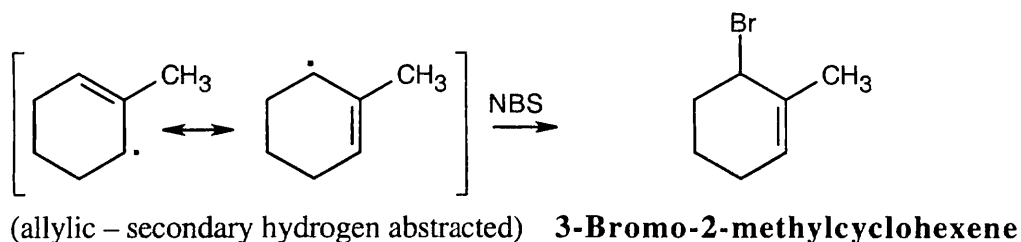


Reaction of the radical intermediates with a bromine source leads to a mixture of products:

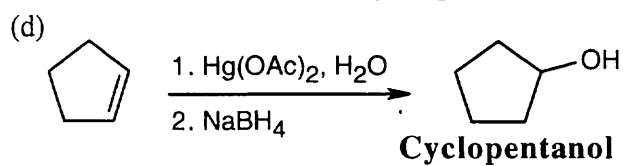
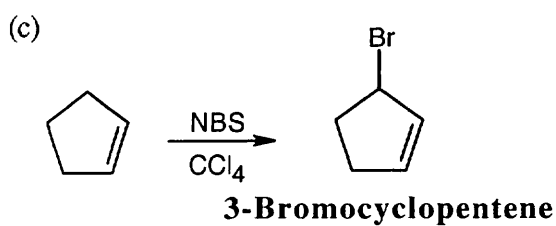
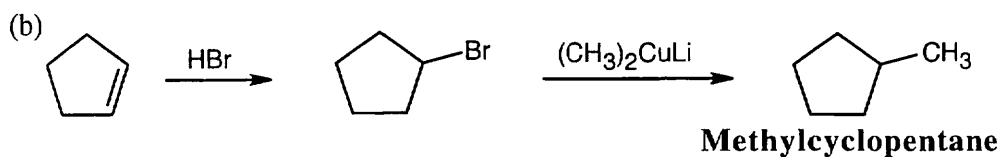
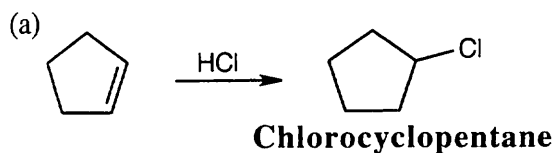


The major product is 4-bromo-2-pentene, instead of the desired product, 1-bromo-2-pentene.

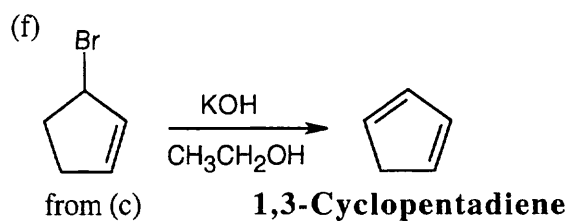
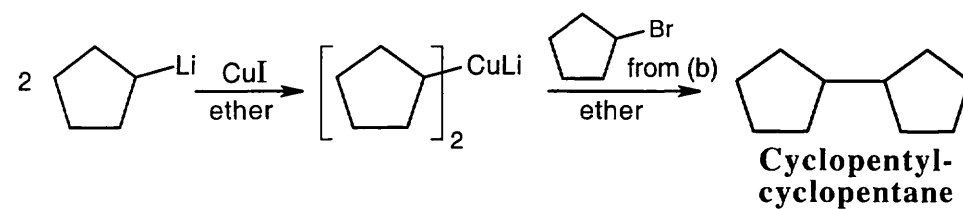
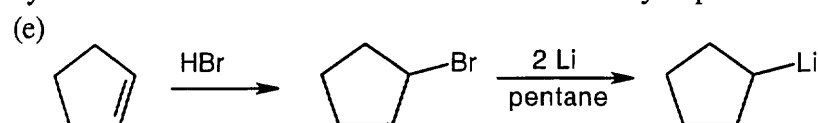
**10.21** Three different allylic radical intermediates can be formed. Bromination of these intermediates can yield as many as five bromoalkenes. This is definitely not a good reaction to use in a synthesis.



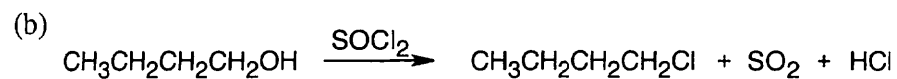
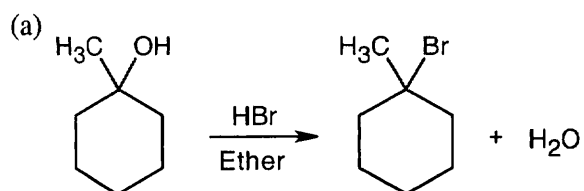
## 10.22



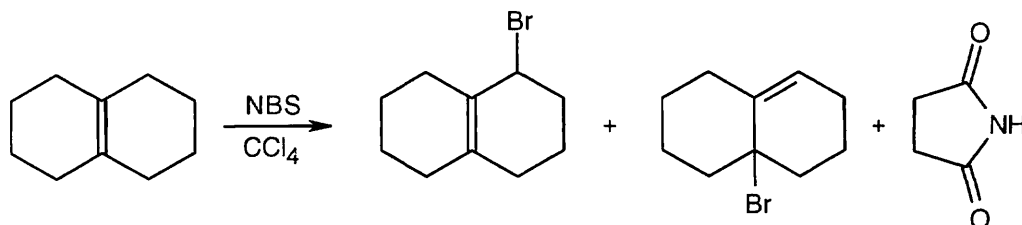
Hydroboration/oxidation can also be used to form cyclopentanol.



## 10.23

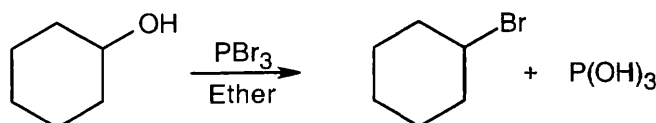


(c)

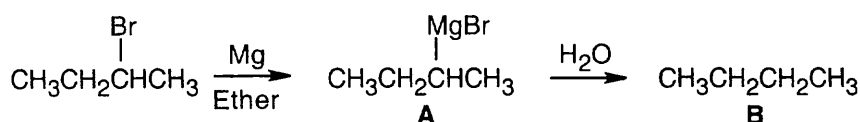


The major product contains a tetrasubstituted double bond, and the minor product contains a trisubstituted double bond.

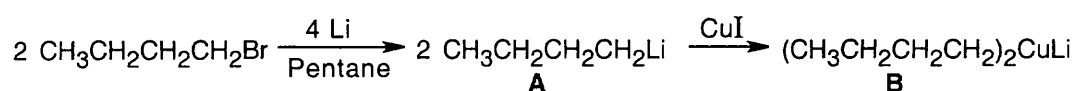
(d)



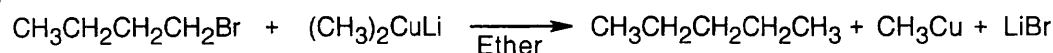
(e)



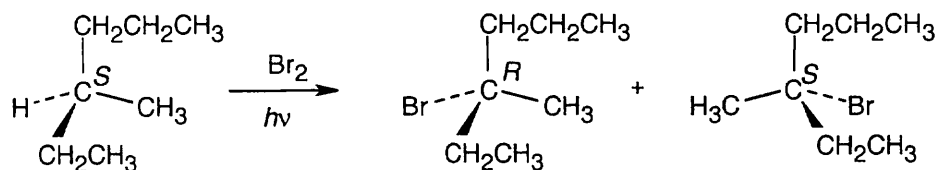
(f)



(g)

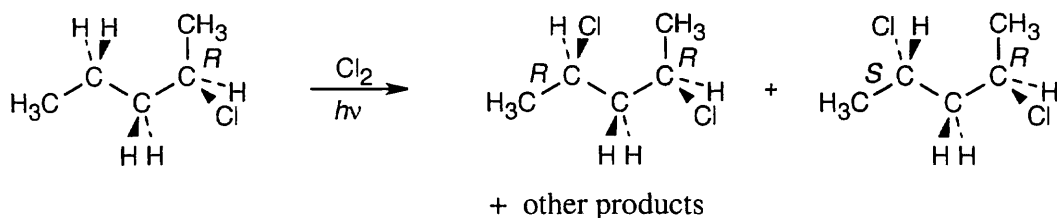


## 10.24



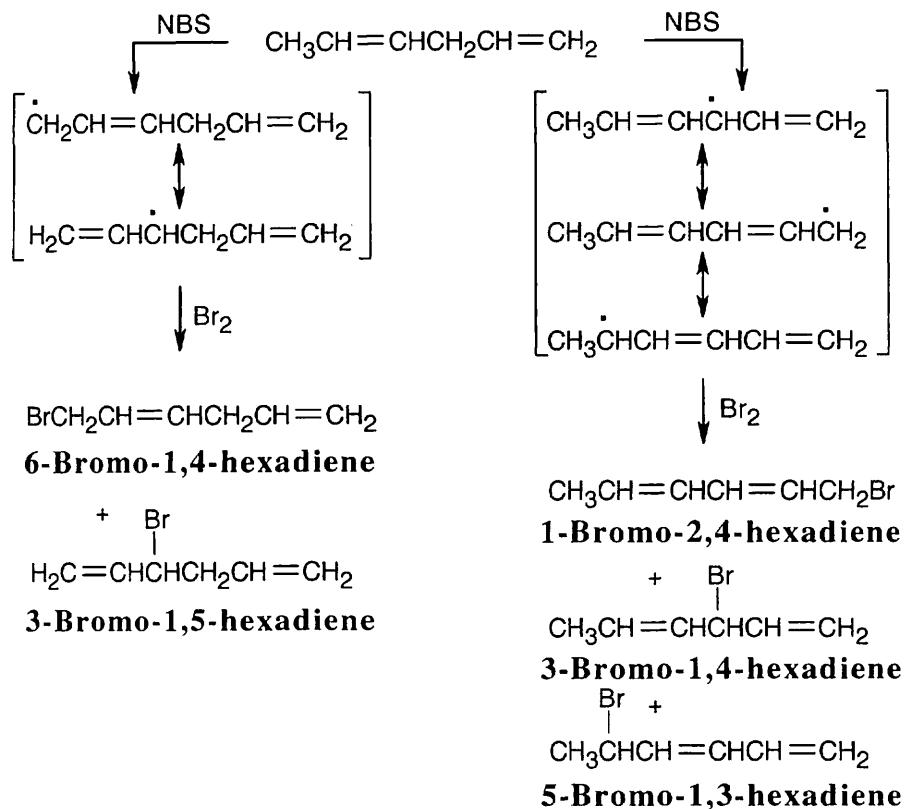
Abstraction of a hydrogen atom from the chirality center of (S)-3-methylhexane produces an achiral radical intermediate, which reacts with bromine to form a 1:1 mixture of *R* and *S* enantiomeric, chiral bromoalkanes. The product mixture is optically inactive.

## 10.25



Abstraction of a hydrogen atom from carbon 4 yields a chiral radical intermediate. Reaction of this intermediate with chlorine does not occur with equal probability from each side, and the two diastereomeric products are not formed in 1:1 ratio. The first product is optically active, and the second product is a meso compound.

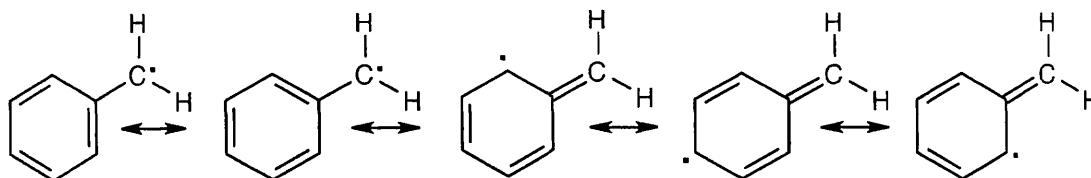
## 10.26



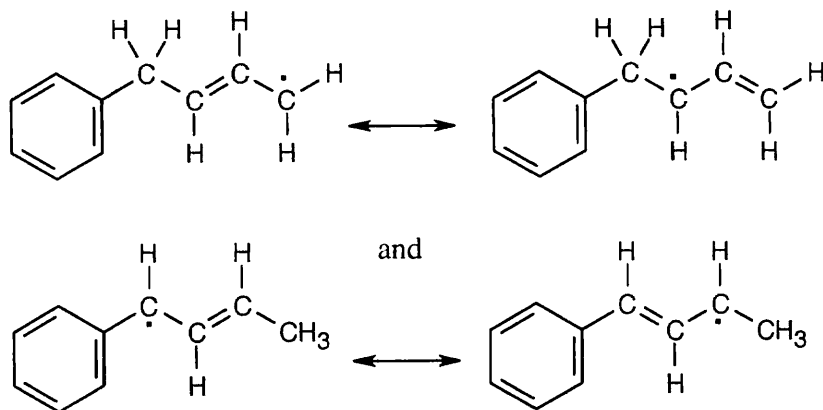
The intermediate on the right is more stable because the unpaired electron is delocalized over more atoms.

**10.27** Table 5.3 shows that the bond dissociation energy for  $\text{C}_6\text{H}_5\text{CH}_2\text{-H}$  is 368 kJ/mol. This value is comparable in size to the bond dissociation energy for a bond between carbon and an allylic hydrogen, and thus it is relatively easy to form the  $\text{C}_6\text{H}_5\text{CH}_2\cdot$  radical. The high bond dissociation energy for formation of  $\text{C}_6\text{H}_5\cdot$ , 464 kJ/mol, indicates the bromination on the benzene ring will not occur. The only product of reaction with NBS is  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ .

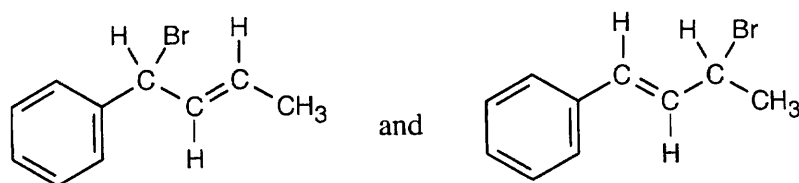
## 10.28



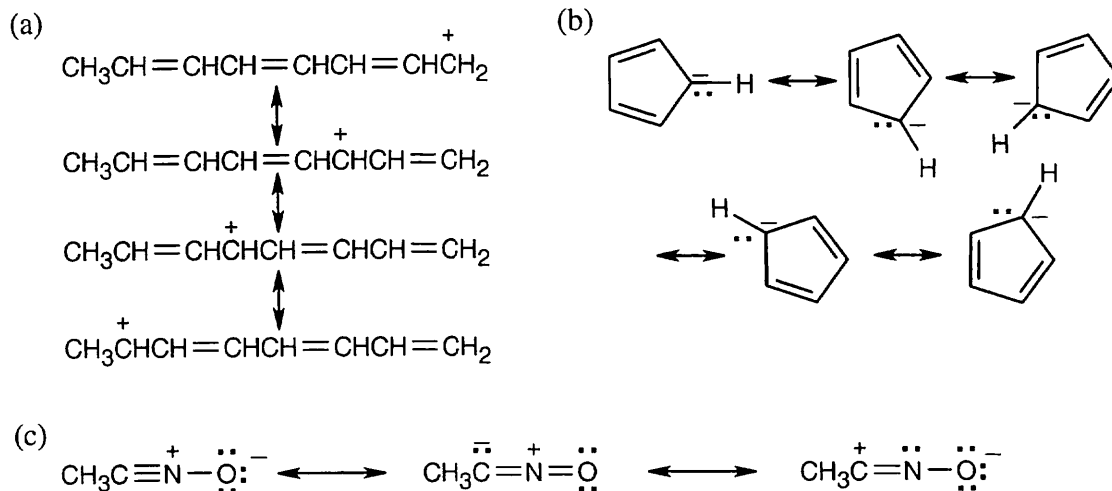
10.29 Two allylic radicals can form:



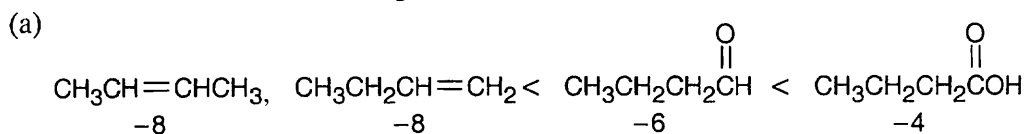
The second radical is much more likely to form because it is both allylic and benzylic, and it yields the following products:



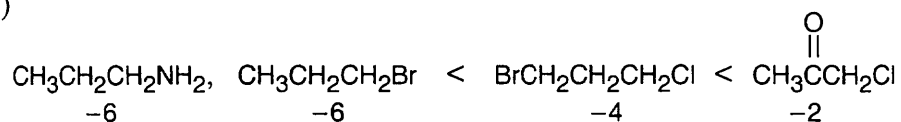
10.30



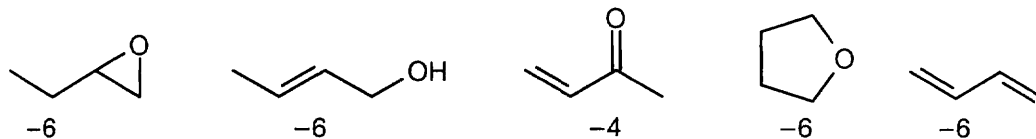
10.31 Remember that the oxidation level is found by subtracting the number of C-H bonds from the number of C-O, C-N, and C-X bonds. The oxidation levels are shown beneath the structures. In order of increasing oxidation level:



(b)



## 10.32



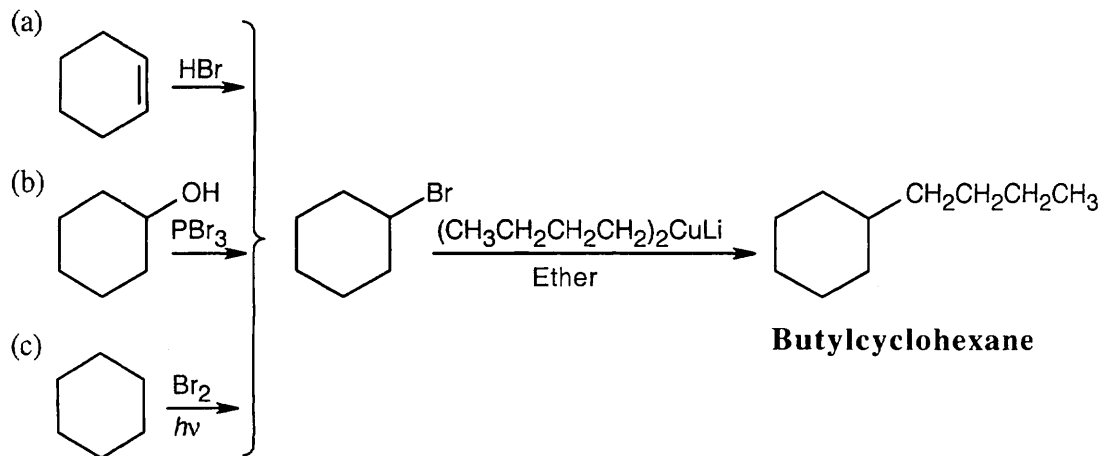
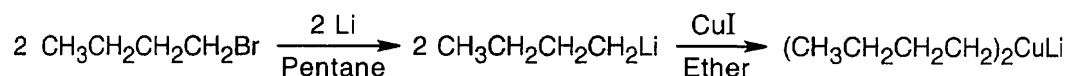
All of the compounds except **3** have the same oxidation level.

10.33 (a) This reaction is an oxidation.

(b) The reaction is neither an oxidation nor a reduction because the oxidation level of the reactant is the same as the oxidation level of the product.

(c) This reaction is a reduction.

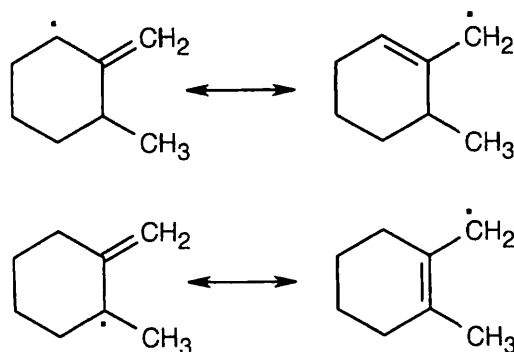
10.34 All these reactions involve addition of a dialkylcopper reagent  $[(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{CuLi}]$  to an alkyl halide. The dialkylcopper is prepared by treating 1-bromobutane with lithium, followed by addition of  $\text{CuI}$ :





**10.35** (a) Fluoroalkanes don't usually form Grignard reagents.

(b) Two allylic radicals can be produced.

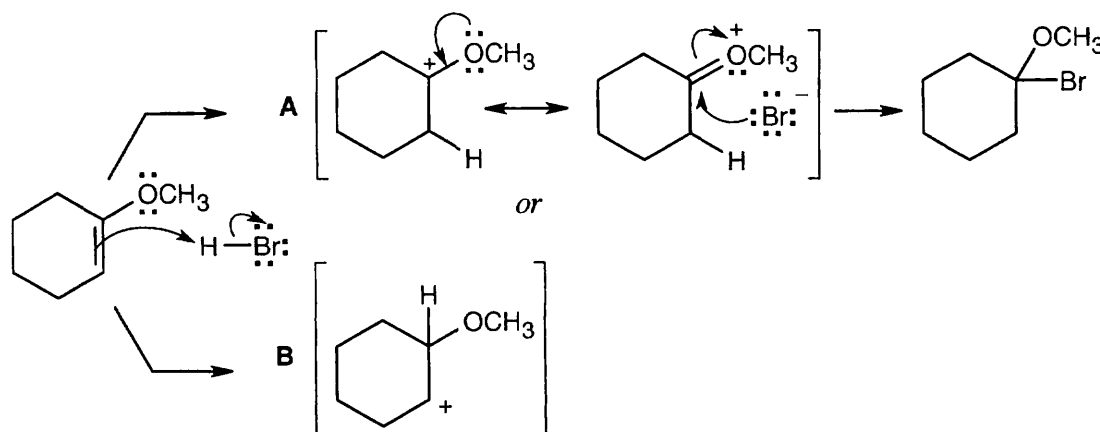


Instead of a single product, as many as four bromoalkene products may result.

(c) Dialkylcopper reagents don't react with fluoroalkanes.

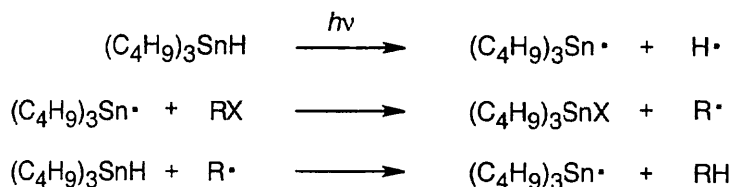
**10.36** A Grignard reagent can't be prepared from a compound containing an acidic functional group because the Grignard reagent is immediately quenched by the proton source. For example, the  $-\text{CO}_2\text{H}$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ , and  $\text{RC}\equiv\text{CH}$  functional groups are too acidic to be used for preparation of a Grignard reagent.  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  is another compound that doesn't form a Grignard reagent.

**10.37**

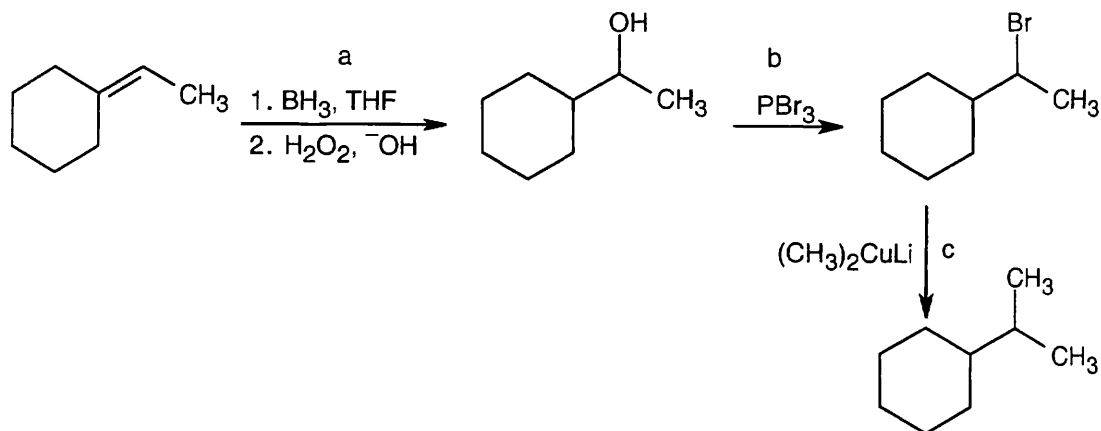


Reaction of the ether with  $\text{HBr}$  can occur by either path A or path B. Path A is favored because its cation intermediate can be stabilized by resonance.

## 10.38

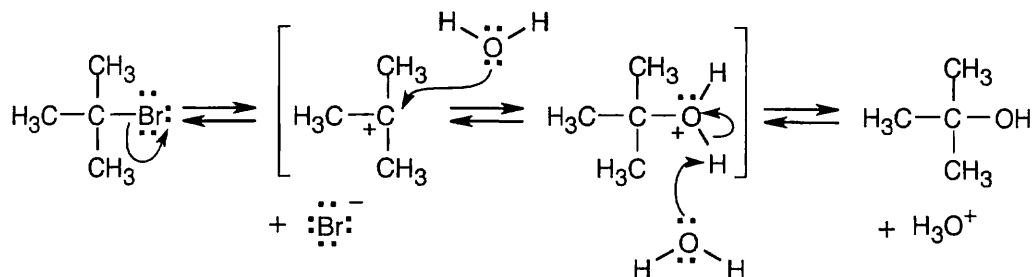


## 10.39

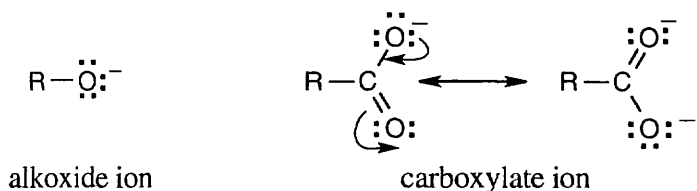


**10.40** As we saw in Chapter 6, tertiary carbocations ( $\text{R}_3\text{C}^+$ ) are more stable than either secondary or primary carbocations, due to the ability of the three alkyl groups to stabilize positive charge. If the substrate is also allylic, as in the case of  $\text{H}_2\text{C}=\text{CHC}(\text{CH}_3)_2\text{Br}$ , positive charge can be further delocalized. Thus,  $\text{H}_2\text{C}=\text{CHC}(\text{CH}_3)_2\text{Br}$  should form a carbocation faster than  $(\text{CH}_3)_3\text{CBr}$  because the resulting carbocation is more stable.

## 10.41



## 10.42



Carboxylic acids are more acidic than alcohols because the negative charge of a carboxylate ion is stabilized by resonance. This resonance stabilization favors formation of carboxylate anions over alkoxide anions, and increases  $K_a$  for carboxylic acids.