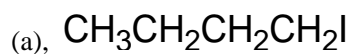
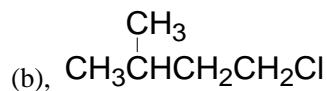


Chapter 10

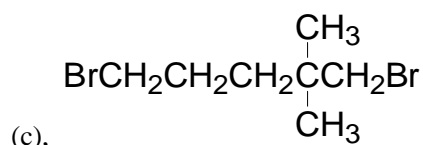
10.1 Give IUPAC names for the following alkyl halides:



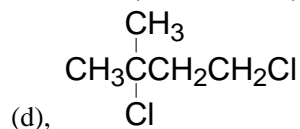
Solution: 1-iodobutane



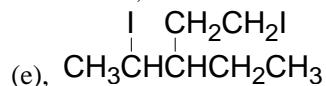
Solution: 1-chloro-3-methylbutane



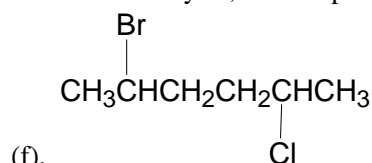
Solution: 1,5-Dibromo-2,2-dimethylpentane



Solution: 1,3-Dichloro-3-methylbutane



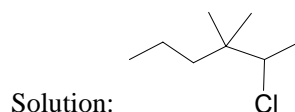
Solution: 3-Ethyl-1,4-diiodopentane



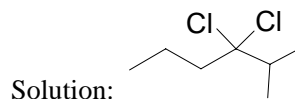
Solution: 2-Bromo-5-chlorohexane

10.2 Draw structures corresponding to the following IUPAC names:

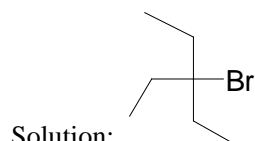
(a), 2-Chloro-3,3-dimethylhexane



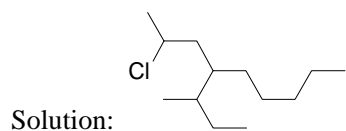
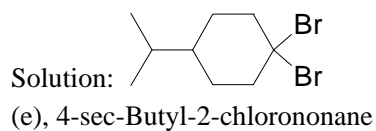
(b), 3,3-Dichloro-2-methylhexane



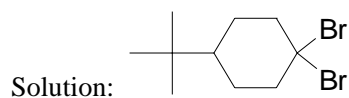
(c), 3-Bromo-3-ethylpentane



(d), 1,1-Dibromo-4-isopropylcyclohexane

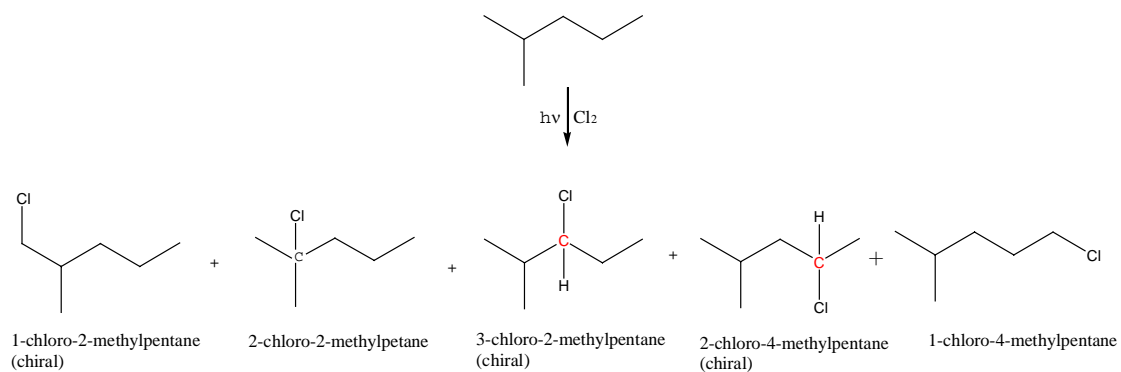


(f), 1,1-Dibromo-4-tert-butylcyclohexane



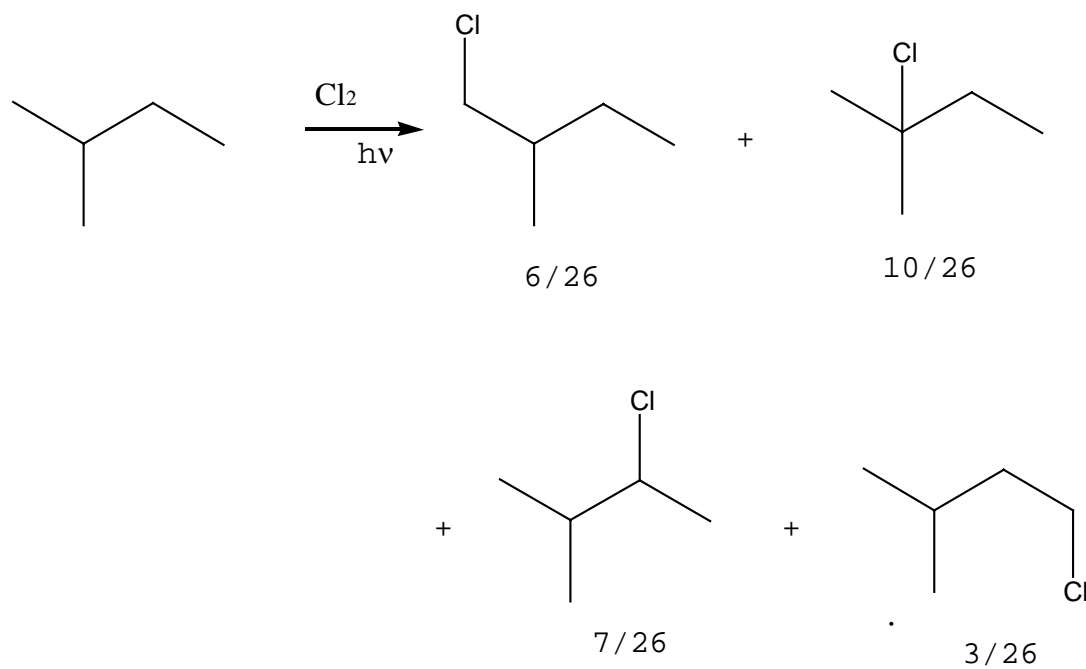
10.3 Draw and name all monochloro products you would expect to obtain from radical chlorination of 2-methylpentane. Which, if any, are chiral?

Solution:

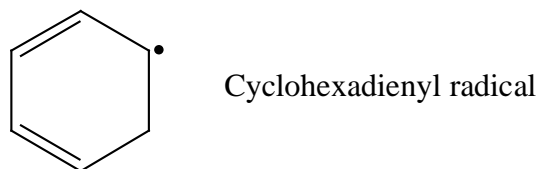


10.4 Taking the relative reactivities of 1° , 2° , 3° hydrogen atoms into account, what products would you expect to obtain from monochlorination of 2-methylbutane? What would the approximate percentage of each product be?

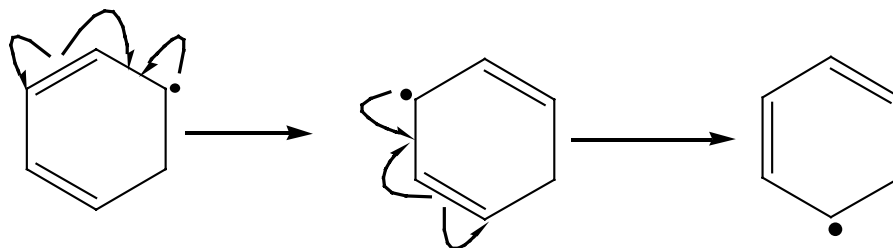
Solution:



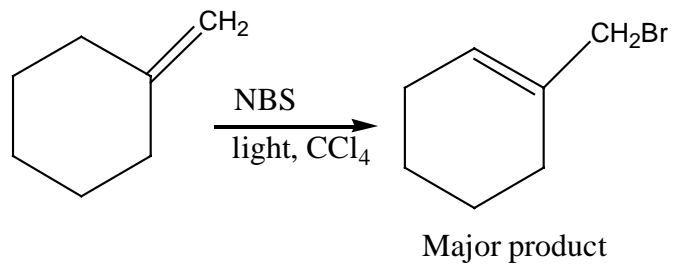
10.5 Draw three resonance forms for the cyclohexadienyl radical.



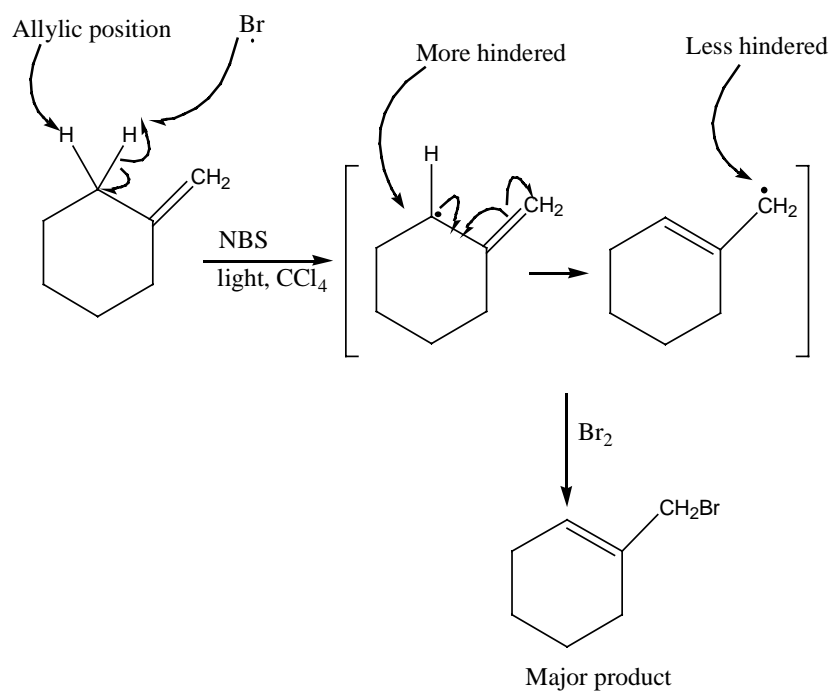
Solution:



10.6 The major product of the reaction of methylenecyclohexane with N-bromosuccinimide is 1-(bromomethyl)cyclohexene. Explain.



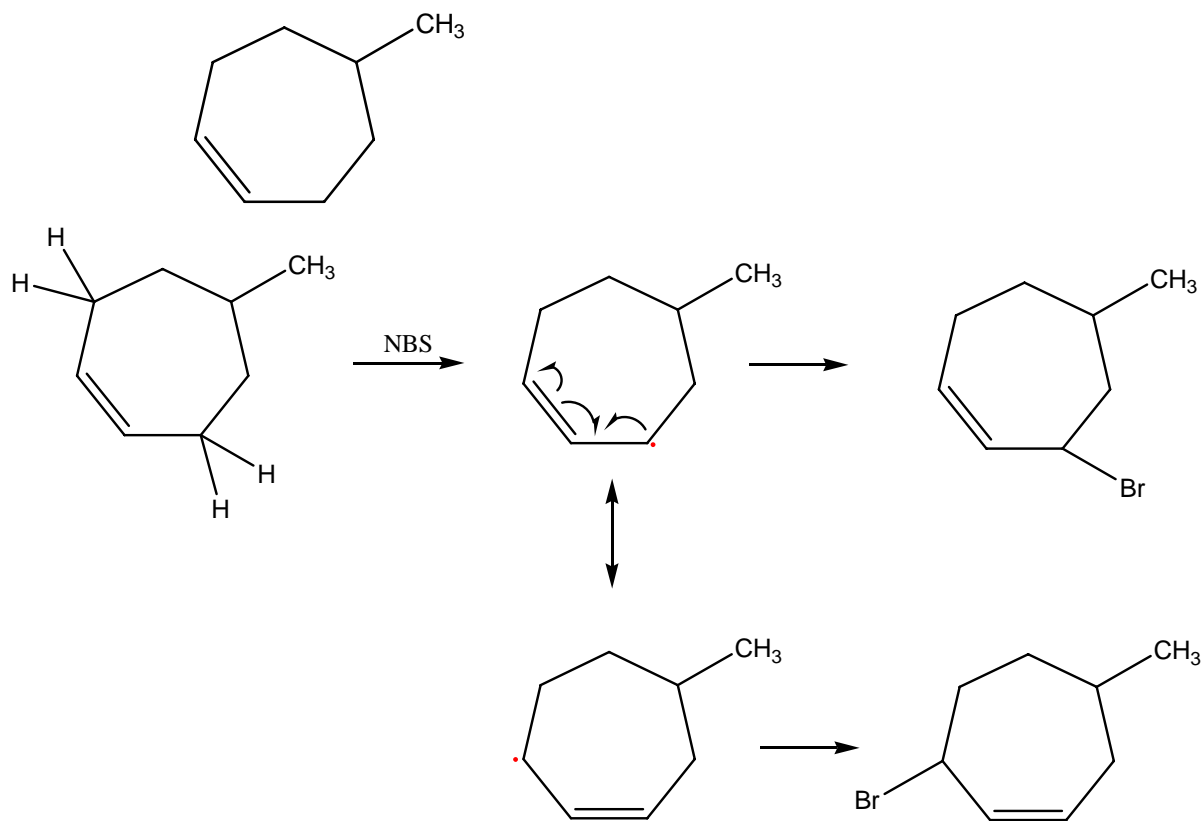
Solution:



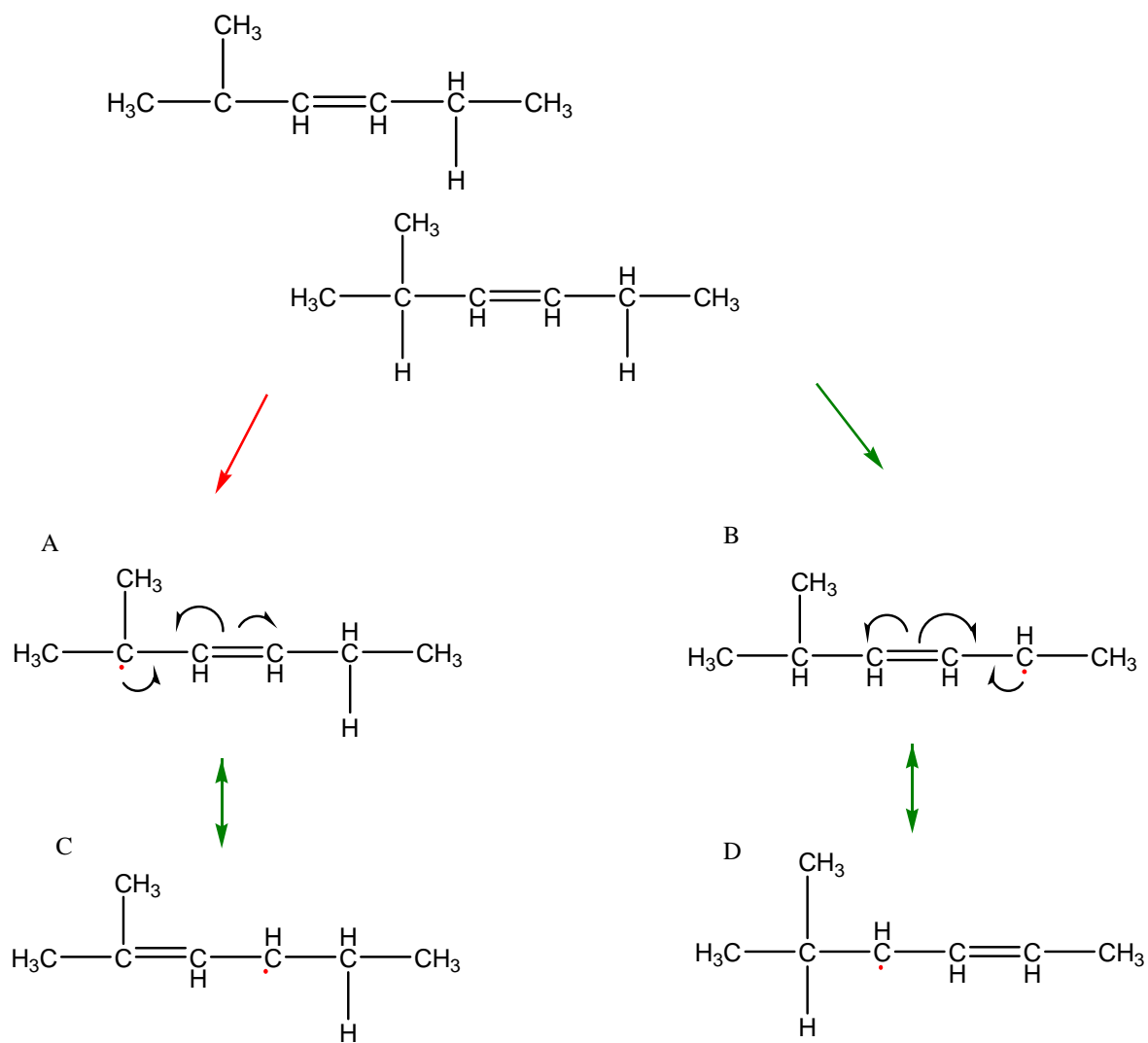
One more reason is the relative stability of alkene.

10.7 What products would you expect from the reaction of the following alkenes with NBS? If more than one product is formed, show the structures of all.

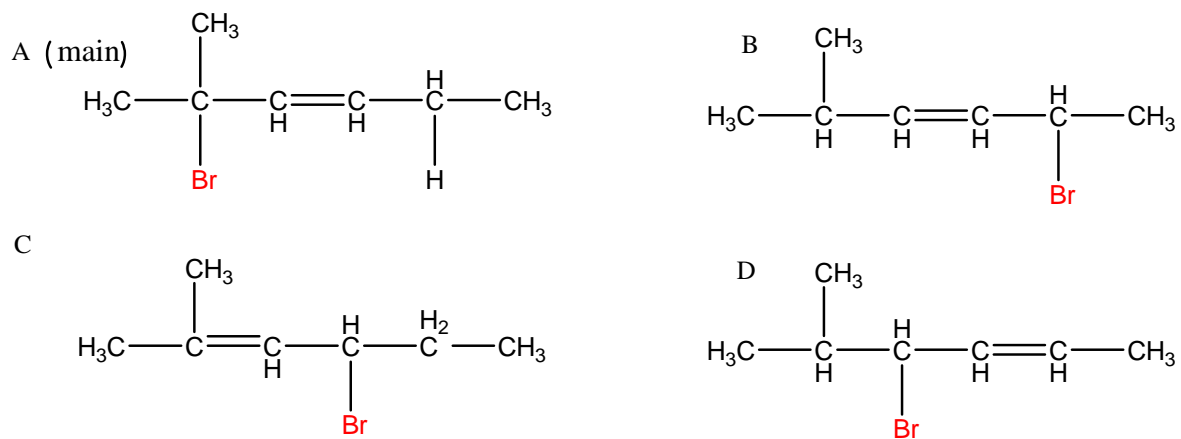
(a)



(b)

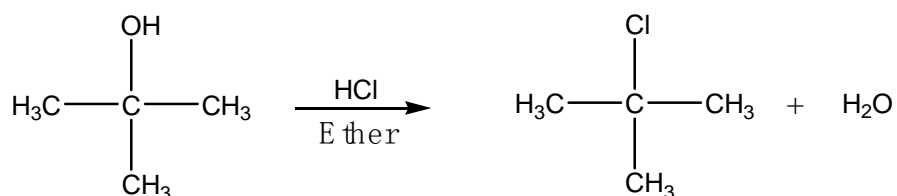
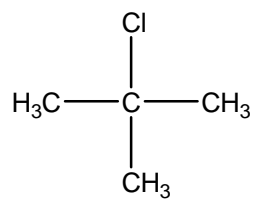


From the four radicals above, we can get four products drawn below:

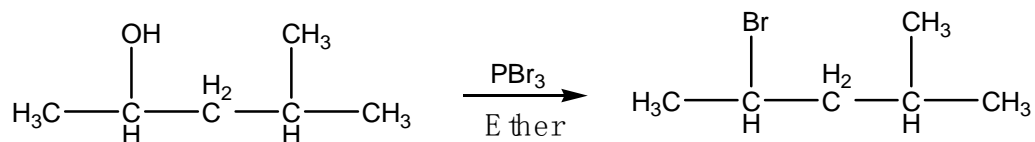
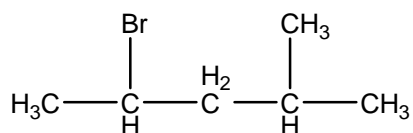


How do you prepare the following alkyl halides from the corresponding alcohols?

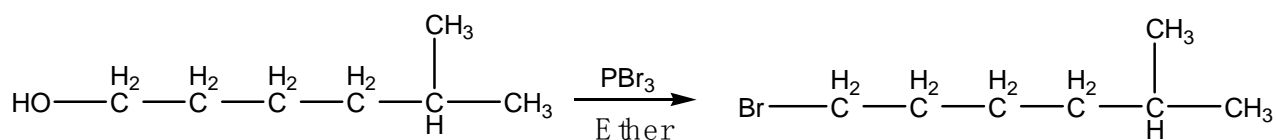
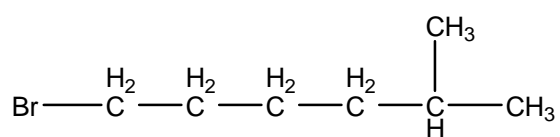
(a)



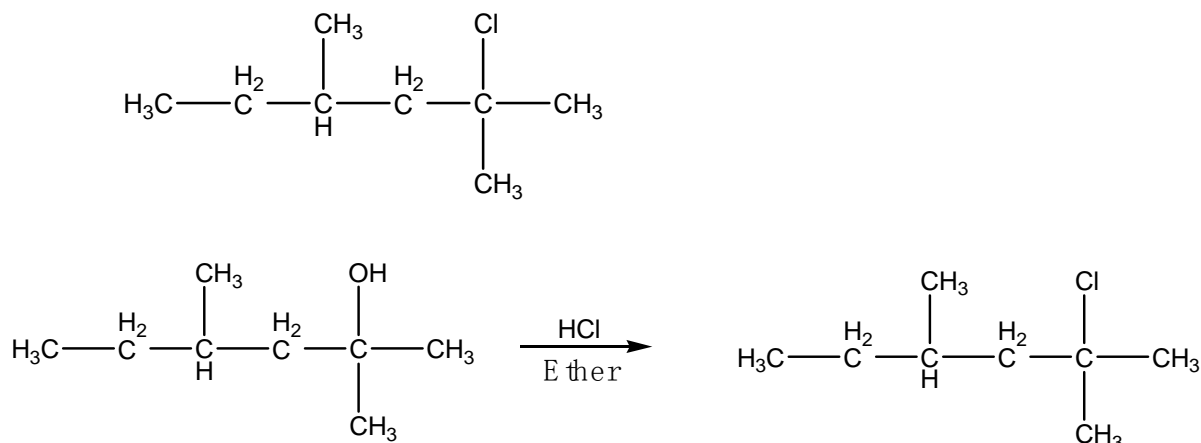
(b)



(c)

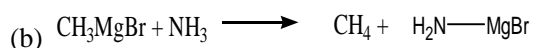
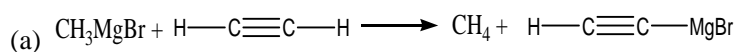


(d)



10.9

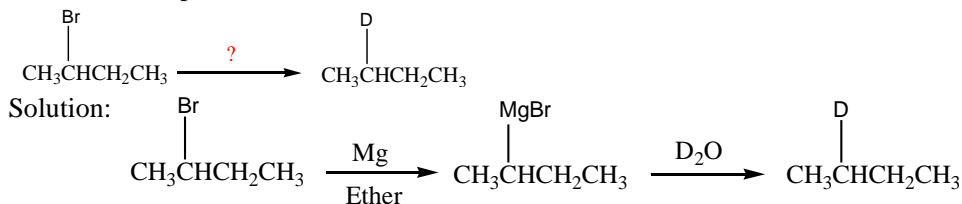
Just how strong a base would you expect a Grignard reagent to be? Look at Table 8.1, and predict whether the following reactions will occur as written. (The pK_a of NH_3 is 35)



Solution: The Grignard reagent can be thought of as the magnesium salt of a hydrocarbon acid. Because hydrocarbons are very weak (pK_a 's in the range 44 to 60), it is very strong base. All the two reactions can occur.

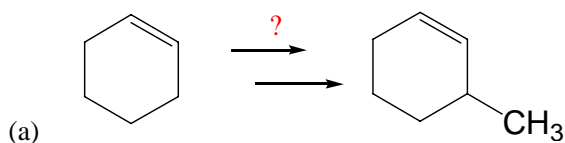
10.10

How might you replace a halogen substituent by a deuterium atom if you wanted to prepare a deuterated compound?

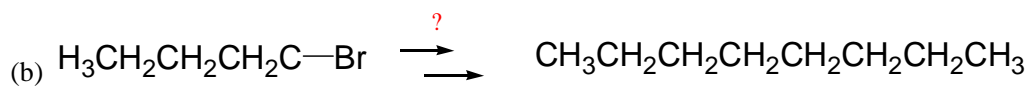
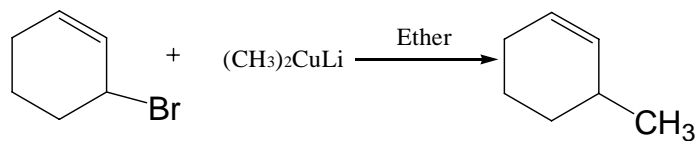
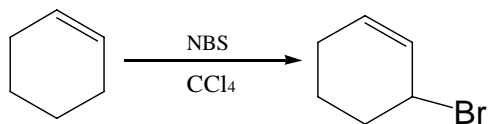


10.11

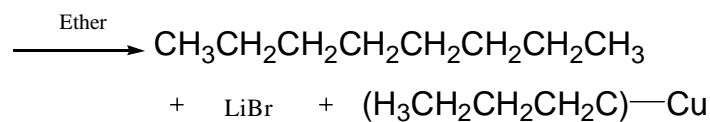
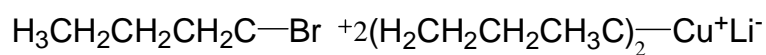
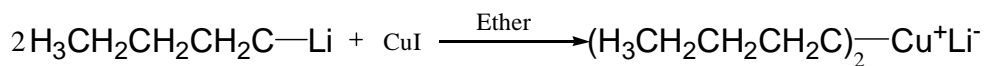
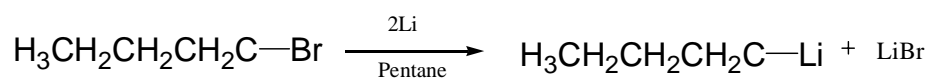
How would you carry out the following transformations using an organocopper coupling reaction? More than one step is required in each case.



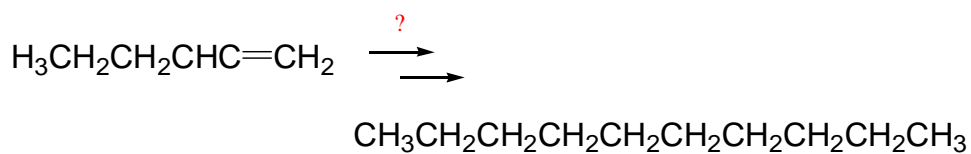
Solution:



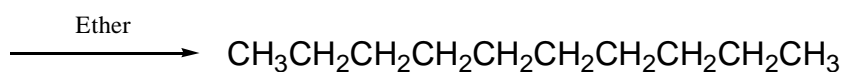
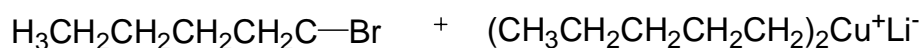
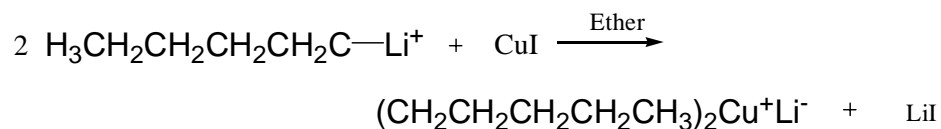
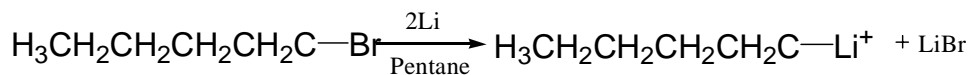
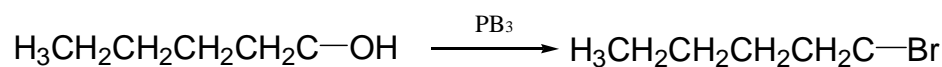
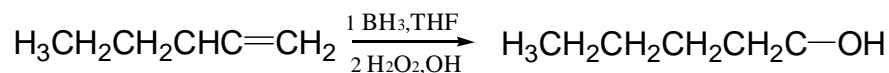
Solution:



(c)



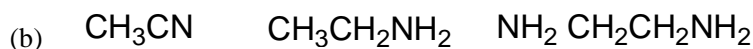
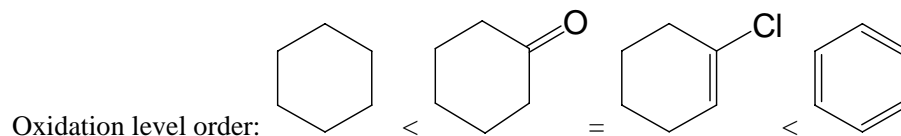
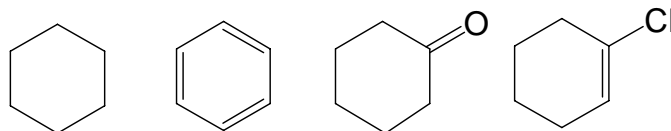
Solution:



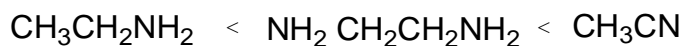
10.12

Rank each of the following series of compounds in order of increasing oxidation level:

(a)



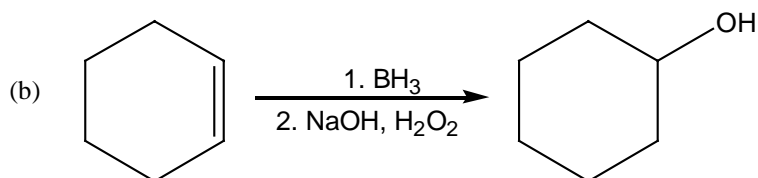
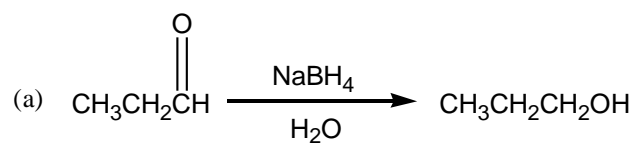
Oxidation level order:



10.13

Tell whether each of the following reaction is an oxidation, a reduction, or neither.

Explain your answer.



Solution: (a) Because of breaking one C-O, so it is reduction.

(b) Because of forming one C-O and forming one C-H, so it is neither reduction nor oxidation.

10.14

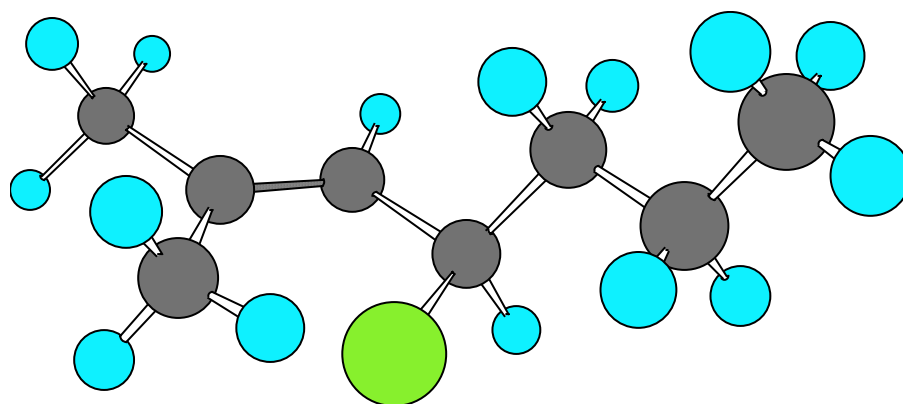
Give an IUPAC name for each of the following alkyl halides (yellow-green=Cl):

(a)



cis-1-Chloro-3-methyl-cyclohexane

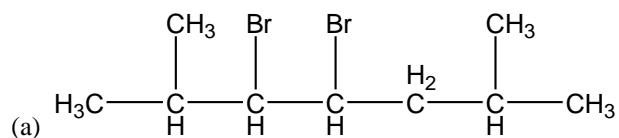
(b)



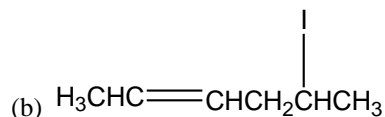
4-chloro-2-methyl-2-heptene

10.17

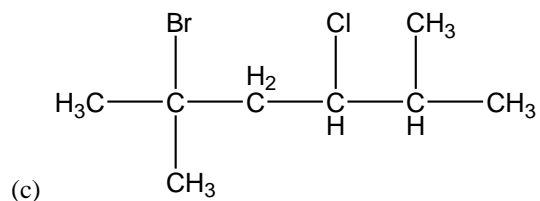
Name the following alkyl halides according to IUPAC rules:



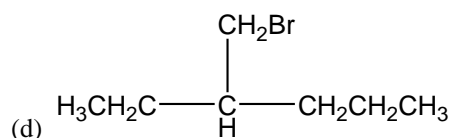
Solution: 3,4-dibromo-2,6-dimethyl-heptane



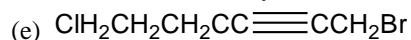
Solution: 5-iodo-2-hexene



Solution: 2-bromo-4-chloro-2,5-dimethyl-hexane



Solution: 3-bromomethylhexane

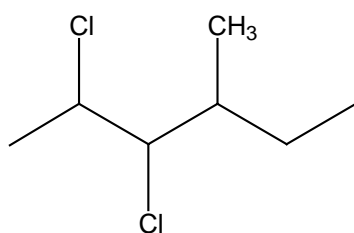


Solution: 1-bromo-6-chloro-2-hexyne

10.18

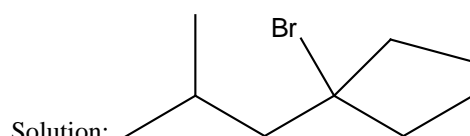
Draw structures corresponding to the following IUPAC names:

(a) 2,3-Dichloro-4-methylhexane



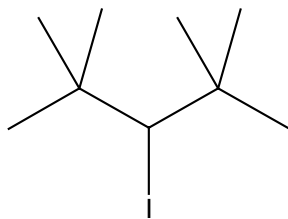
Solution:

(b) 4-bromo-4-ethyl-2-methylhexane



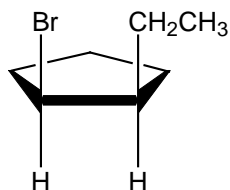
Solution:

(c) 3-iodo-2,2,4,4-tetramethylpentane



Solution:

(d) cis-1-bromo-2-ethylcyclopentane



Solution:

10.19:

Draw and name the monochlorination products you might obtain by radical chlorination of 2-methylbutane. Which of the products are chiral? Are any of the products optically active?

Solution: As there are four kinds of hydrogen atoms, so there should be four kinds of products, which are (a):1-chloro-2-methylbutane, (b):2-chloro-2-methylbutane, (c):3-chloro-2-methylbutane and (d):4-chloro-2-methylbutane.

The products (a) and (c) are chiral. And the products (a) and (c) are optically active.

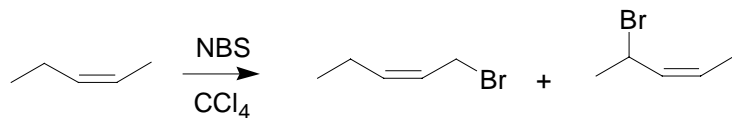
10.20:

A chemist requires a large amount of 1-bromo-2-pentene as starting material for a synthesis and decides to carry out an NBS allylic bromination reaction:



What is wrong with this synthesis plan? What side products would form in addition to the desired product?

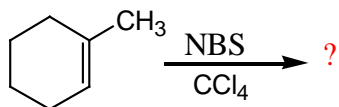
Solution:

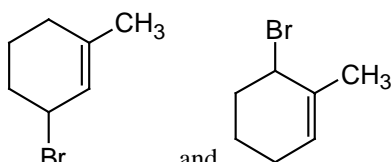


Mixture will be obtained.

10.21

What product(s) would you expect from the reaction of 1-methylcyclohexene with NBS? Would you use this reaction as part of a synthesis?





Solution: The products will be

and

As a part of synthesis I will not use this reaction. Because from this reaction I will get two mixed products. But usually in synthesis we only need one single product.

10.22

How would you prepare the following compounds, starting with cyclopentene and any other reagents needed?

(a) Chlorocyclopentane

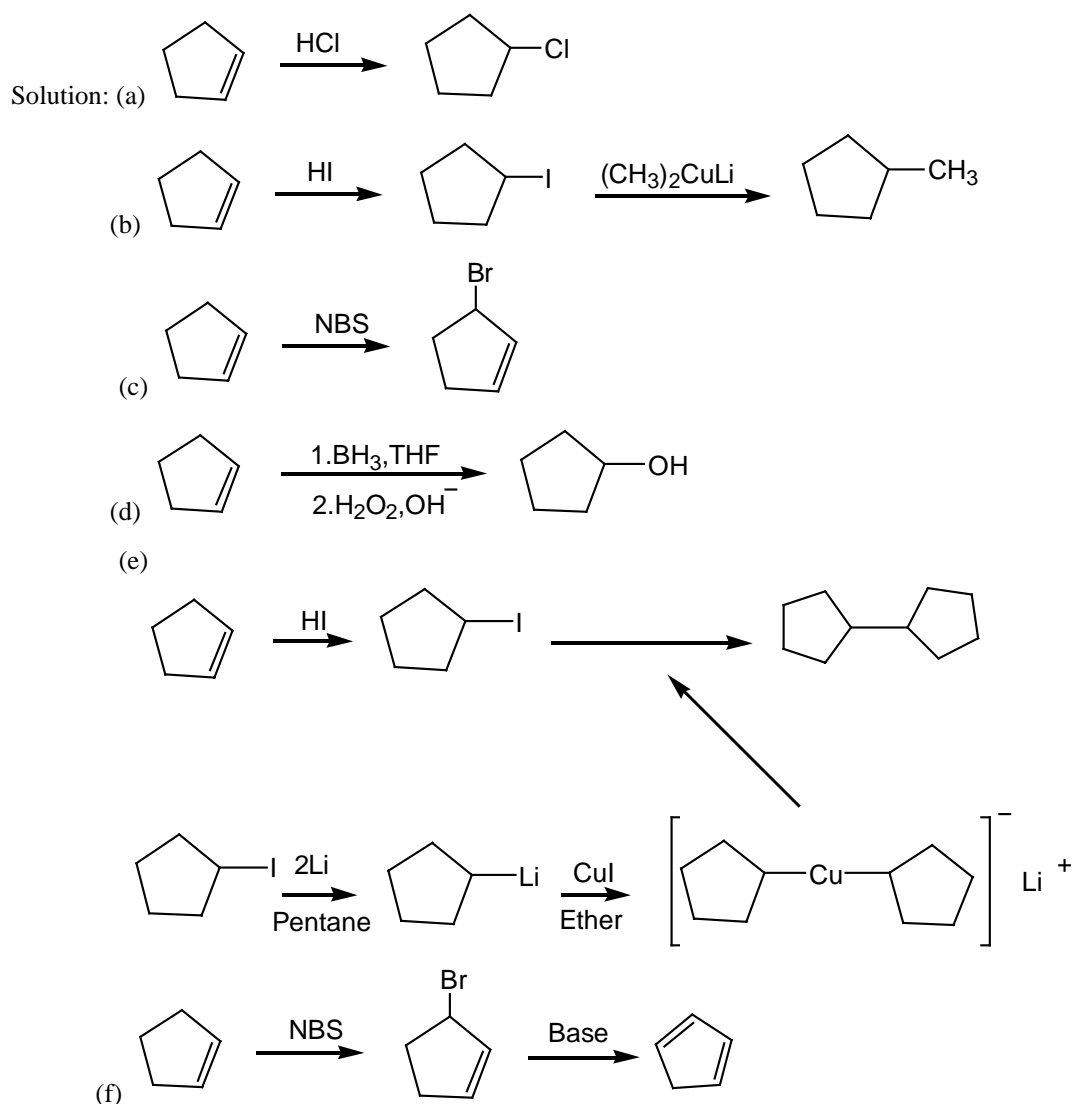
(b) Methylcyclopentane

(c) 3-Bromocyclopentene

(d) Cyclopentanol

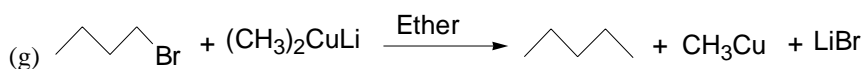
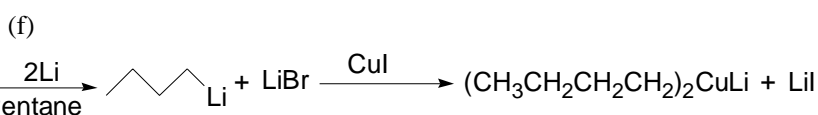
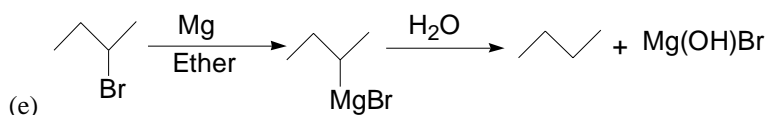
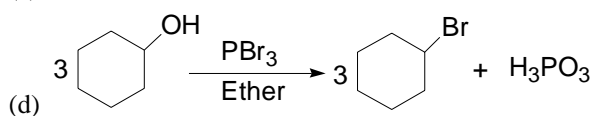
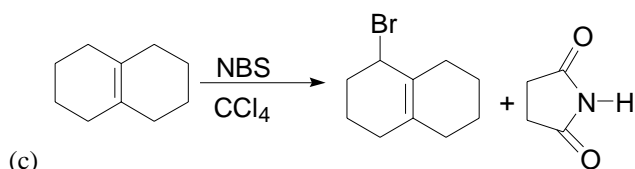
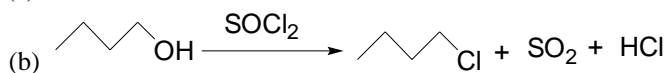
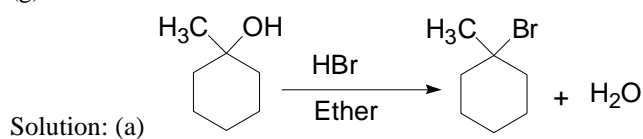
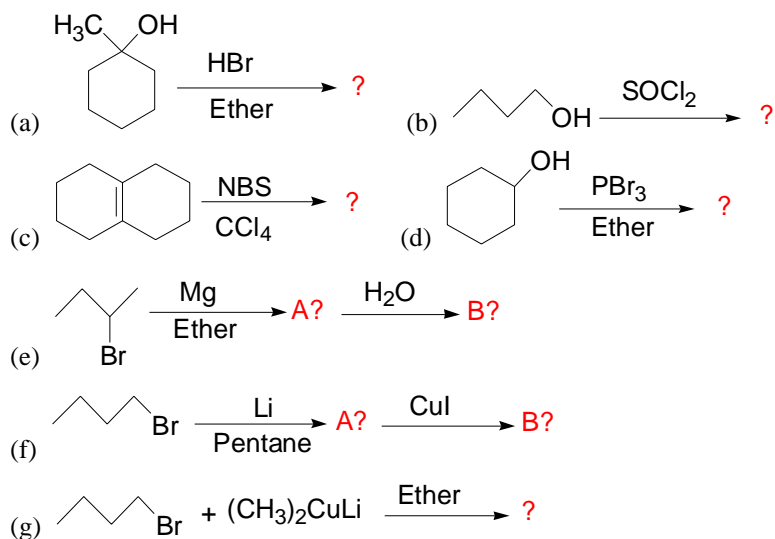
(e) Cyclopentylcyclopentane

(f) 1,3-Cyclopentadiene



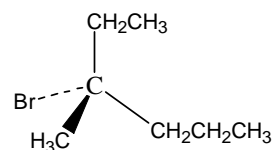
10.23

Predict the product(s) of the following reactions:

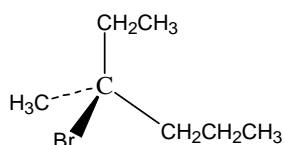


10.24

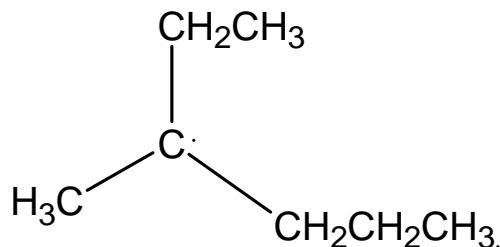
(S)-3-Methylhexane undergoes radical bromination to yield optically inactive 3-bromo-3-methylhexane as the major product. Is the product chiral? What conclusions can you draw about the radical intermediate?



Solution: Two stereoisomers of the product are formed. (R)-3-bromo-3-methylhexane and



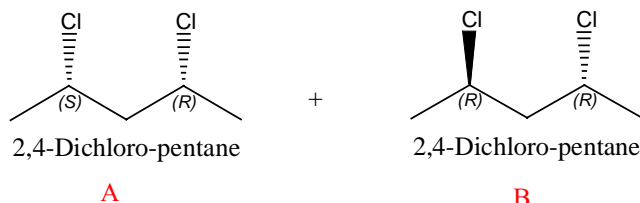
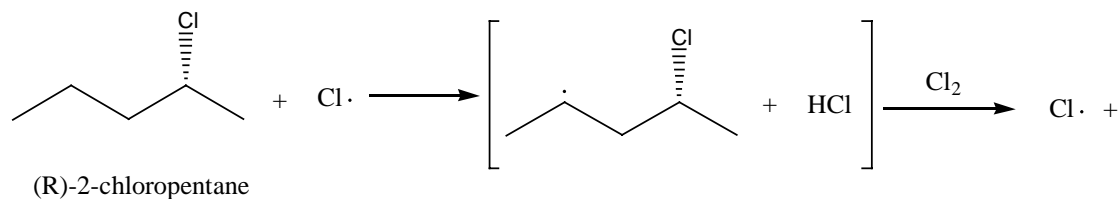
(S)-3-bromo-3-methylhexane. They are all chiral and form in a ratio of 1:1.



Conclusions: The radical intermediate is and the two sides have equal chance to be attacked.

10.25

Assume that you have carried out a radical chlorination reaction on (R)-2-chloropentane and have isolated (in low yield) 2,4-dichloropentane. How many stereoisomers of the product are formed and in what ratio? Are any of the isomers optically active? (See Problem 10.24)



Solution:

Two stereoisomers of the product are formed in 1 : 1 ratio. The first one (A) is a meso compound, so it is optically inactive. The second one (B) is optically active.

10.26

Calculate ΔH for the reactions of $\text{Cl}\cdot$ and $\text{Br}\cdot$ with CH_4 , and then draw a reaction energy diagram showing both processes. Which reaction is likely to be faster?

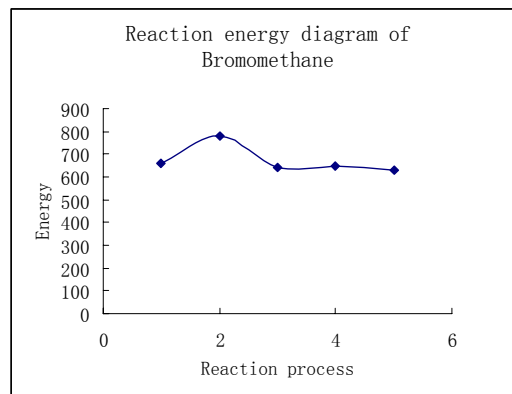
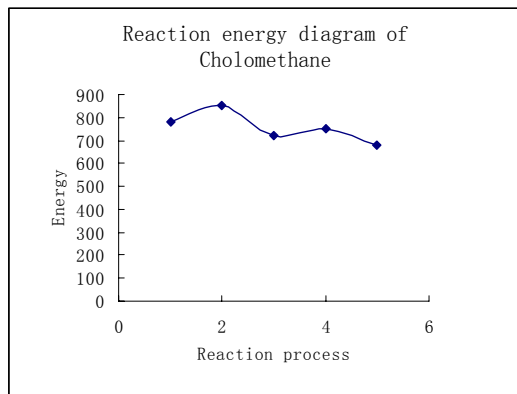
Solution:

Product bonds formed		Reactant bonds broken	
C-Cl	D=351kJ/mol	C-H	D=438kJ/mol
H-Cl	D=432kJ/mol	Cl-Cl	D=243kJ/mol
Total	D=783kJ/mol	Total	D=681kJ/mol
$\Delta H = 681 - 783 = -102\text{kJ/mol}$			
Product bonds formed		Reactant bonds broken	

C-Br	D=293kJ/mol	C-H	D=438kJ/mol
H-Br	D=366kJ/mol	Br-Br	D=193kJ/mol
Total	D=659kJ/mol	Total	D=631kJ/mol

$$\Delta H = 631 - 659 = -28 \text{ kJ/mol}$$

The reaction energy diagram:



The reaction between Chlorine radical and methane is much faster.

10.27

Use the bond dissociation energies listed in Table 5.3 on page 154 to calculate ΔH^0 for the reactions of Cl^\cdot and Br^\cdot with a secondary hydrogen atom of propane. Which reaction would you expect to be more selective?

$$\text{For Cl}^\cdot: \Delta H^0 = 401 - 339 = 62 \text{ kJ/mol}$$

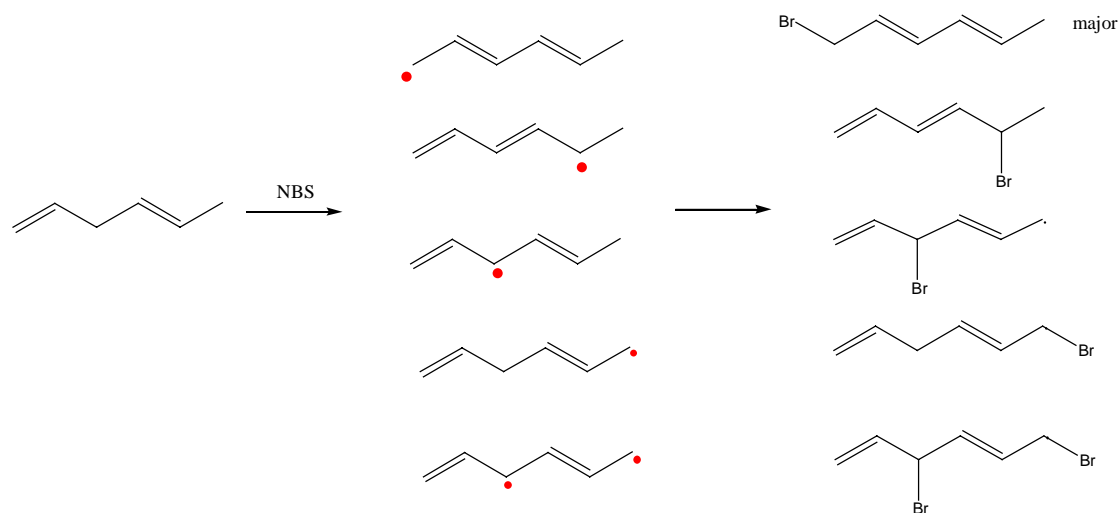
$$\text{For Br}^\cdot: \Delta H^0 = 401 - 274 = 127 \text{ kJ/mol}$$

It is clear that Cl^\cdot has higher reactivity while Br^\cdot has lower reactivity; thus according to "lower reactivity higher selectivity", the reaction of Br^\cdot with a secondary hydrogen atom of propane is more selective.

10.28

What product(s) would you expect from the reaction of 1, 4-hexdiene with NBS? What is the structure of the most stable radical intermediate?

Solution: The reaction will be following:

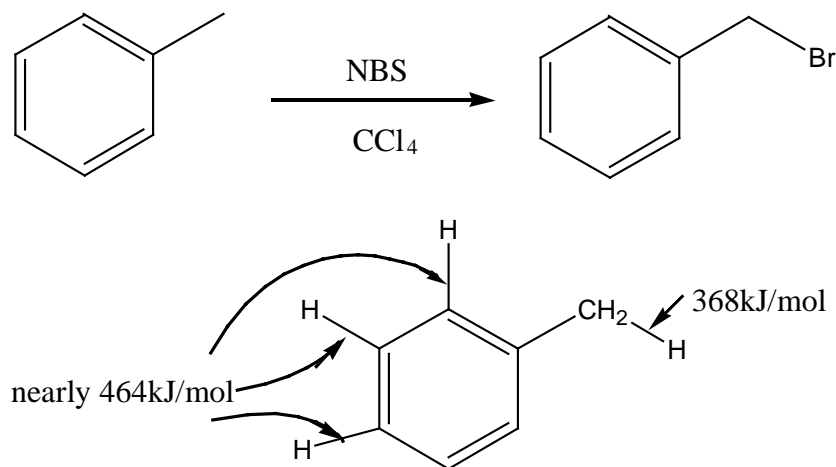


That's because of relative stability of conjugated diene.

10.29

Alkyl benzenes such as toluene (methylbenzene) react with NBS to give products in which bromine substitution has occurred at the position next to the aromatic ring (the benzylic position). Explain, based on the bond dissociation energies in Table 5.3

The reason is show bellow:

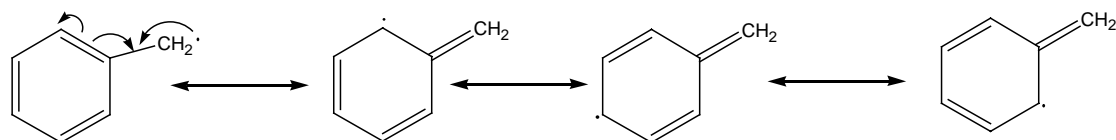


The carbon hydrogen bond of the methyl has the lowest bond dissociation energy, so this bond is most likely to be broken and yields the most stable radical.

10.30:

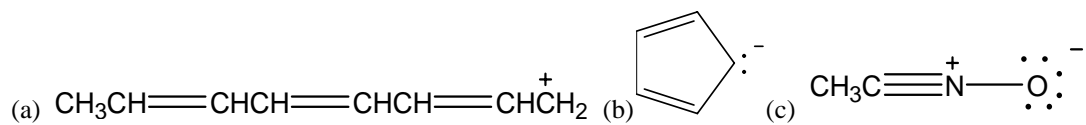
Draw resonance structures for the benzyl radical, $C_6H_5CH_2\cdot$, the intermediate produced in the NBS bromination reaction of toluene (Problem 10.29)

Solution:



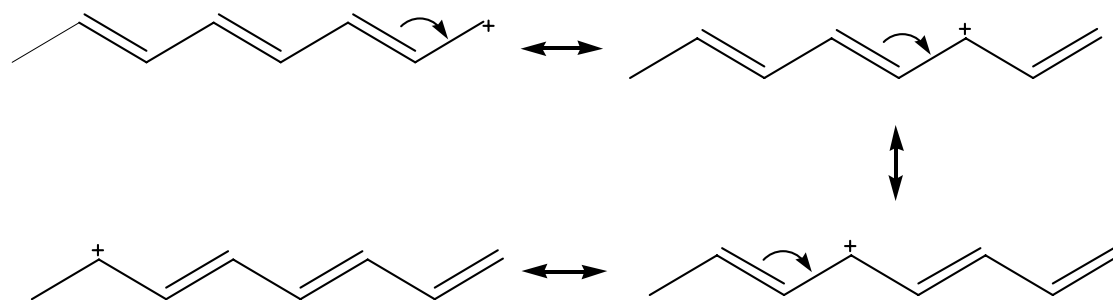
10.32

Draw resonance structure for the following species:

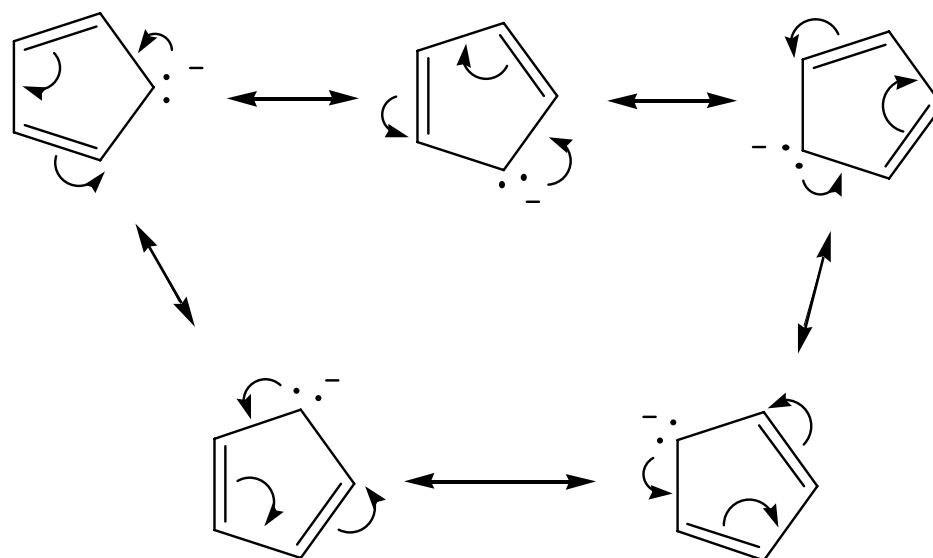


Solution:

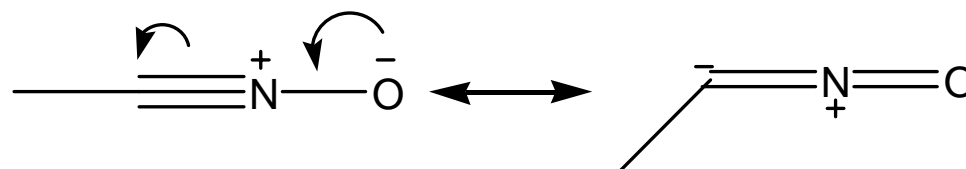
(a).



(b).

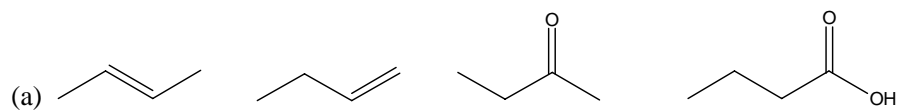


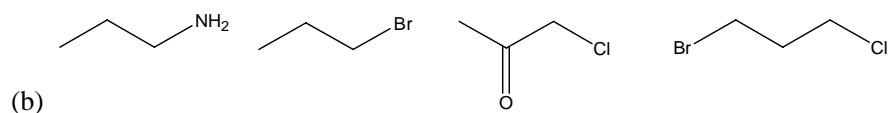
(c).



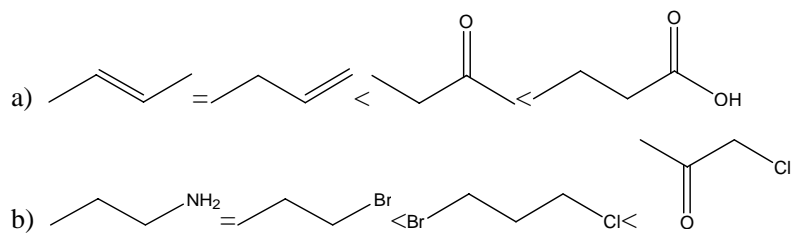
10.33

Rank the compounds in each of the following series in order of increasing oxidation level:



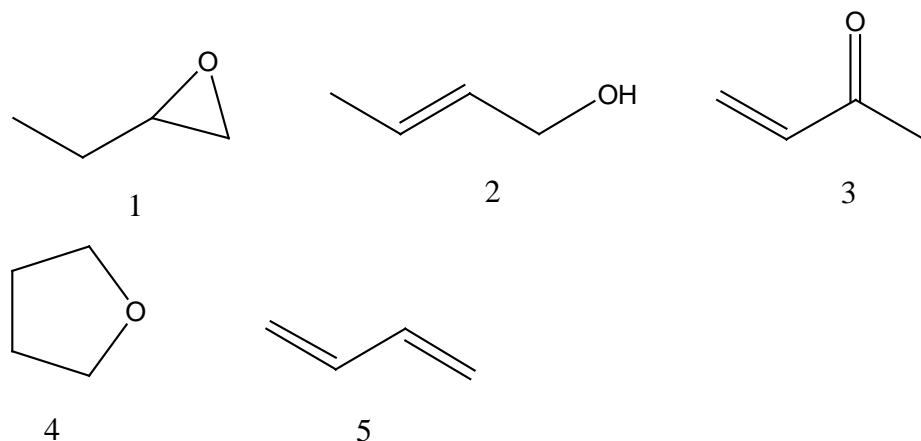


Solution:



10.34.

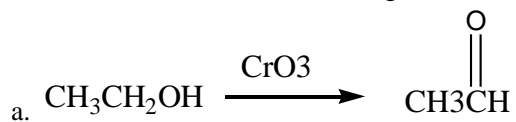
Which of the following compounds have the same oxidation level and which have different levels?



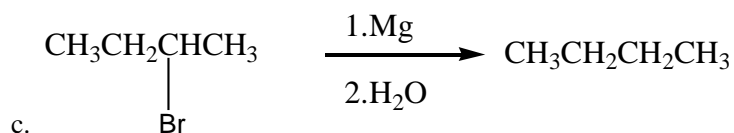
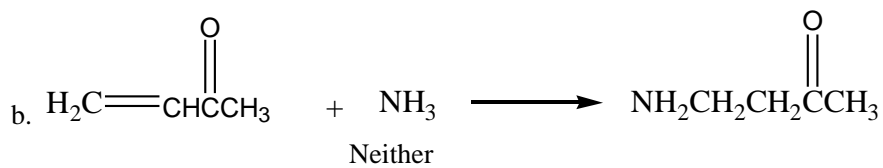
Solution: compound 1, 2, 4 have the same oxidation level and compound 3, 5 has different oxidation level.

10.35

Tell whether each of the following reactions is an oxidation or reduction:



Oxidation

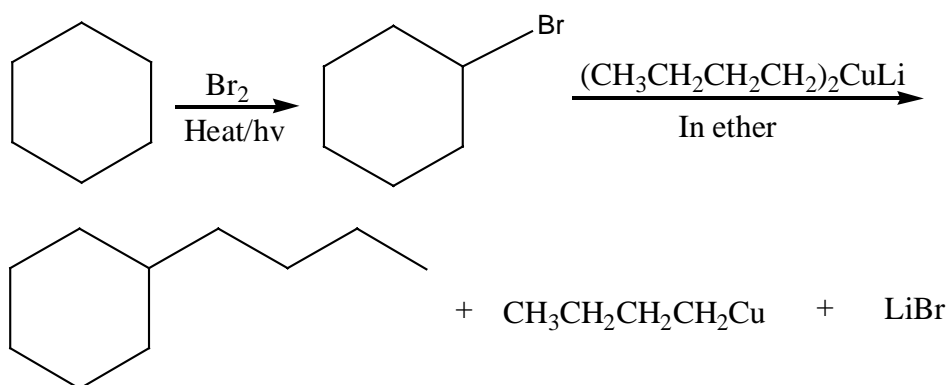
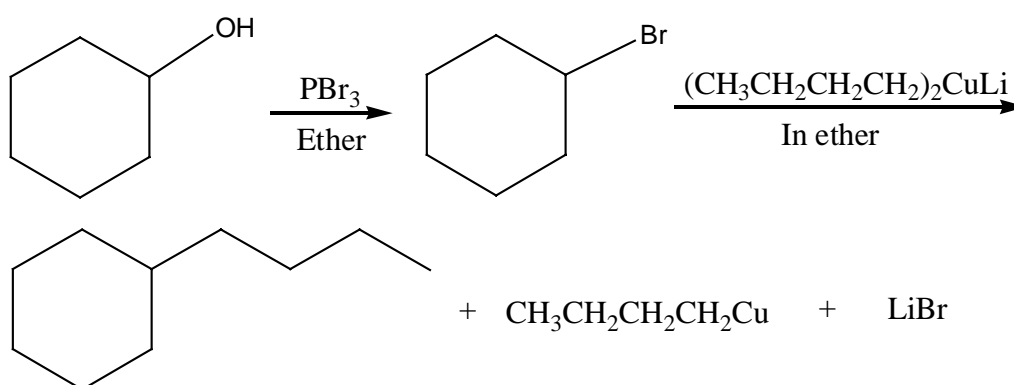
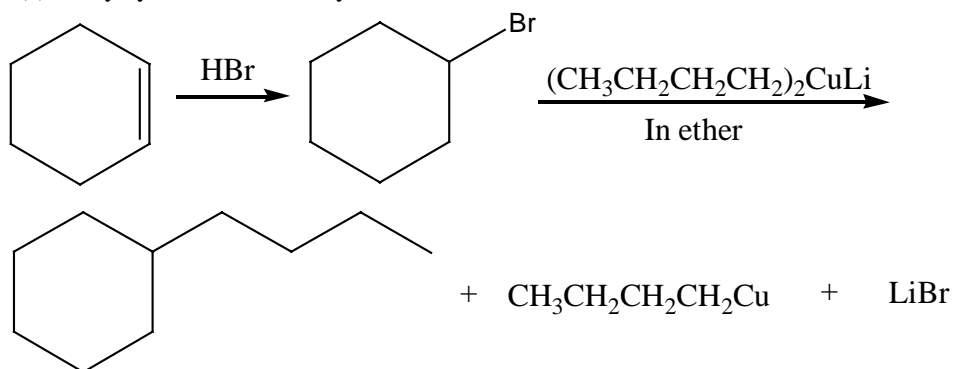


Reduction

10.36

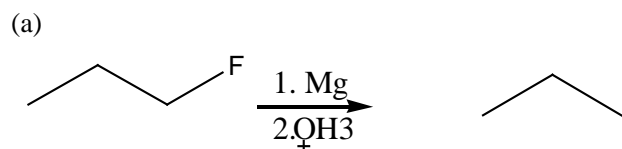
How would you carry out the following syntheses?

- (a) Butylcyclohexane from cyclohexene
- (b) Butylcyclohexane from cyclohexanol
- (c) Butylcyclohexane from cyclohexane

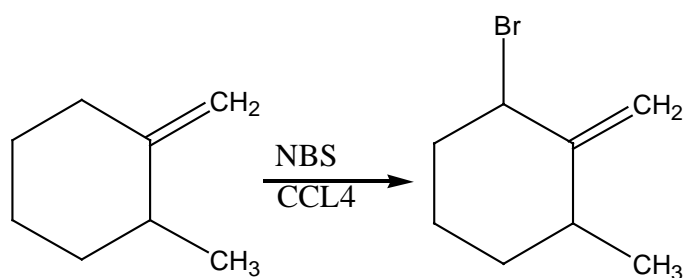


10.37

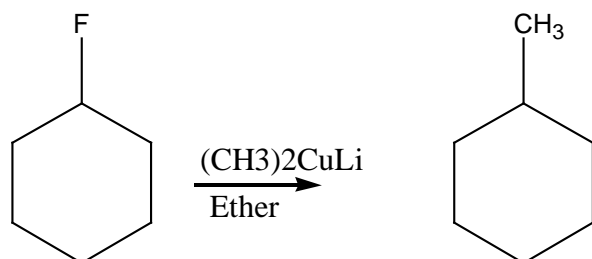
The syntheses shown here are unlikely to occur as written. What is wrong with each?



(b)



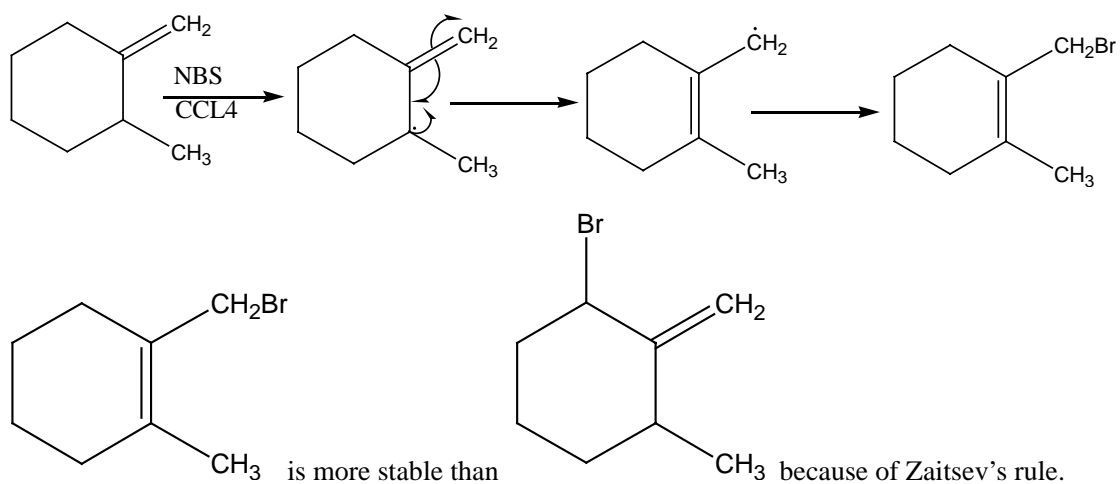
(c)



Solution:

(a) Organofluorides rarely react with magnesium. So there is no alkyl magnesium fluorides.

(b) The reaction reacts as follow:

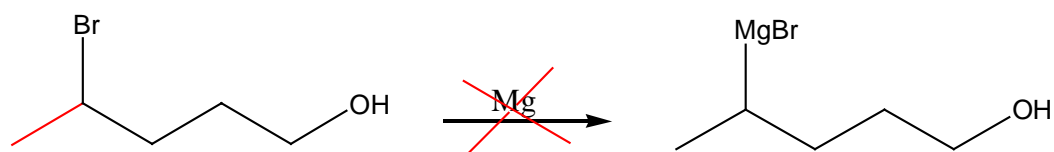


(c)

Gilman reagents couldn't react with fluorides because of high density of electron on fluorine atom. So this reaction could not occur.

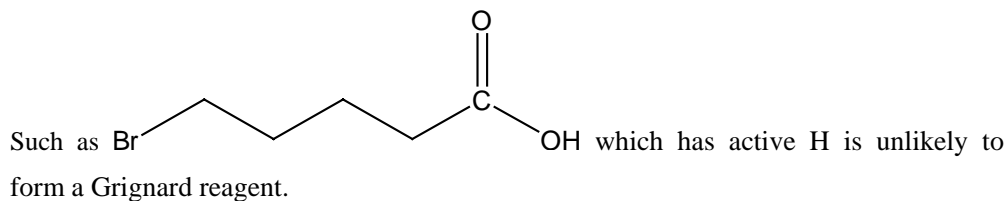
10.38

Why do you suppose it's not possible to prepare a Grignard reagent from a bromo alcohol such as 4-bromo-1-pentanol?



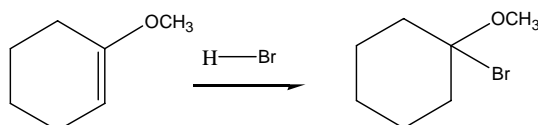
Give another example of a molecule that is unlikely to form a Grignard reagent.

Solution: If 4-bromo-1-pentanol can form a Grignard reagent, it will nucleophilically attack the active atom H in $-OH$, so it's not possible to prepare a Grignard reagent.



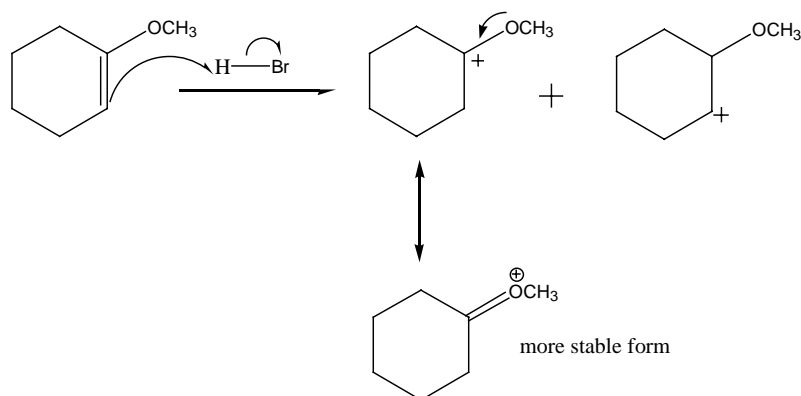
10.39

Addition of HBr to a double bond with an ether substituent occurs regioselectively to give a product in which the Br and OR are bonded to the same carbon:



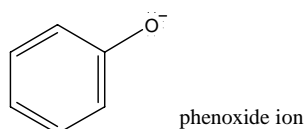
Draw two possible carbocation intermediates in this electrophilic addition reaction, and explain using resonance why the observed product is formed.

Answer:

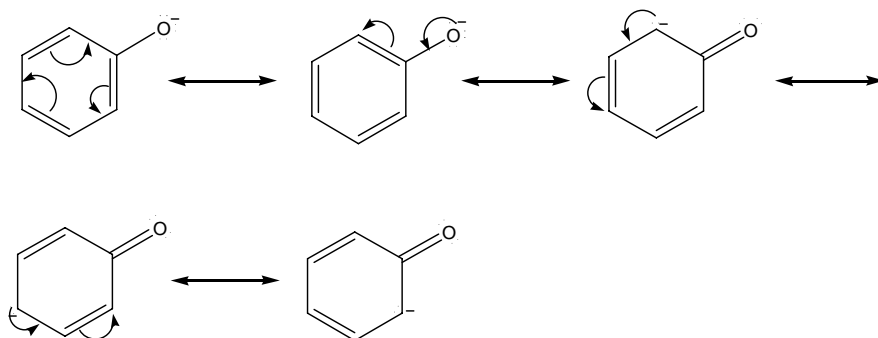


10.40

Phenols, compounds that have an $-OH$ group bonded to a benzene ring, are relatively acidic because their anions are stabilized by resonance. Draw resonance structures for the phenoxide ion.

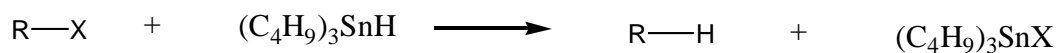


Solution:



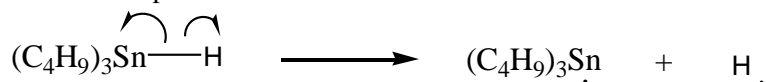
10.41

Alkyl halides can be reduced to alkanes by a radical reaction with tributyltin hydride, $(C_4H_9)_3SnH$, in the presence of light ($h\nu$):

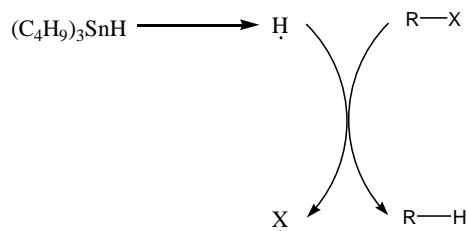


solution:

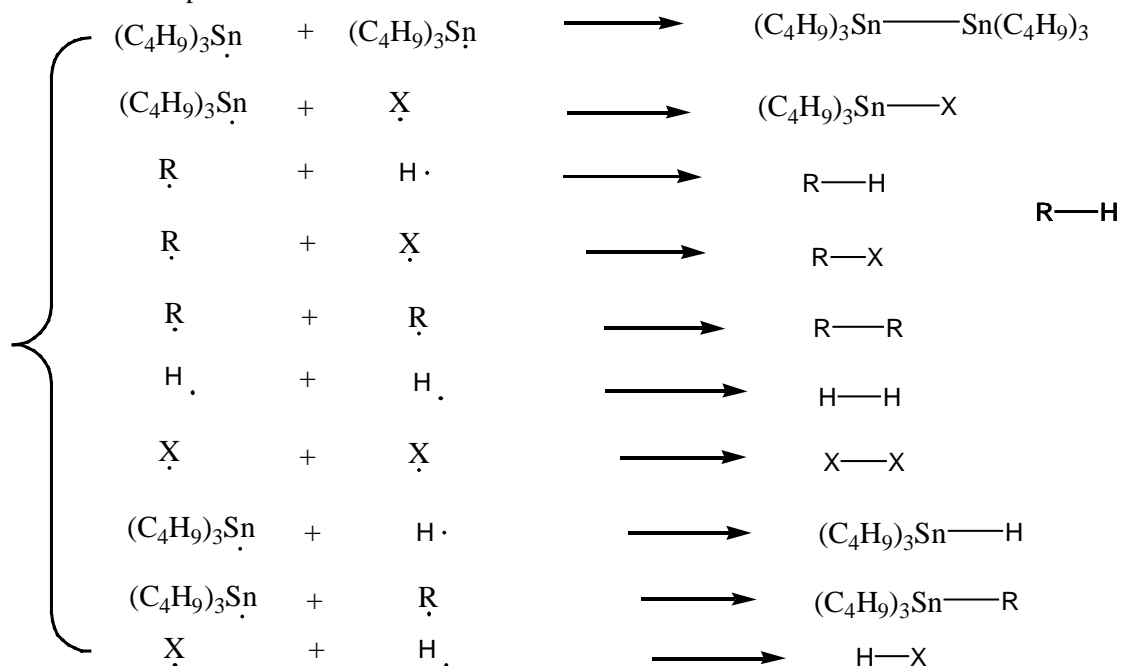
Initiation step:



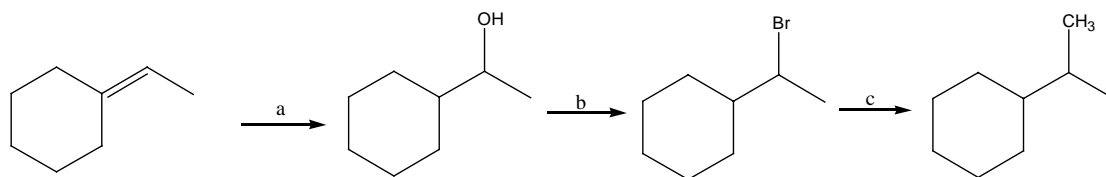
Propagation steps:



Termination steps:



10.42 Identify the reagents a-c in the following scheme:



Solution: a, 1) BH_3 , 2) OH^- , H_2O_2 ; b, PBr_3 ; c, 1) Li , 2) CuI , 3) CH_3I

10.43

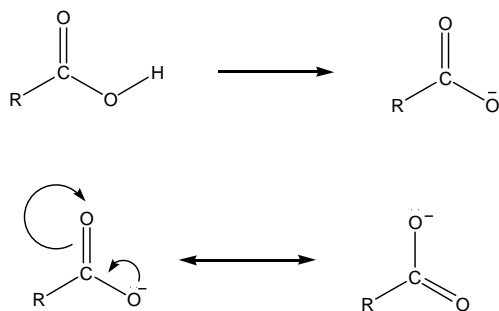
Tertiary alkyl halides, R_3CX , undergo spontaneous dissociation to yield a carboncation, R_3C^+ . Which do you think reacts faster, $(\text{CH}_3)_3\text{CBr}$, or $\text{H}_2\text{C}=\text{CHC}(\text{CH}_3)_2\text{Br}$? Explain

Solutions: $\text{H}_2\text{C}=\text{CHC}(\text{CH}_3)_2\text{Br}$. Because of double bond's conjugate effect. So the carboncation is more stable. And the ΔG is smaller. And as a result the reaction is faster.

10.44

Carboxylic acids (RCO_2H ; $\text{pK}_a \approx 5$) are approximately 10^{11} times more acidic than alcohols (ROH ; $\text{pK}_a \approx 16$). In other words, a carboxylate ion (RCO_2^-) is more stable than an alkoxide ion (RO^-). Explain, using resonance.

Solution:



The carboxylate ion has two resonance forms, which is rather than the alkoxide ion, only one

Form. Thus the RCO_2^- is much stable than RO^- .