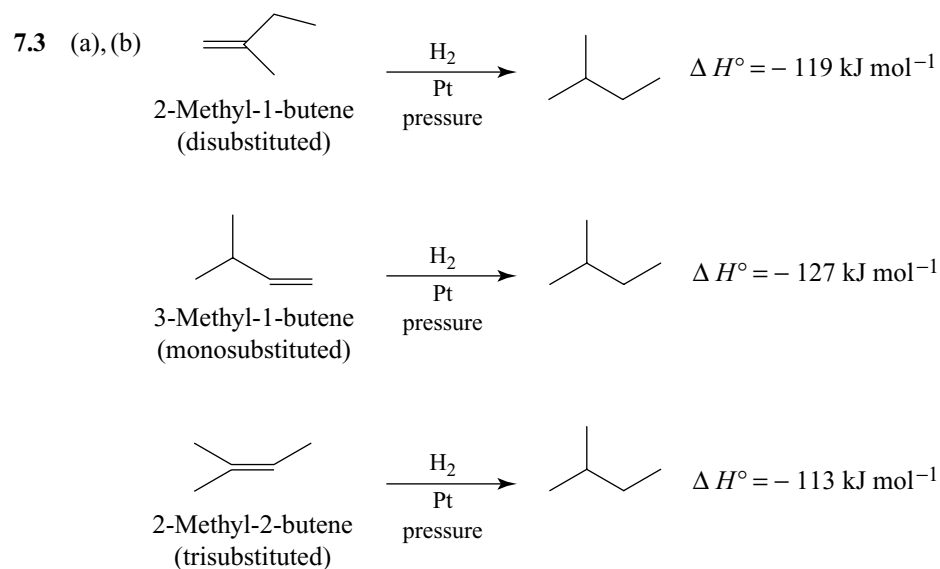
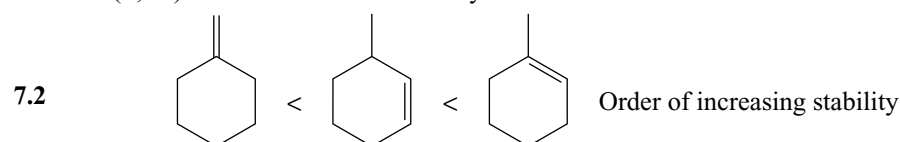


# 7

## ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS. ELIMINATION REACTIONS OF ALKYL HALIDES

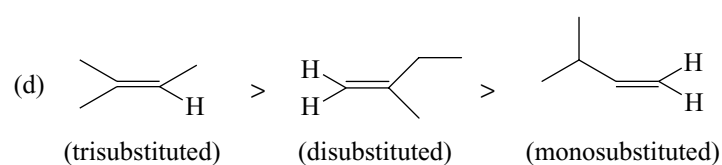
### SOLUTIONS TO PROBLEMS

- 7.1 (a) (*E*)-1-Bromo-1-chloro-1-pentene or (*E*)-1-Bromo-1-chloropent-1-ene  
 (b) (*E*)-2-Bromo-1-chloro-1-iodo-1-butene or (*E*)-2-Bromo-1-chloro-1-iodobut-1-ene  
 (c) (*Z*)-3,5-Dimethyl-2-hexene or (*Z*)-3,5-Dimethylhex-2-ene  
 (d) (*Z*)-1-Chloro-1-iodo-2-methyl-1-butene or (*Z*)-1-Chloro-1-iodo-2-methylbut-1-ene  
 (e) (*Z*,4*S*)-3,4-Dimethyl-2-hexene or (*Z*,4*S*)-3,4-Dimethylhex-2-ene  
 (f) (*Z*,3*S*)-1-Bromo-2-chloro-3-methyl-1-hexene or  
 (*Z*,3*S*)-1-Bromo-2-chloro-3-methylhex-1-ene

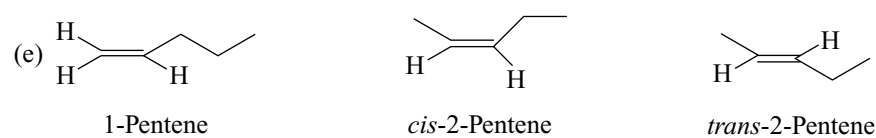


- (c) Yes, because hydrogenation converts each alkene into the same product.

## ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 107



Notice that this predicted order of stability is confirmed by the heats of hydrogenation. 2-Methyl-2-butene evolves the least heat; therefore, it is the most stable. 3-Methyl-1-butene evolves the most heat; therefore, it is the least stable.

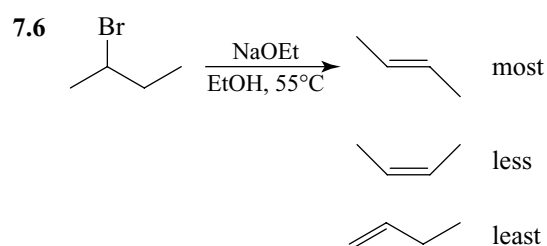


(f) Order of stability: *trans*-2-pentene > *cis*-2-pentene > 1-pentene

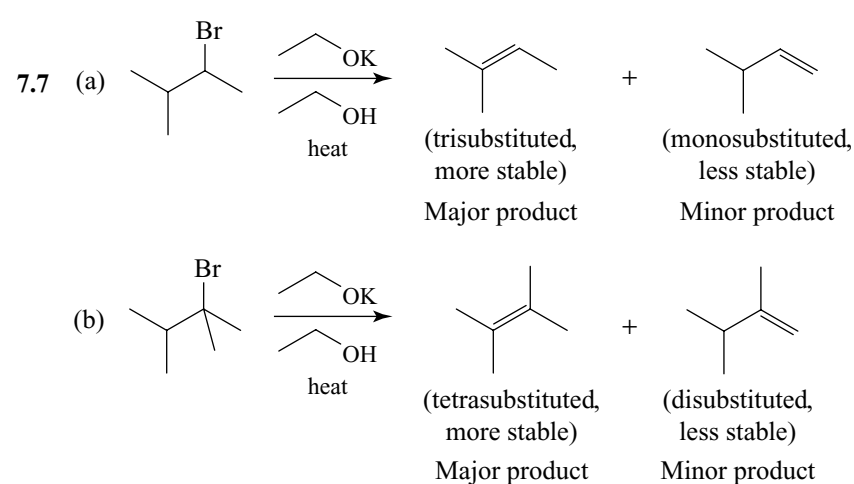
- 7.4** (a) 2,3-Dimethyl-2-butene would be the more stable because the double bond is tetra-substituted. 2-Methyl-2-pentene has a trisubstituted double bond.
- (b) *trans*-3-Hexene would be the more stable because alkenes with trans double bonds are more stable than those with cis double bonds.
- (c) *cis*-3-Hexene would be more stable because its double bond is disubstituted. The double bond of 1-hexene is monosubstituted.
- (d) 2-Methyl-2-pentene would be the more stable because its double bond is trisubstituted. The double bond of *trans*-2-hexene is disubstituted.

**7.5** The location of IR absorptions between  $600\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$  due to out-of-plane bending of alkene C—H bonds can be the basis of differentiation.

- (a) 2-Methyl-2-pentene,  $\sim 800\text{ cm}^{-1}$   
 2,3-Dimethyl-2-butene, no alkene C—H bonds
- (b) *cis*-3-Hexene,  $650\text{--}750\text{ cm}^{-1}$   
*trans*-3-Hexene,  $\sim 960\text{ cm}^{-1}$
- (c) 1-Hexene,  $\sim 900\text{ cm}^{-1}$  and  $\sim 1000\text{ cm}^{-1}$   
*cis*-3-Hexene,  $650\text{--}750\text{ cm}^{-1}$
- (d) *trans*-2-Hexene,  $\sim 960\text{ cm}^{-1}$   
 2-Methyl-2-pentene,  $\sim 800\text{ cm}^{-1}$

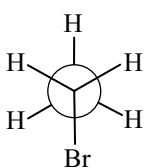


## 108 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

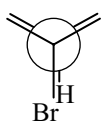


### 7.8 *t*-BuOK in *t*-BuOH

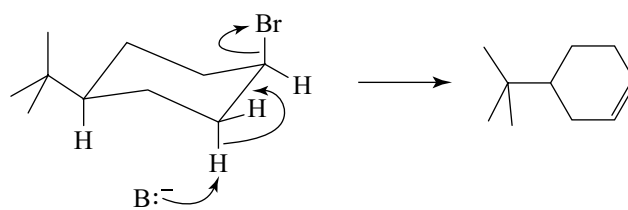
7.9 An anti coplanar transition state allows the molecule to assume the more stable staggered conformation,



whereas a syn coplanar transition state requires the molecule to assume the less stable eclipsed conformation.



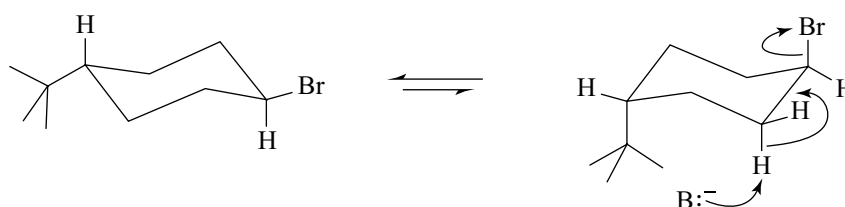
7.10 *cis*-1-Bromo-4-*tert*-butylcyclohexane can assume an anti coplanar transition state in which the bulky *tert*-butyl group is equatorial.



The conformation (above), because it is relatively stable, is assumed by most of the molecules present, and, therefore, the reaction is rapid.

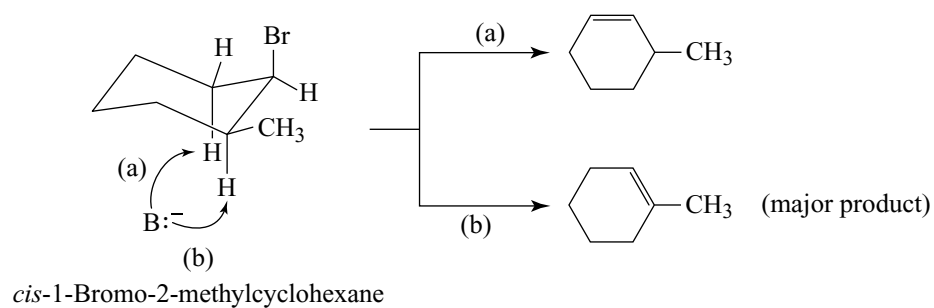
## ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 109

On the other hand, for *trans*-1-bromo-4-*tert*-butylcyclohexane to assume an anti coplanar transition state, the molecule must assume a conformation in which the large *tert*-butyl group is axial:

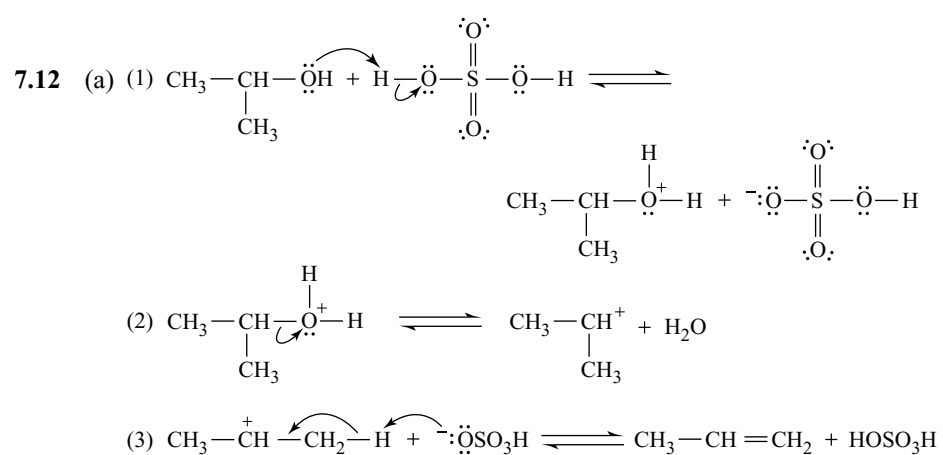
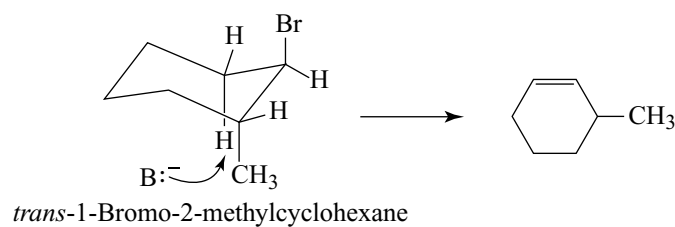


Such a conformation is of high energy; therefore, very few molecules assume this conformation. The reaction, consequently, is very slow.

**7.11** (a) Anti coplanar elimination can occur in two ways with the *cis* isomer.

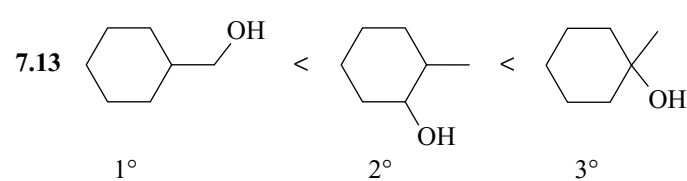


(b) Anti coplanar elimination can occur in only one way with the *trans* isomer.

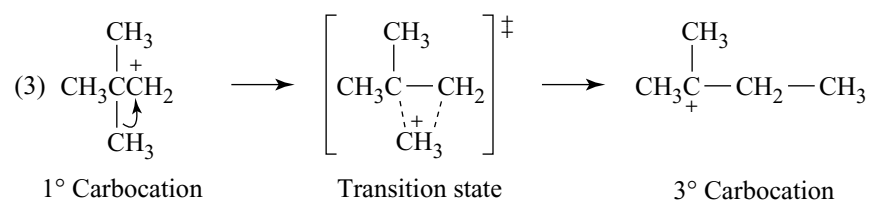
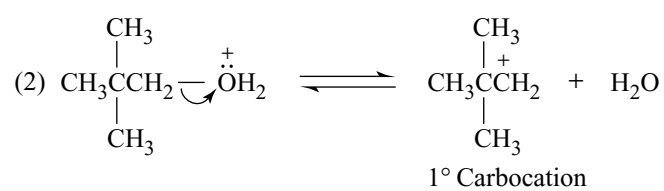
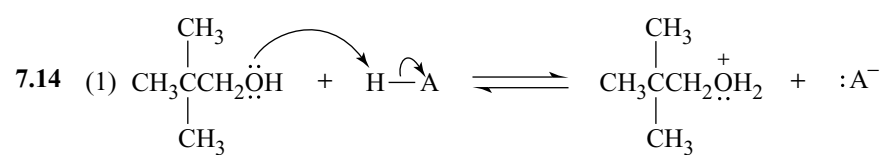


## 110 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

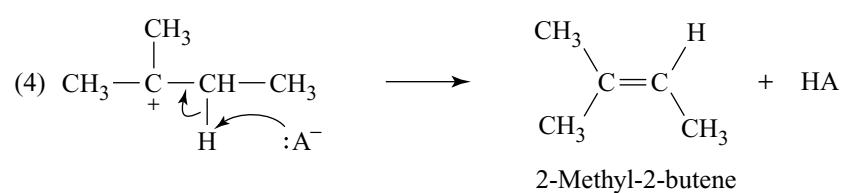
(b) By donating a proton to the —OH group of the alcohol in step (1), the acid allows the loss of a relatively stable, weakly basic, leaving group ( $\text{H}_2\text{O}$ ) in step (2). In the absence of an acid, the leaving group would have to be the strongly basic  $\text{OH}^-$  ion, and such steps almost never occur.



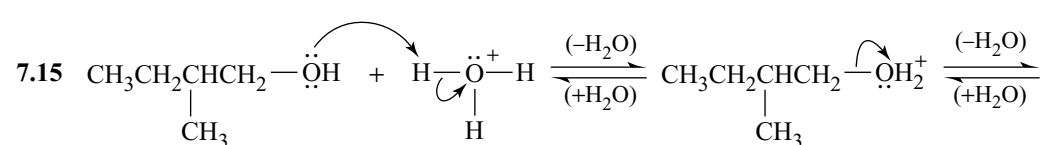
Order of increasing ease of dehydration



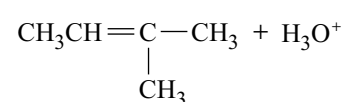
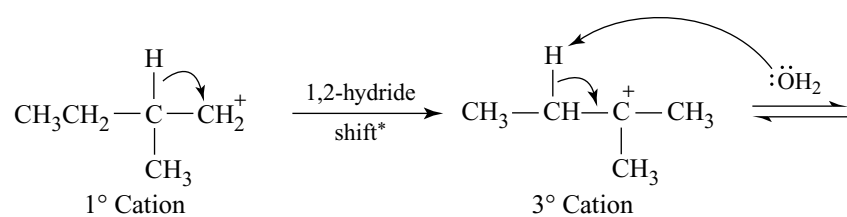
[Steps (2) and (3), ionization and rearrangement, may occur simultaneously.]



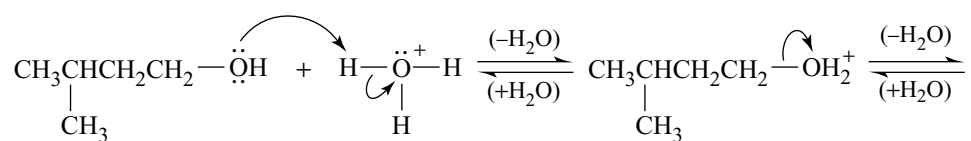
# ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 111



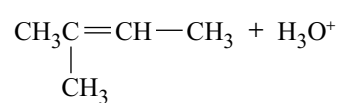
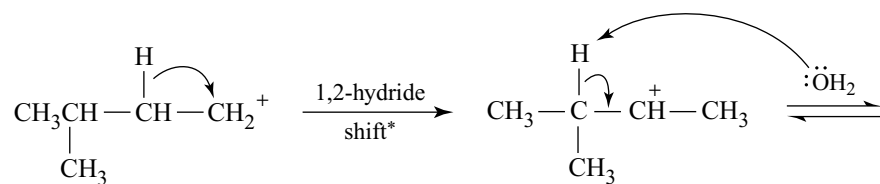
2-Methyl-1-butanol



2-Methyl-2-butene

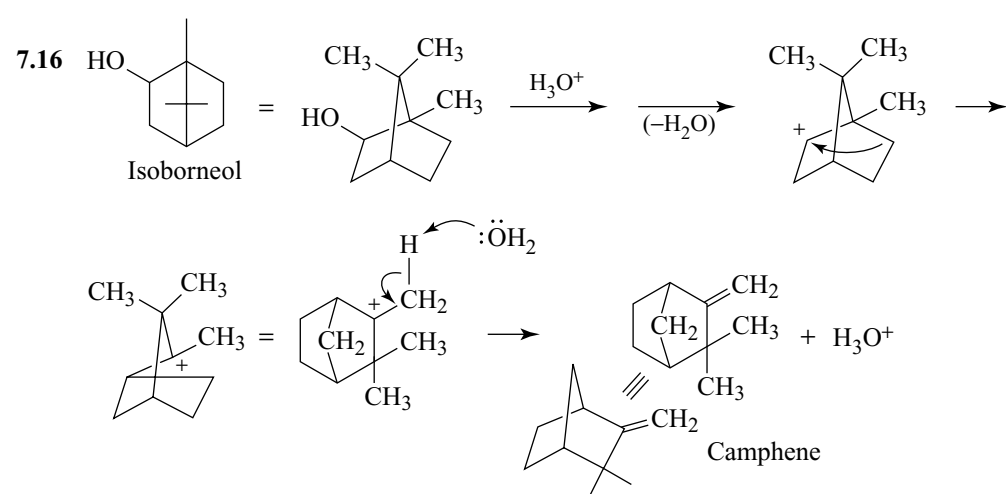


3-Methyl-1-butanol

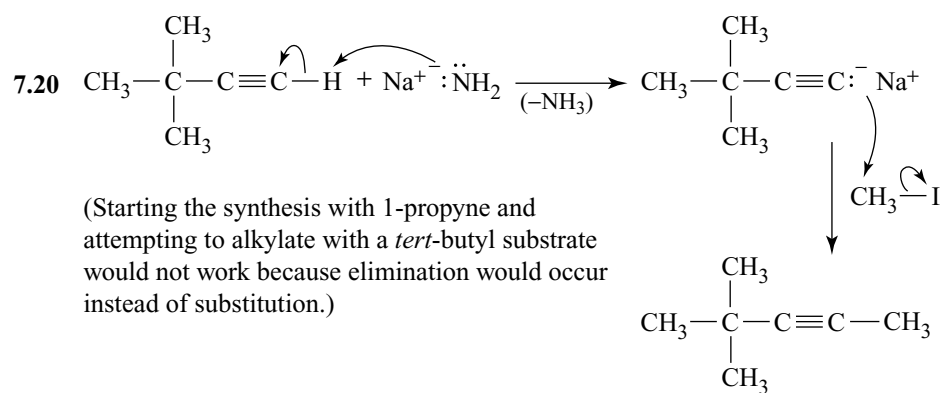
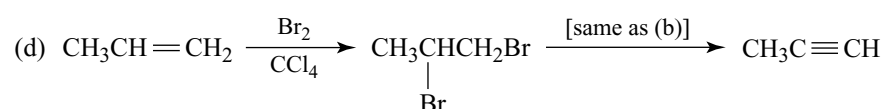
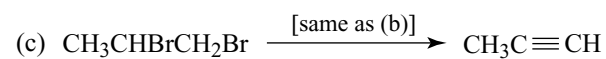
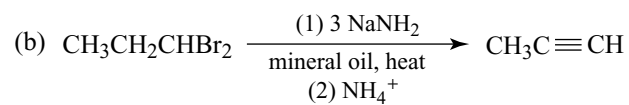
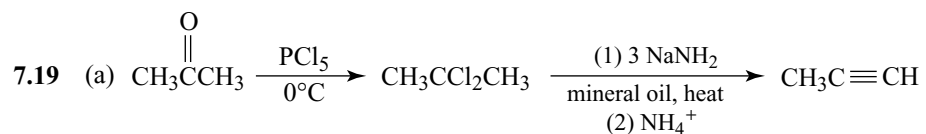
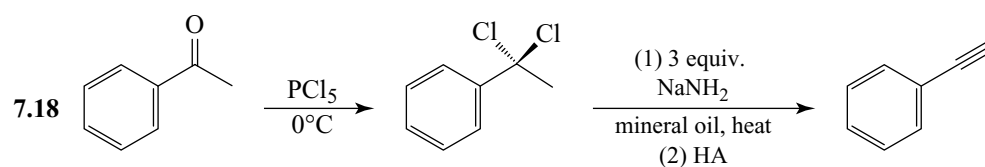
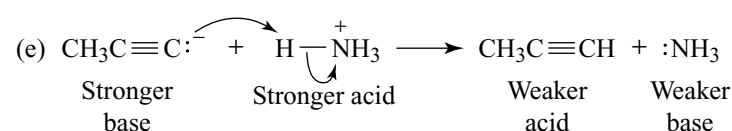
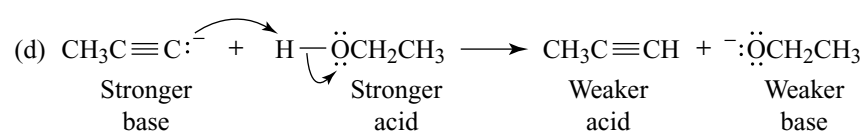
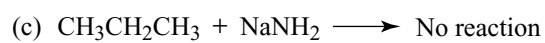
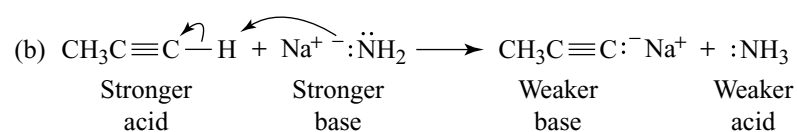
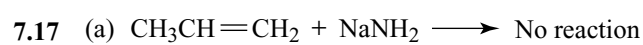


2-Methyl-2-butene

\* The hydride shift may occur simultaneously with the preceding step.



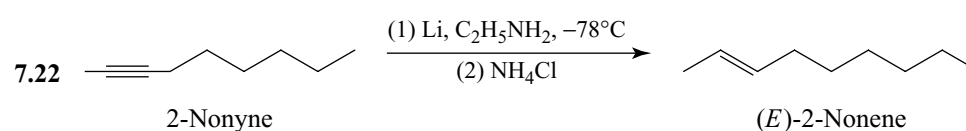
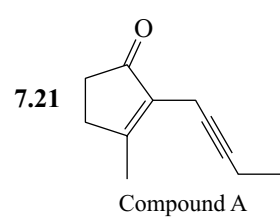
## 112 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS



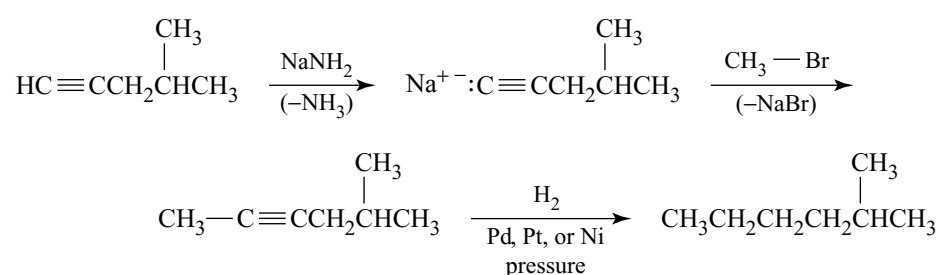
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 JWCL234-07 JWCL234-Solomons-v1

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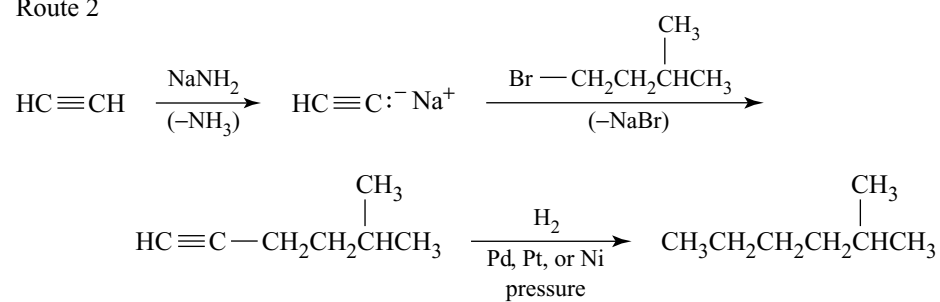
## ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 113



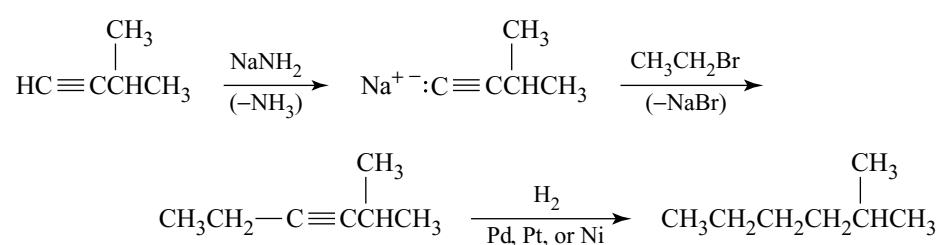
**7.23** Route 1



Route 2

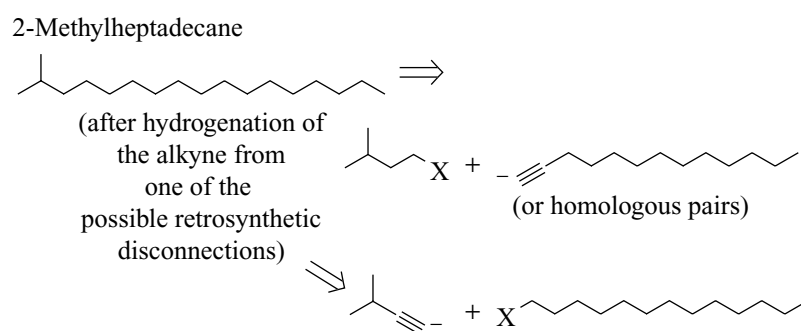
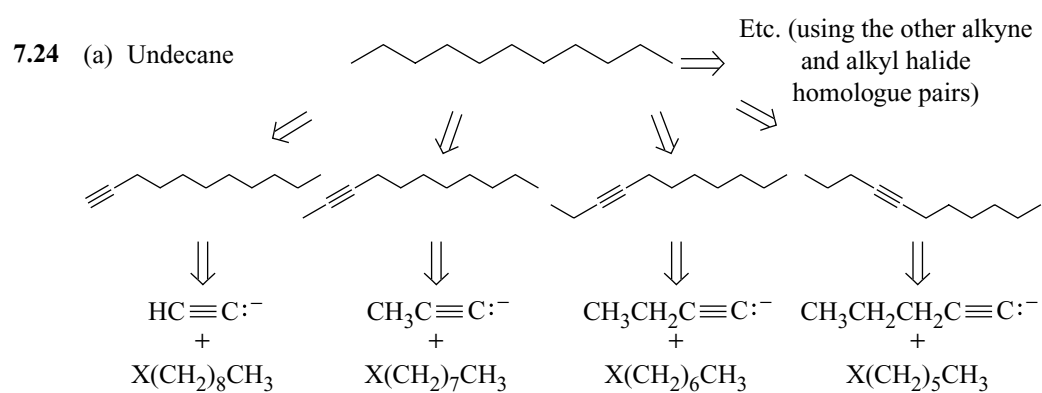


Route 3





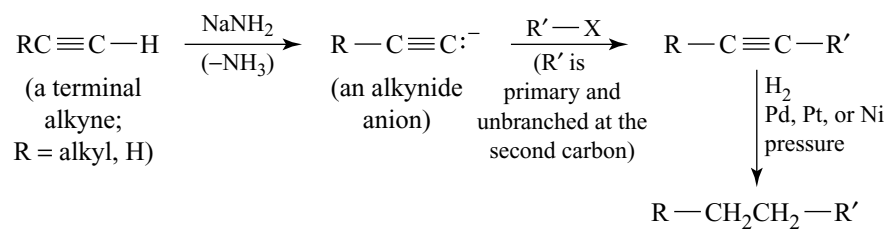
## 114 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS



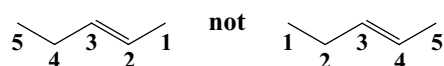
(Note that  $(\text{CH}_3)_2\text{CHX} + \text{C}\equiv\text{C}(\text{CH}_2)_6\text{CH}_3^-$  is not a good choice because the alkyl halide is branched at the carbon adjacent to the one which bears the halogen.)

Neither would  $(\text{CH}_3)_2\text{CHX} + \text{C}\equiv\text{C}(\text{CH}_2)_6\text{CH}_3^-$  work because the alkyl halide is secondary. Both of these routes would lead to elimination instead of substitution.)

(b) For any pair of reactants above that is a feasible retrosynthetic disconnection, the steps for the synthesis would be



**7.25** (a) We designate the position of the double bond by using the *lower* number of the two numbers of the doubly bonded carbon atoms, and the chain is numbered from the end nearer the double bond. The correct name is *trans*-2-pentene.

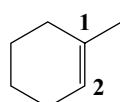


## ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 115

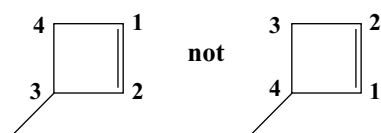
- (b) We must choose the longest chain for the base name. The correct name is 2-methylpropene.



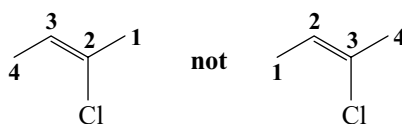
- (c) We use the lower number of the two doubly bonded carbon atoms to designate the position of the double bond. The correct name is 1-methylcyclohexene.



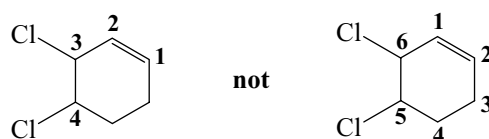
- (d) We must number the ring starting with the double bond in the direction that gives the substituent the lower number. The correct name is 3-methylcyclobutene.



- (e) We number in the way that gives the double bond *and the substituent* the lower number. The correct name is (Z)-2-chloro-2-butene or (Z)-2-chlorobut-2-ene.



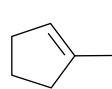
- (f) We number the ring starting with the double bond so as to give the substituents the lower numbers. The correct name is 3,4-dichlorocyclohexene.



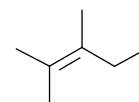
7.26 (a)



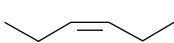
(b)



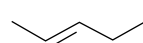
(c)



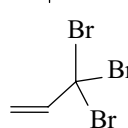
(d)



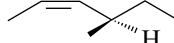
(e)



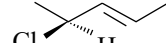
(f)



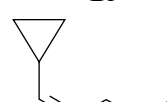
(g)



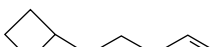
(h)



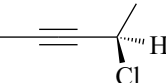
(i)



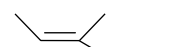
(j)



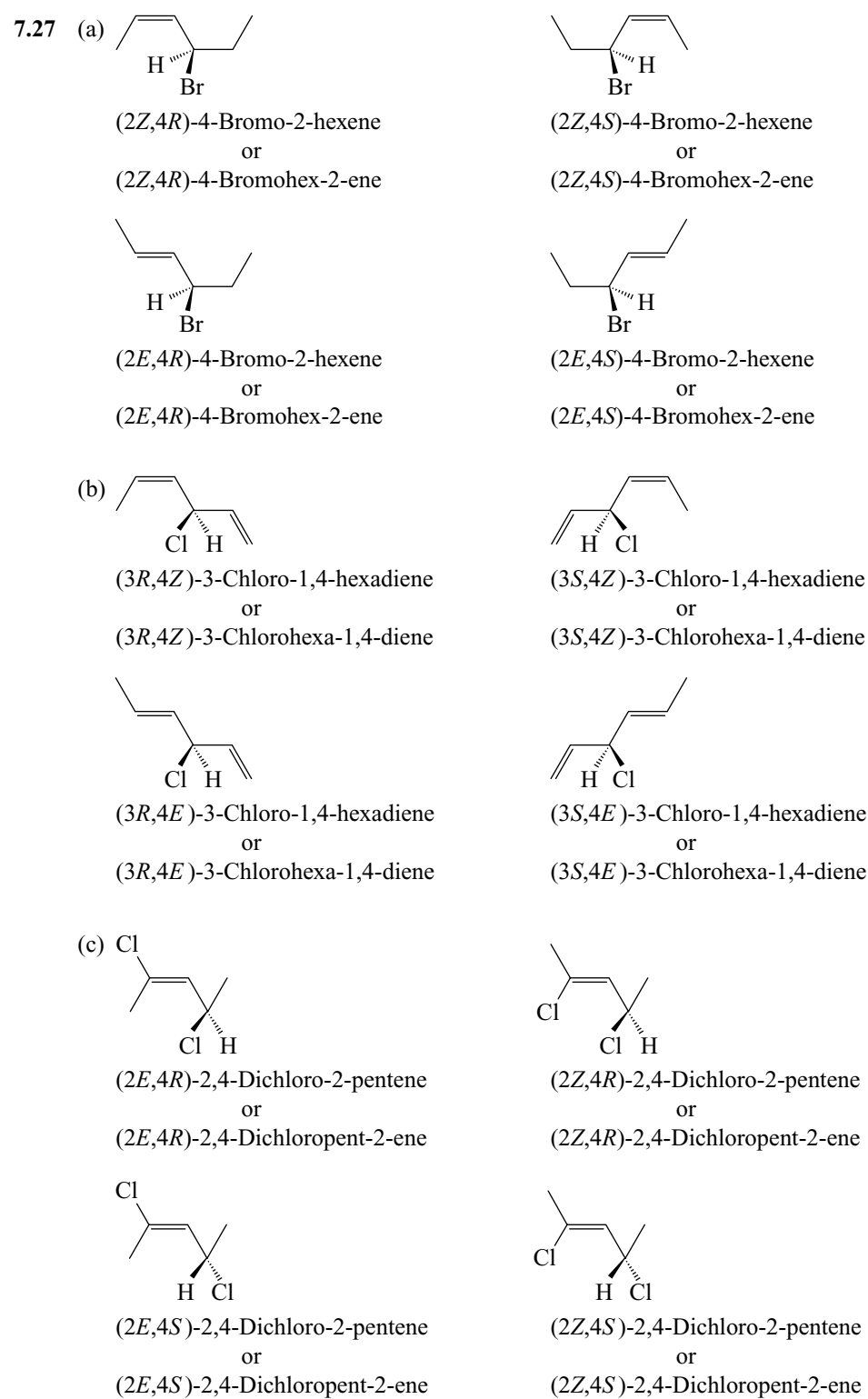
(k)



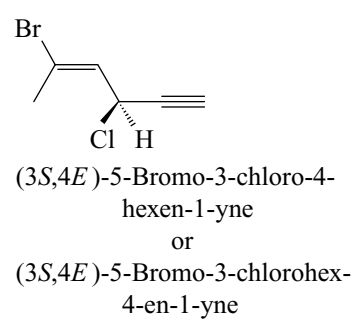
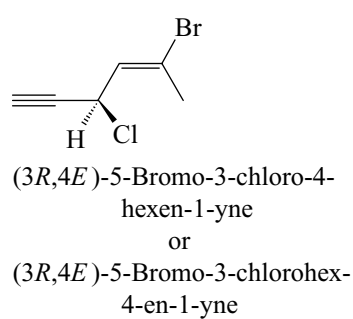
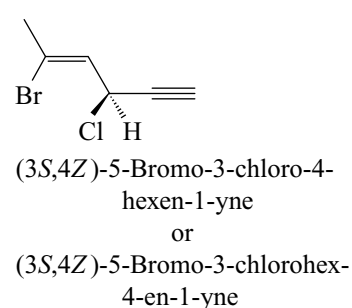
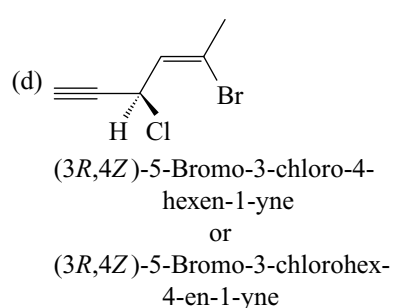
(l)



## 116 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS



## ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 117



An IUPAC rule covers those cases in which a double bond and a triple bond occur in the same molecule:

Numbers as low as possible are given to double and triple bonds as a set, even though this may at times give “-yne” a lower number than “-ene.” If a choice remains, preference for low locants is given to the double bonds.\*

\*International Union of Pure and Applied Chemistry, [http://www.acdlabs.com/iupac/nomenclature/93/r93\\_280.htm](http://www.acdlabs.com/iupac/nomenclature/93/r93_280.htm) (accessed March 2003).

- 7.28** (a) (*E*)-3,5-Dimethyl-2-hexene or (*E*)-3,5-dimethylhex-2-ene  
 (b) 4-Chloro-3-methylcyclopentene  
 (c) 6-Methyl-3-heptyne or 6-methylhept-3-yne  
 (d) 1-*sec*-Butyl-2-methylcyclohexene or 1-methyl-2-(1-methylpropyl)cyclohexene  
 (e) (4*Z*,3*R*)-3-Chloro-4-hepten-1-yne or (4*Z*,3*R*)-3-chlorohept-4-en-1-yne  
 (f) 2-Pentyl-1-heptene or 2-pentylhept-1-ene

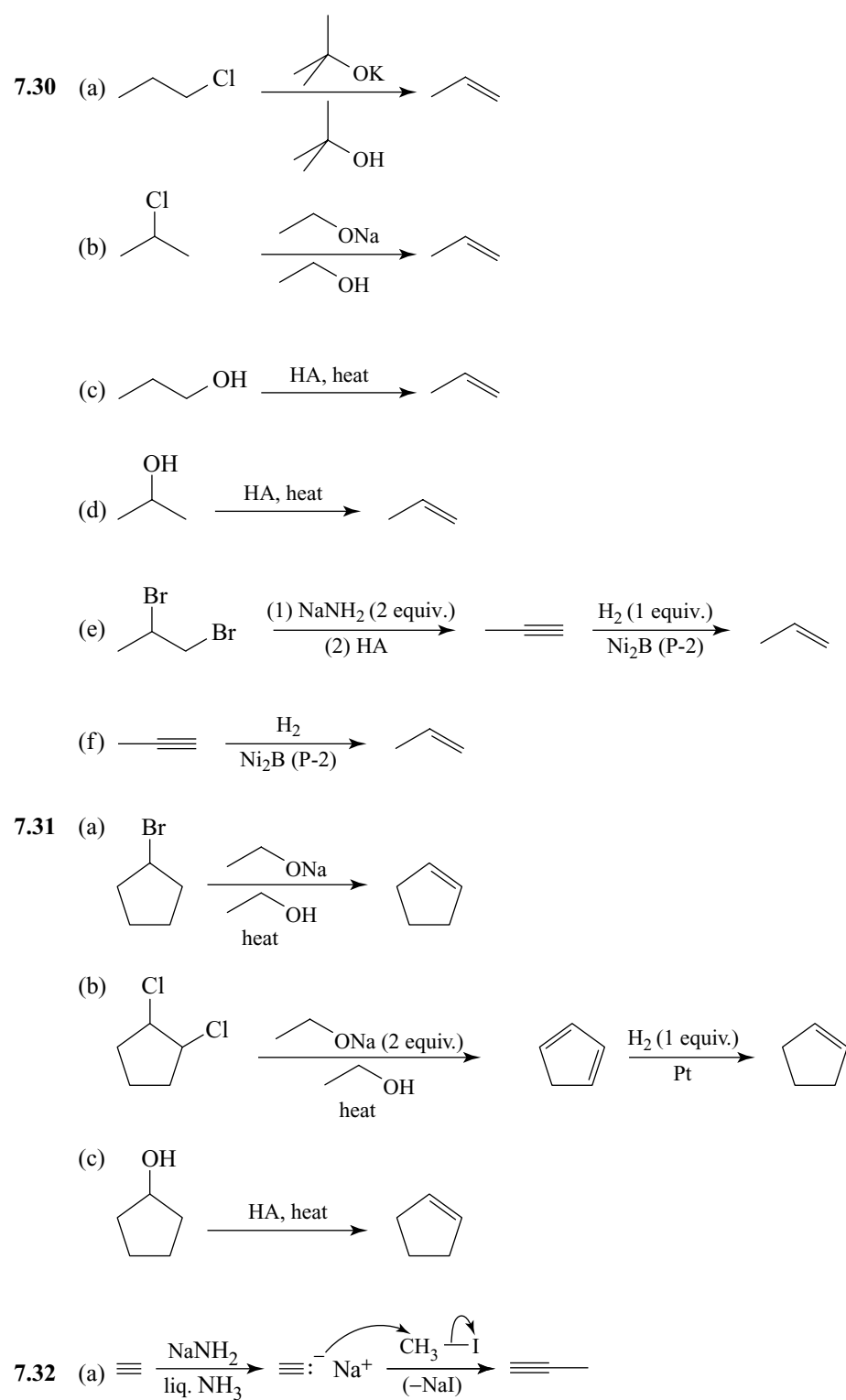
- 7.29** 1-Pentanol > 1-pentyne > 1-pentene > pentane  
 (See Section 3.8 for the explanation.)

P1: PBU/OVY P2: PBU/OVY QC: PBU/OVY T1: PBU  
 JWCL234-07 JWCL234-Solomons-v1

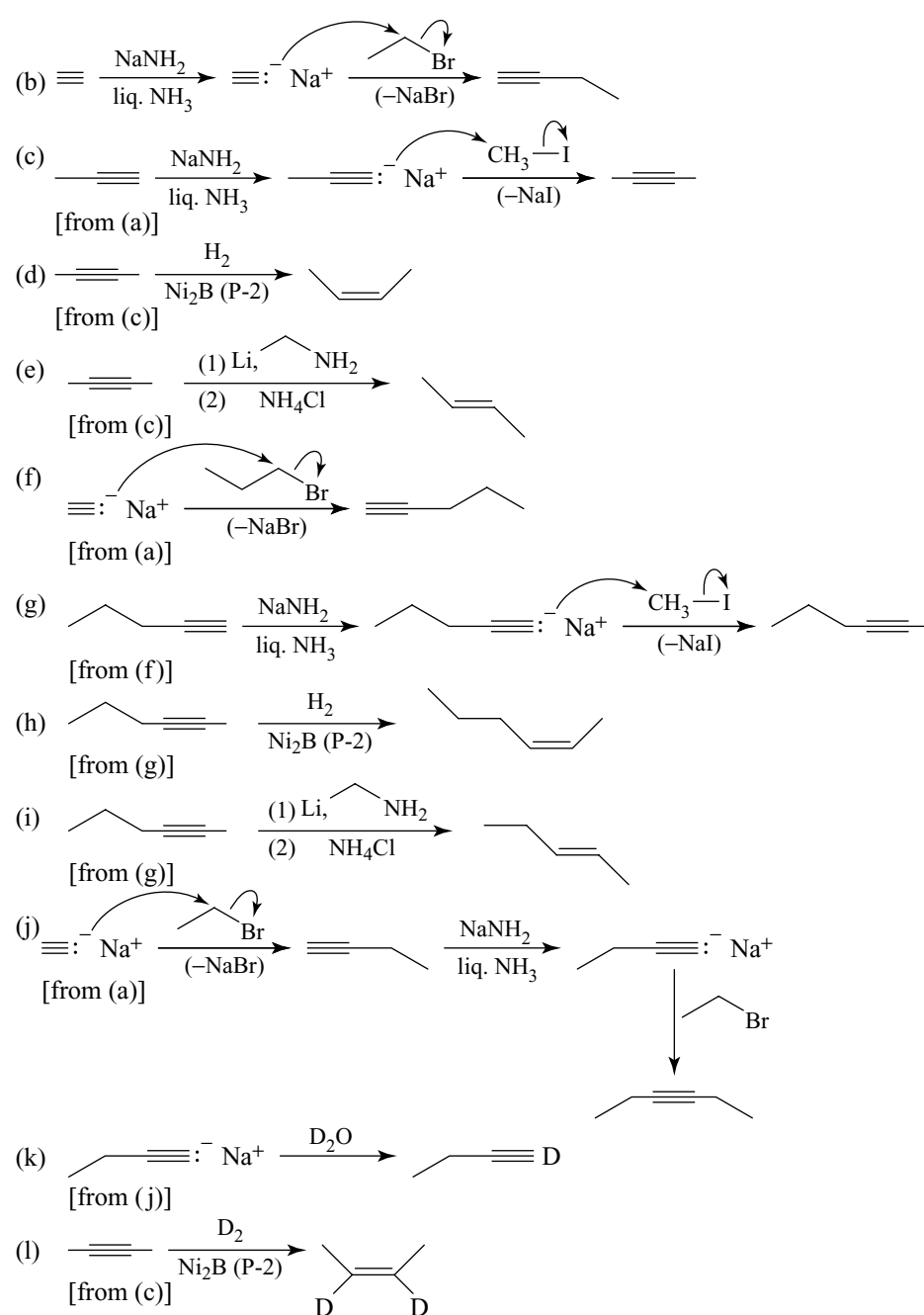
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## 118 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

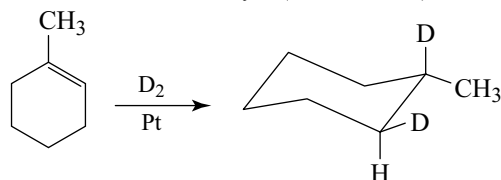
### Synthesis



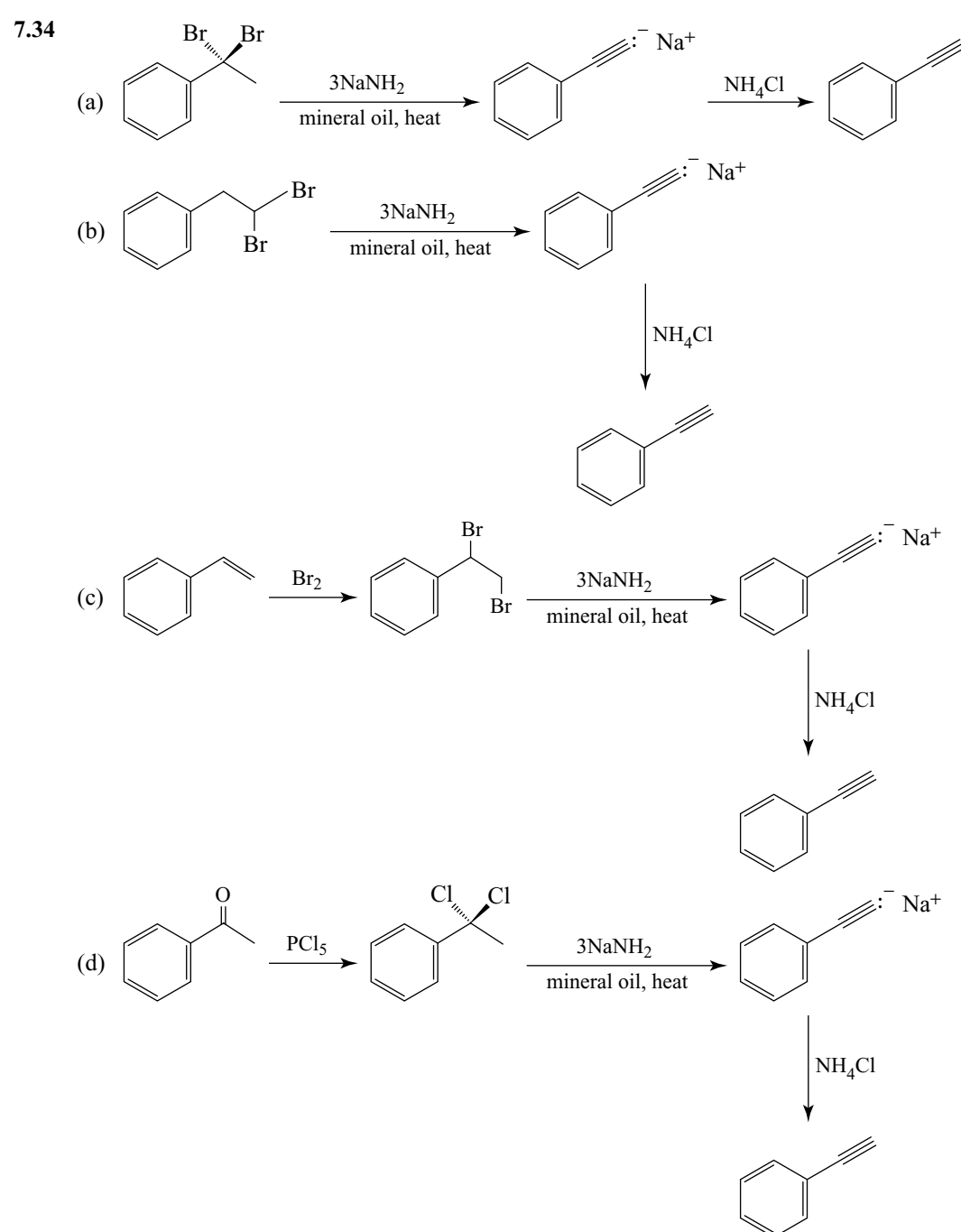
# ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 119



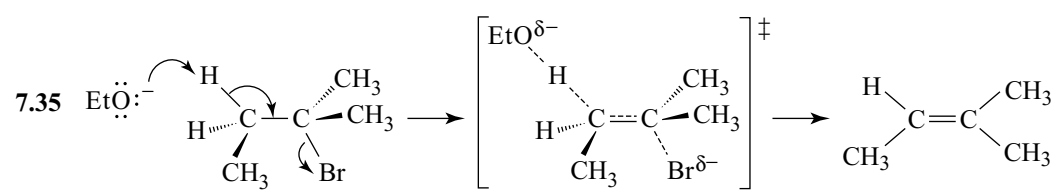
**7.33** We notice that the deuterium atoms are cis to each other, and we conclude, therefore, that we need to choose a method that will cause a syn addition of deuterium. One way would be to use  $\text{D}_2$  and a metal catalyst (Section 7.14)



## 120 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

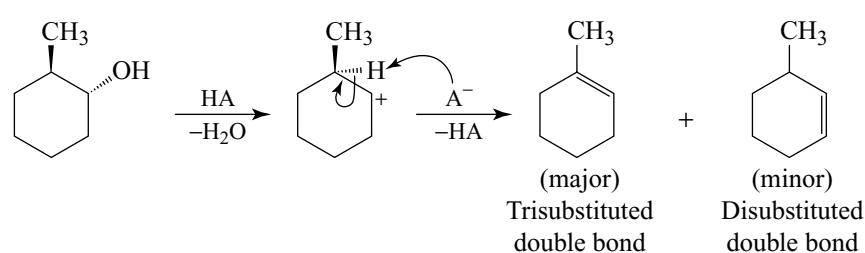


### Dehydrohalogenation and Dehydration

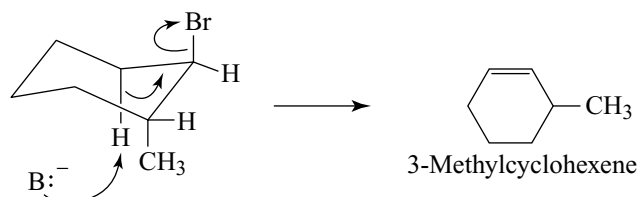


## ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 121

- 7.36** Dehydration of *trans*-2-methylcyclohexanol proceeds through the formation of a carbocation (through an E1 reaction of the protonated alcohol) and leads preferentially to the more stable alkene. 1-Methylcyclohexene (below) is more stable than 3-methylcyclohexene (the minor product of the dehydration) because its double bond is more highly substituted.



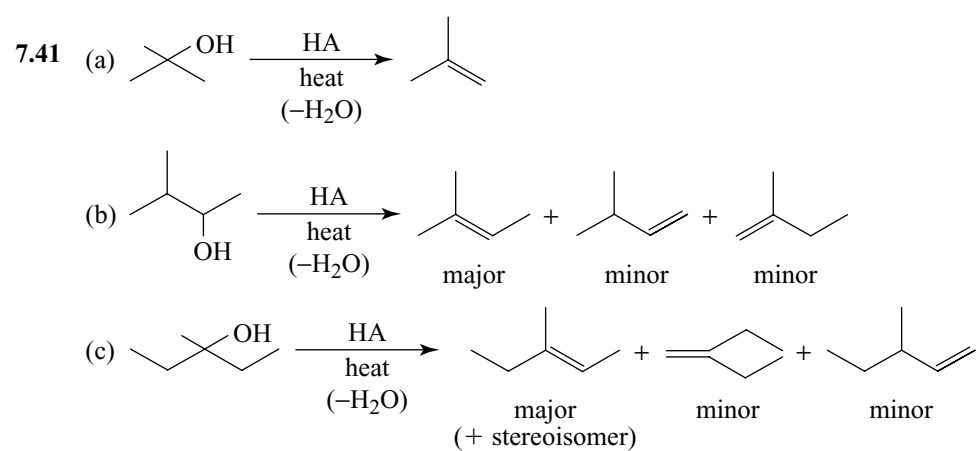
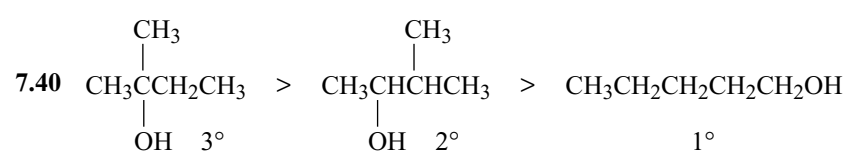
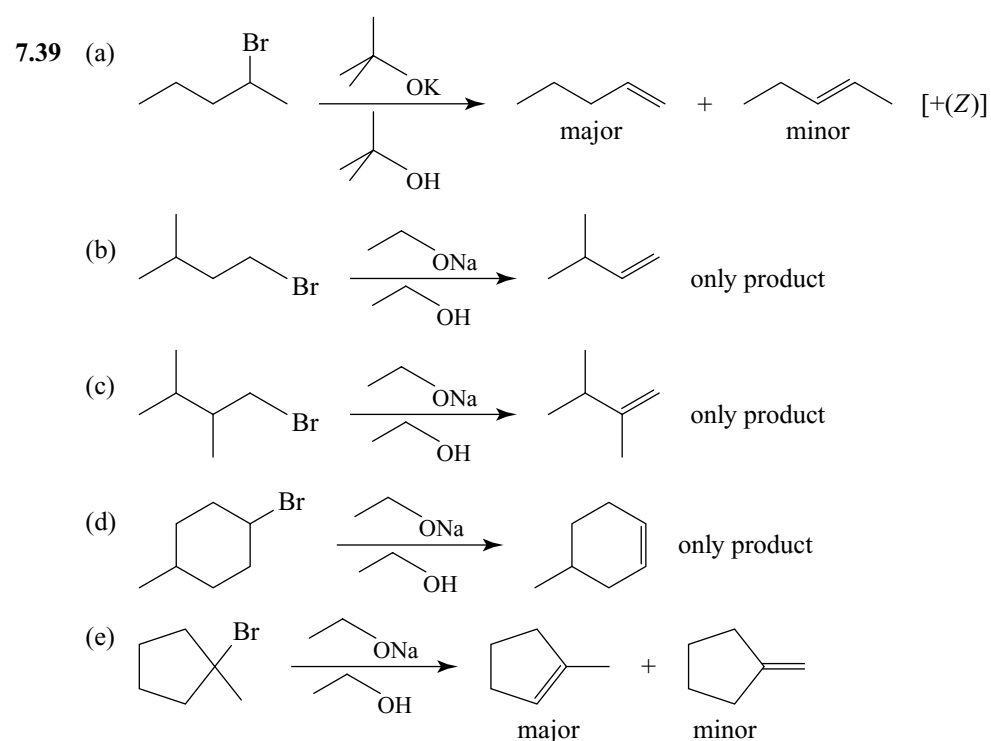
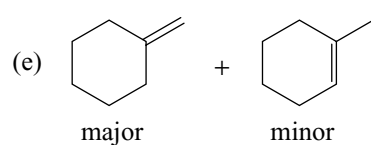
Dehydrohalogenation of *trans*-1-bromo-2-methylcyclohexane is an E2 reaction and must proceed through an anti coplanar transition state. Such a transition state is possible only for the elimination leading to 3-methylcyclohexene (cf. Review Problem 7.11).



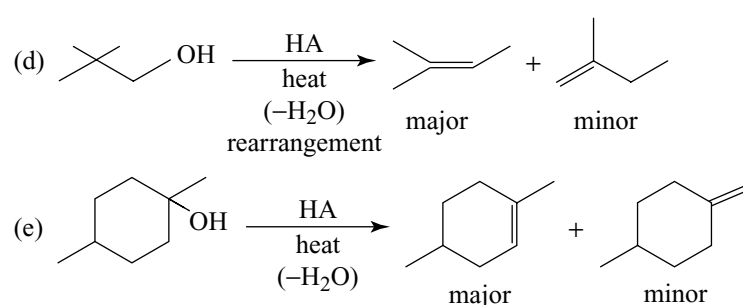
- 7.37** (a) major minor
- (b) only product
- (c) major (+ stereoisomer) minor
- (d) major minor
- (e) major minor
- (f) only product
- 7.38** (a) major minor
- (b) only product
- (c) major minor (+ stereoisomer)
- (d) major minor (+ stereoisomer)



## 122 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

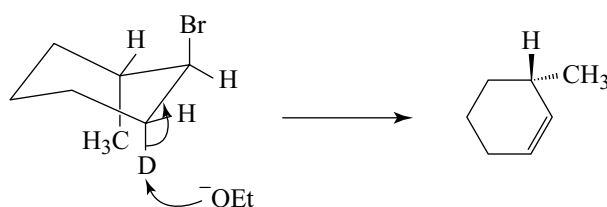


# ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 123

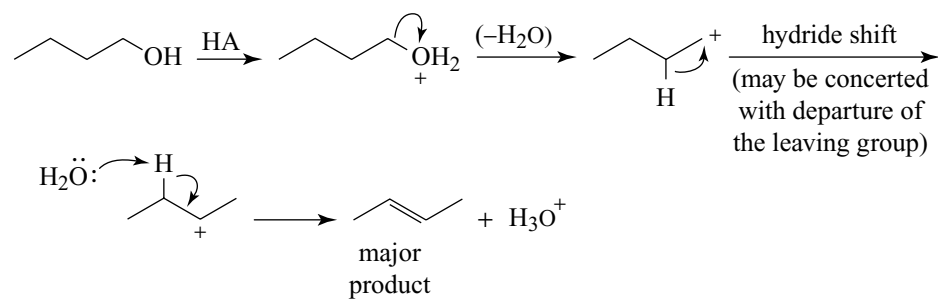


**7.42** The alkene cannot be formed because the double bond in the product is too highly strained. Recall that the atoms at each carbon of a double bond prefer to be in the same plane.

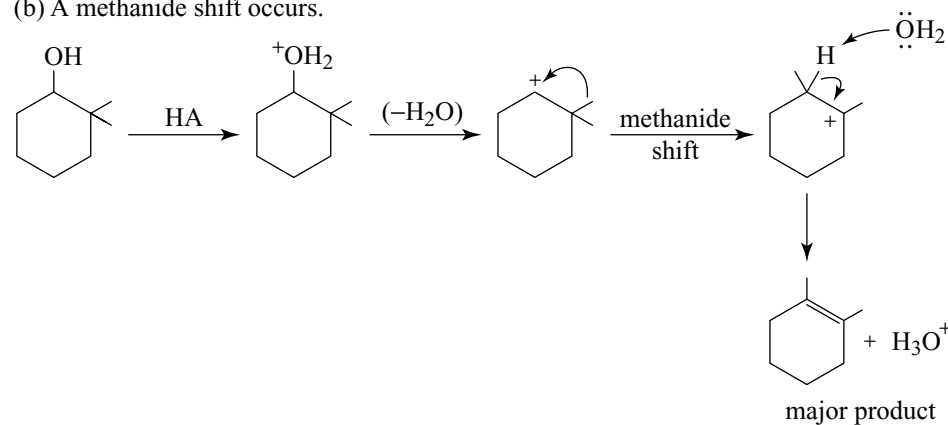
**7.43** Only the deuterium atom can assume the anti coplanar orientation necessary for an E2 reaction to occur.



**7.44** (a) A hydride shift occurs.

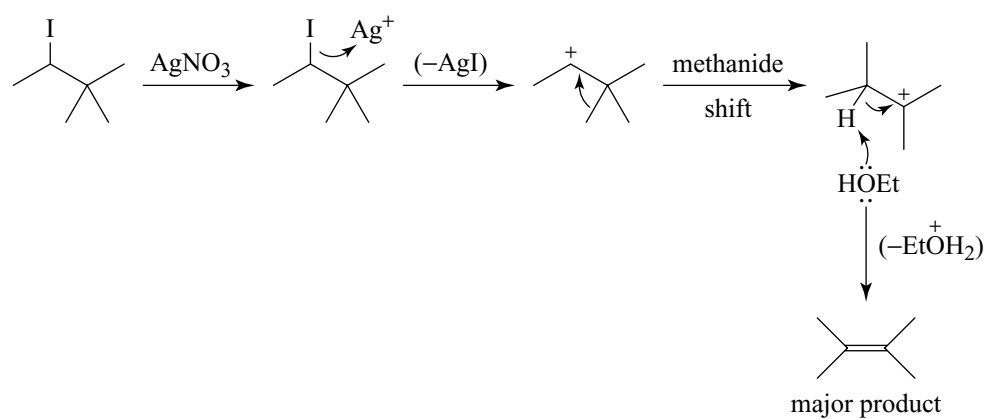


(b) A methanide shift occurs.

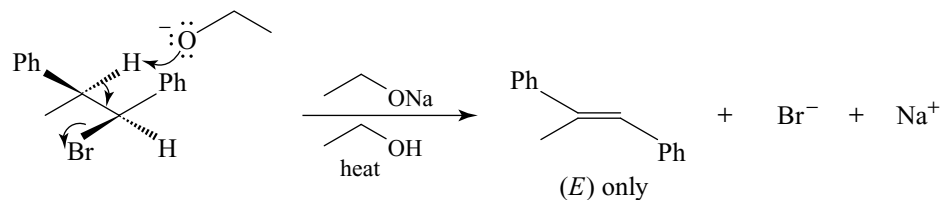


## 124 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

(c) A methanide shift occurs.



(d) The required anti coplanar transition state leads only to (*E*) alkene:



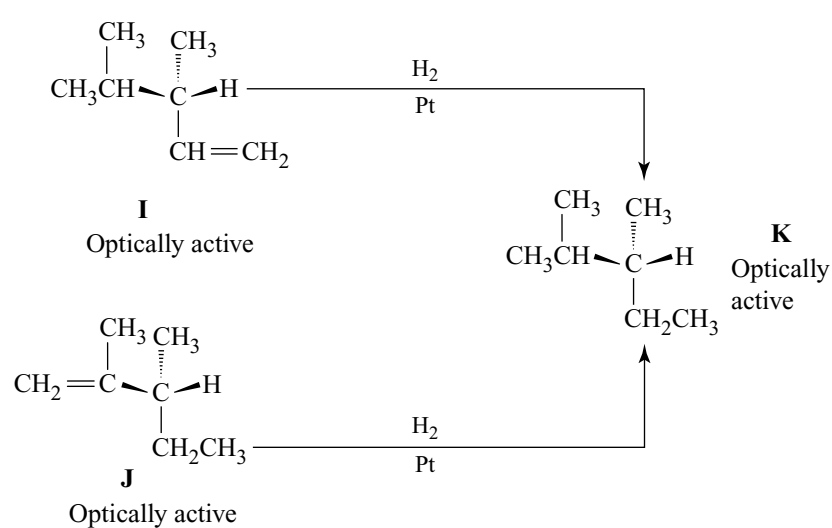
### Index of Hydrogen Deficiency

- 7.45** (a) Caryophyllene has the same molecular formula as zingiberene (Review Problem 4.21); thus it, too, has an index of hydrogen deficiency equal to 4. That 1 mol of caryophyllene absorbs 2 mol of hydrogen on catalytic hydrogenation indicates the presence of two double bonds per molecule.
- (b) Caryophyllene molecules must also have two rings. (See Review Problem 23.2 for the structure of caryophyllene.)
- 7.46** (a)  $C_{30}H_{62}$  = formula of alkane  
 $C_{30}H_{50}$  = formula of squalene  
 $H_{12}$  = difference = 6 pairs of hydrogen atoms  
 Index of hydrogen deficiency = 6
- (b) Molecules of squalene contain six double bonds.
- (c) Squalene molecules contain no rings. (See Review Problem 23.2 for the structural formula of squalene.)

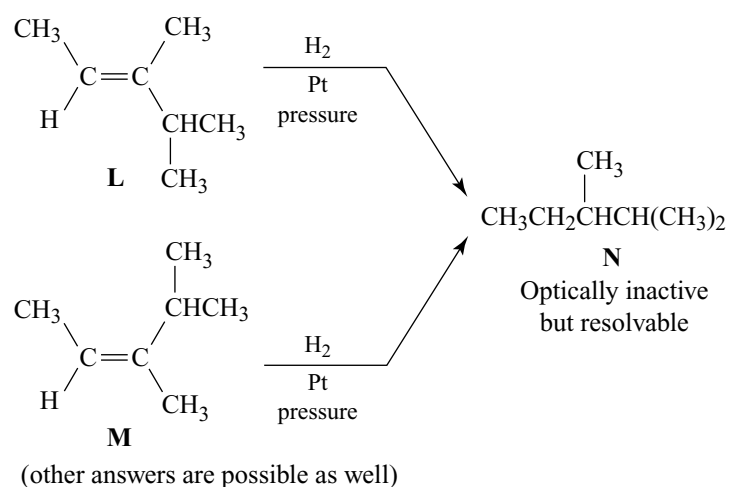
### Structure Elucidation

- 7.47** That **I** and **J** rotate plane-polarized light in the same direction tells us that **I** and **J** are not enantiomers of each other. Thus, the following are possible structures for **I**, **J**, and **K**. (The enantiomers of **I**, **J**, and **K** would form another set of structures, and other answers are possible as well.)

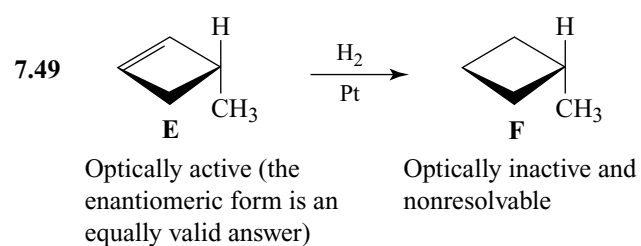
# ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 125



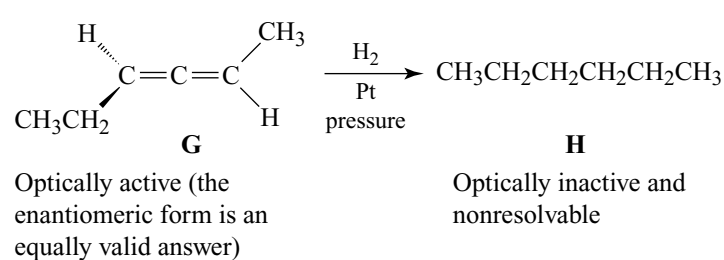
7.48 The following are possible structures:



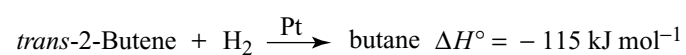
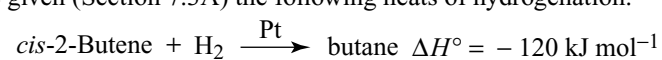
## Challenge Problems



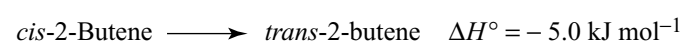
## 126 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS



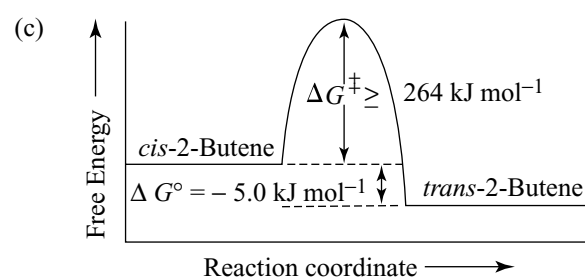
**7.50** (a) We are given (Section 7.3A) the following heats of hydrogenation:



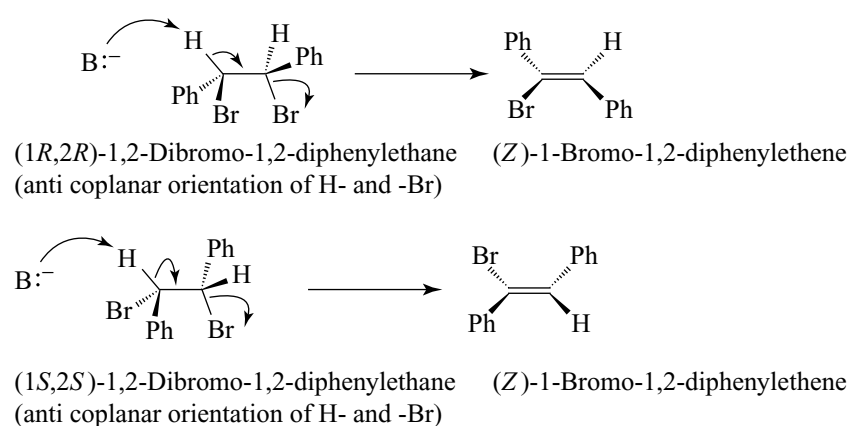
Thus, for



(b) Converting *cis*-2-butene into *trans*-2-butene involves breaking the  $\pi$  bond. Therefore, we would expect the energy of activation to be at least as large as the  $\pi$ -bond strength, that is, at least  $264 \text{ kJ mol}^{-1}$ .

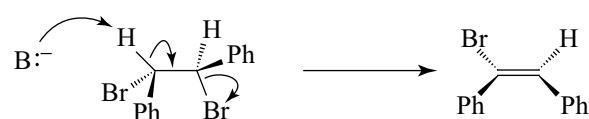


**7.51** (a) With either the (1*R*,2*R*)- or the (1*S*,2*S*)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti coplanar arrangement of the H- and Br-. In either case, the elimination leads only to (*Z*)-1-bromo-1,2-diphenylethene:



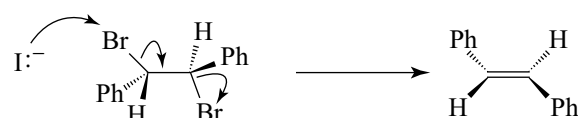
# ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 127

(b) With (1*R*,2*S*)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti coplanar arrangement of the H- and Br-. In either case, the elimination leads only to (*E*)-1-bromo-1,2-diphenylethene:

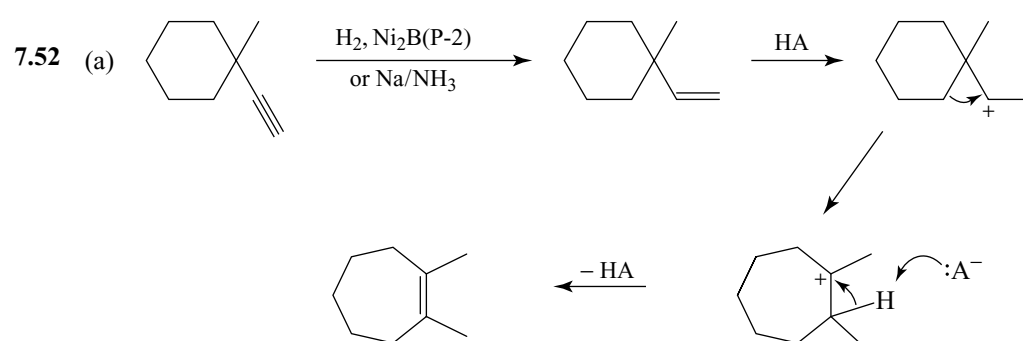


(1*R*,2*S*)-1,2-Dibromo-1,2-diphenylethane (*E*)-1-Bromo-1,2-diphenylethene  
 (anti coplanar orientation of H and Br)

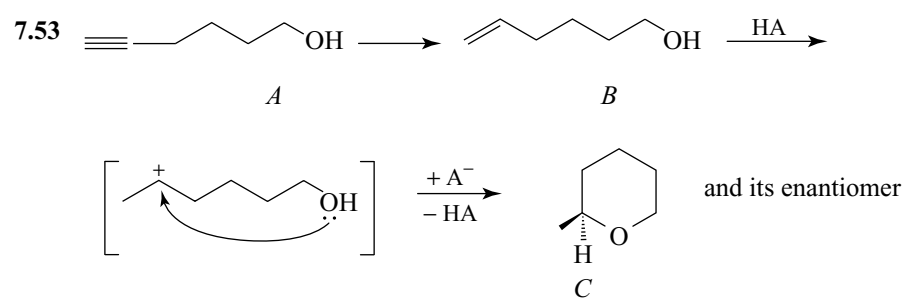
(c) With (1*R*,2*S*)-1,2-dibromo-1,2-diphenylethane, only one conformation will allow an anti coplanar arrangement of both bromine atoms. In this case, the elimination leads only to (*E*)-1,2-diphenylethene:



(1*R*,2*S*)-1,2-Dibromo-1,2-diphenylethane (*E*)-1,2-Diphenylethene  
 (anti coplanar orientation of both -Br atoms)



(b) No, tetrasubstituted double bonds usually show no C=C stretching absorption in their infrared spectra.

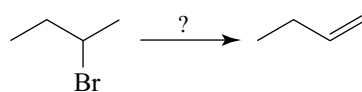


- 7.54 (a) Three  
 (b) Six

## 128 ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS

### QUIZ

- 7.1 Which conditions/reagents would you employ to obtain the best yields in the following reaction?

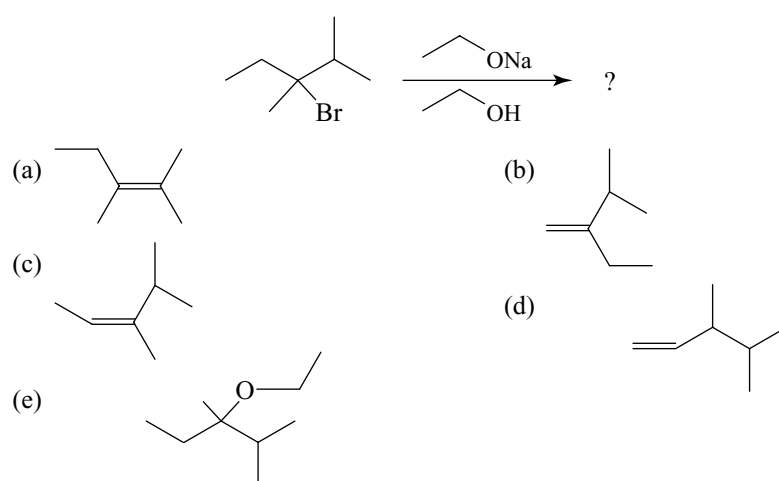


- (a)  $\text{H}_2\text{O}/\text{heat}$  (c)  $\text{t-BuOK} / \text{t-BuOH}, \text{heat}$   
 (b)  $\text{CH}_3\text{CH}_2\text{ONa} / \text{CH}_3\text{CH}_2\text{OH}$  (d) Reaction cannot occur as shown

- 7.2 Which of the following names is incorrect?

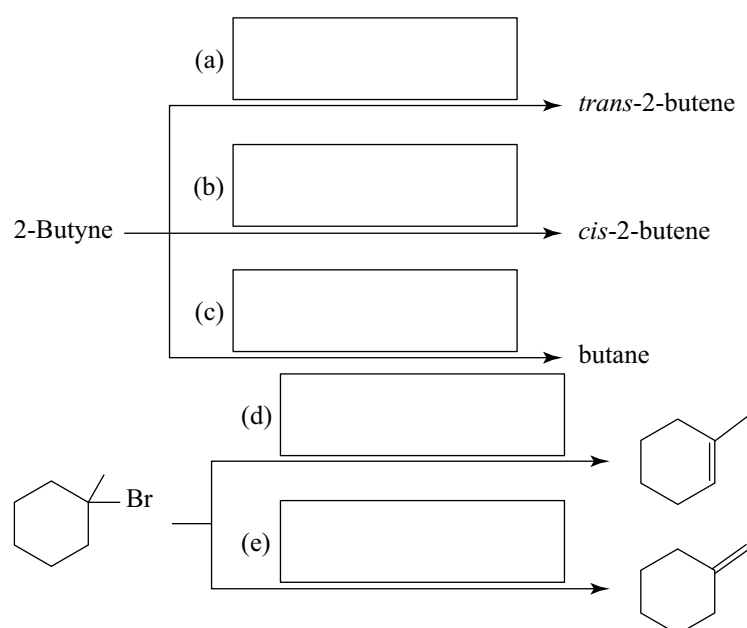
- (a) 1-Butene (b) *trans*-2-Butene (c) (*Z*)-2-Chloro-2-pentene  
 (d) 1,1-Dimethylcyclopentene (e) Cyclohexene

- 7.3 Select the major product of the reaction

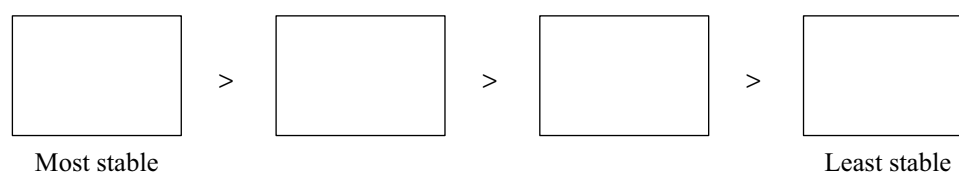


## ALKENES AND ALKYNES I: PROPERTIES AND SYNTHESIS 129

7.4 Supply the missing reagents.



7.5 Arrange the following alkenes in order of decreasing stability. 1-Pentene, *cis*-2-pentene, *trans*-2-pentene, 2-methyl-2-butene



7.6 Complete the following synthesis.

