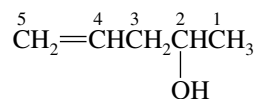
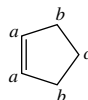


- (e) When a hydroxyl group is present in a compound containing a double bond, the hydroxyl takes precedence over the double bond in numbering the longest carbon chain.

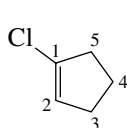


4-Penten-2-ol

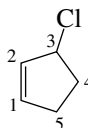
- 5.2 There are three sets of nonequivalent positions on a cyclopentene ring, identified as *a*, *b*, and *c* on the cyclopentene structure shown:



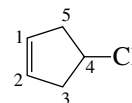
Thus, there are three different monochloro-substituted derivatives of cyclopentene. The carbons that bear the double bond are numbered C-1 and C-2 in each isomer, and the other positions are numbered in sequence in the direction that gives the chlorine-bearing carbon its lower locant.



1-Chlorocyclopentene

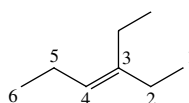


3-Chlorocyclopentene



4-Chlorocyclopentene

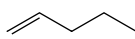
- 5.3 (b) The alkene is a derivative of 3-hexene regardless of whether the chain is numbered from left to right or from right to left. Number it in the direction that gives the lower number to the substituent.



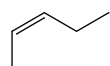
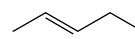
3-Ethyl-3-hexene

- (c) There are only two sp^2 -hybridized carbons, the two connected by the double bond. All other carbons (six) are sp^3 -hybridized.
 (d) There are three sp^2 - sp^3 σ bonds and three sp^3 - sp^3 σ bonds.

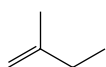
- 5.4 Consider first the C_5H_{10} alkenes that have an unbranched carbon chain:



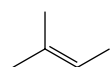
1-Pentene

*cis*-2-Pentene*trans*-2-Pentene

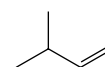
There are three additional isomers. These have a four-carbon chain with a methyl substituent.



2-Methyl-1-butene



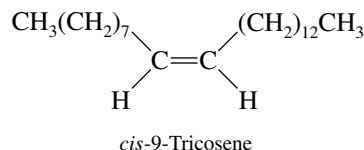
2-Methyl-2-butene



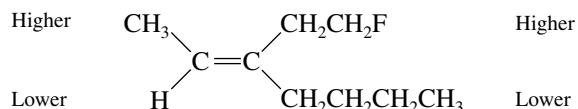
3-Methyl-1-butene

- 5.5 First, identify the constitution of 9-tricosene. Referring back to Table 2.4 in Section 2.8 of the text, we see that tricosane is the unbranched alkane containing 23 carbon atoms. 9-Tricosene, therefore, contains an unbranched chain of 23 carbons with a double bond between C-9 and C-10. Since the

problem specifies that the pheromone has the *cis* configuration, the first 8 carbons and the last 13 must be on the same side of the C-9–C-10 double bond.

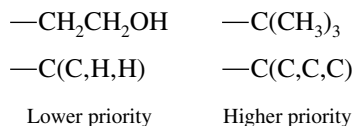


- 5.6 (b) One of the carbons of the double bond bears a methyl group and a hydrogen; methyl is of higher rank than hydrogen. The other doubly bonded carbon bears the groups $\text{—CH}_2\text{CH}_2\text{F}$ and $\text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$. At the first point of difference between these two, fluorine is of higher atomic number than carbon, and so $\text{—CH}_2\text{CH}_2\text{F}$ is of higher precedence.

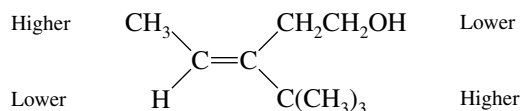


Higher ranked substituents are on the same side of the double bond; the alkene has the *Z* configuration.

- (c) One of the carbons of the double bond bears a methyl group and a hydrogen; as we have seen, methyl is of higher rank. The other doubly bonded carbon bears $\text{—CH}_2\text{CH}_2\text{OH}$ and $\text{—C}(\text{CH}_3)_3$. Let's analyze these two groups to determine their order of precedence.

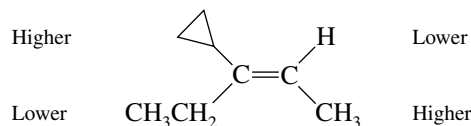


We examine the atoms one by one at the point of attachment before proceeding down the chain. Therefore, $\text{—C}(\text{CH}_3)_3$ outranks $\text{—CH}_2\text{CH}_2\text{OH}$.



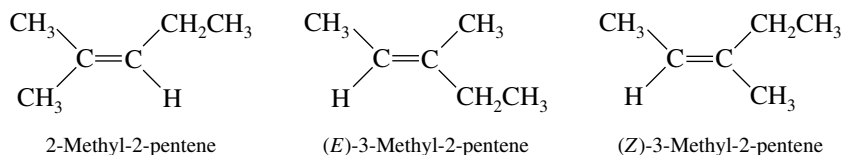
Higher ranked groups are on opposite sides; the configuration of the alkene is *E*.

- (d) The cyclopropyl ring is attached to the double bond by a carbon that bears the atoms (C, C, H) and is therefore of higher precedence than an ethyl group $\text{—C}(\text{C}, \text{H}, \text{H})$.

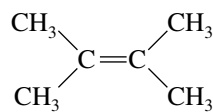


Higher ranked groups are on opposite sides; the configuration of the alkene is *E*.

- 5.7 A trisubstituted alkene has three carbons directly attached to the doubly bonded carbons. There are three trisubstituted C_6H_{12} isomers, two of which are stereoisomers.

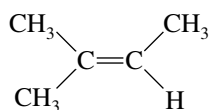
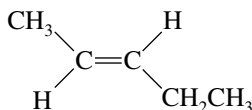
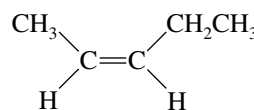
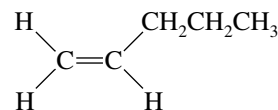


- 5.8 The most stable C_6H_{12} alkene has a tetrasubstituted double bond:

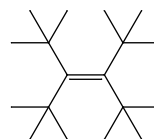


2,3-Dimethyl-2-butene

- 5.9 Apply the two general rules for alkene stability to rank these compounds. First, more highly substituted double bonds are more stable than less substituted ones. Second, when two double bonds are similarly constituted, the trans stereoisomer is more stable than the cis. The predicted order of decreasing stability is therefore:

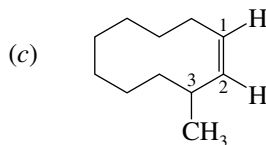
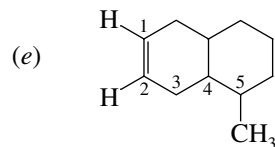
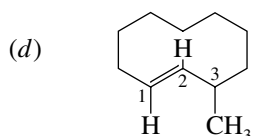
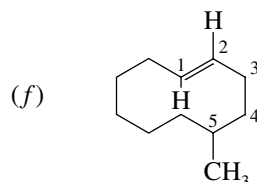
2-Methyl-2-butene
(trisubstituted):
most stable*(E)*-2-Pentene
(disubstituted)*(Z)*-2-Pentene
(disubstituted)1-Pentene
(monosubstituted):
least stable

- 5.10 Begin by writing the structural formula corresponding to the IUPAC name given in the problem. A bond-line depiction is useful here.

3,4-Di-*tert*-butyl-2,2,5,5-tetramethyl-3-hexene

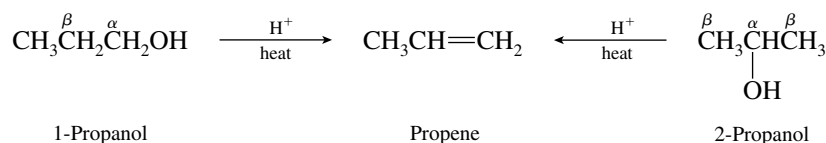
The alkene is extremely crowded and destabilized by van der Waals strain. Bulky *tert*-butyl groups are cis to one another on each side of the double bond. Highly strained compounds are often quite difficult to synthesize, and this alkene is a good example.

- 5.11 Use the zigzag arrangement of bonds in the parent skeleton figure to place *E* and *Z* bonds as appropriate for each part of the problem. From the sample solution to parts (a) and (b), the ring carbons have the higher priorities. Thus, an *E* double bond will have ring carbons arranged and a *Z* double bond .

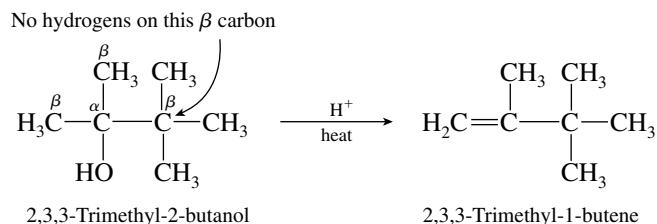
*(Z)*-3-Methylcyclodecene*(Z)*-5-Methylcyclodecene*(E)*-3-Methylcyclodecene*(E)*-5-Methylcyclodecene

- 5.12 Write out the structure of the alcohol, recognizing that the alkene is formed by loss of a hydrogen and a hydroxyl group from adjacent carbons.

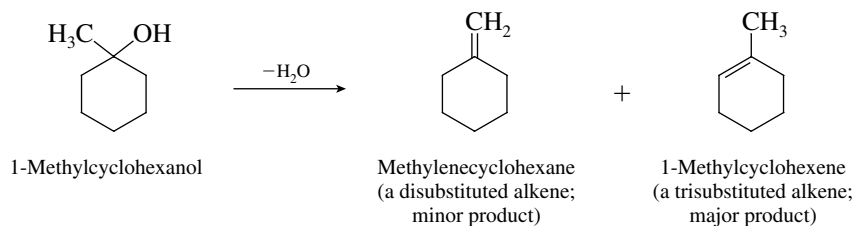
(b, c) Both 1-propanol and 2-propanol give propene on acid-catalyzed dehydration.



(d) Carbon-3 has no hydrogens in 2,3,3-trimethyl-2-butanol. Elimination can involve only the hydroxyl group at C-2 and a hydrogen at C-1.

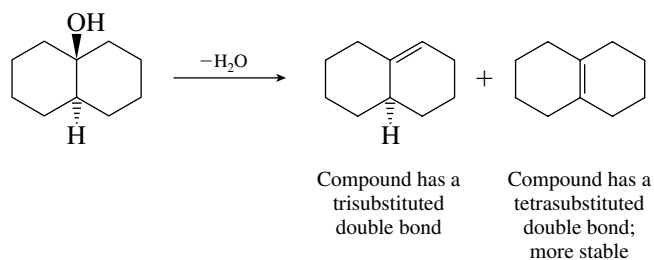


5.13 (b) Elimination can involve loss of a hydrogen from the methyl group or from C-2 of the ring in 1-methylcyclohexanol.



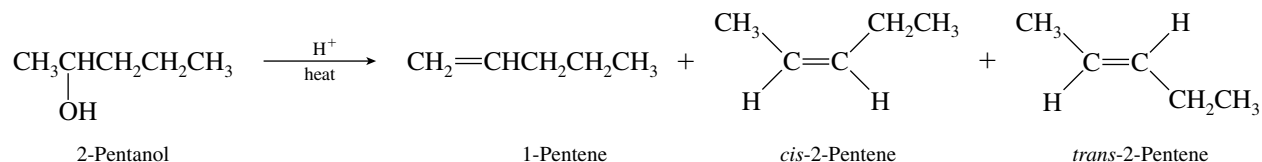
According to the Zaitsev rule, the major alkene is the one corresponding to loss of a hydrogen from the alkyl group that has the smaller number of hydrogens. Thus hydrogen is removed from the methylene group in the ring rather than from the methyl group, and 1-methylcyclohexene is formed in greater amounts than methylenecyclohexane.

(c) The two alkenes formed are as shown in the equation.

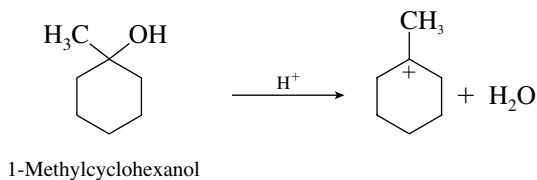


The more highly substituted alkene is formed in greater amounts, as predicted by Zaitsev's rule.

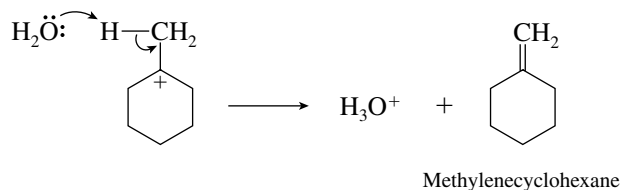
5.14 2-Pentanol can undergo dehydration in two different directions, giving either 1-pentene or 2-pentene. 2-Pentene is formed as a mixture of the cis and trans stereoisomers.



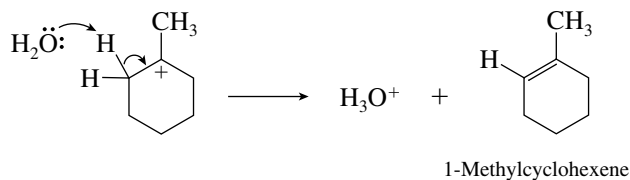
- 5.15 (b) The site of positive charge in the carbocation is the carbon atom that bears the hydroxyl group in the starting alcohol.



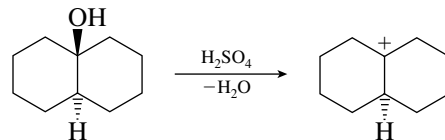
Water may remove a proton from the methyl group, as shown in the following equation:



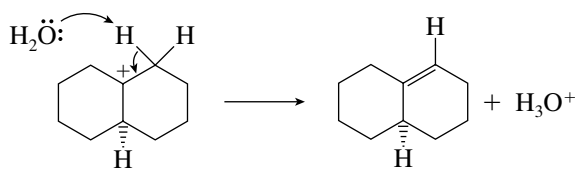
Loss of a proton from the ring gives the major product 1-methylcyclohexene.



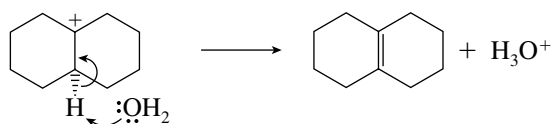
- (c) Loss of the hydroxyl group under conditions of acid catalysis yields a tertiary carbocation.



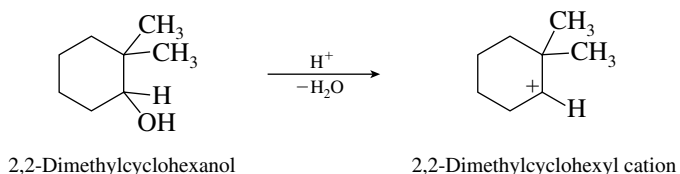
Water may remove a proton from an adjacent methylene group to give a trisubstituted alkene.



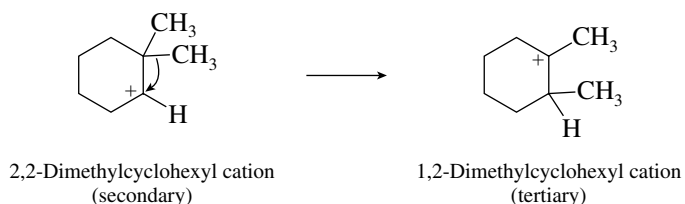
Removal of the methine proton gives a tetrasubstituted alkene.



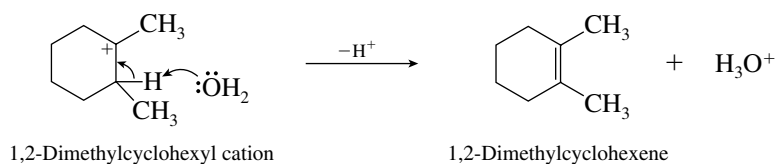
- 5.16 In writing mechanisms for acid-catalyzed dehydration of alcohols, begin with formation of the carbocation intermediate:



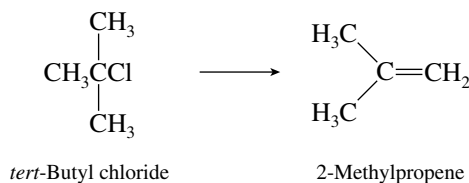
This secondary carbocation can rearrange to a more stable tertiary carbocation by a methyl group shift.



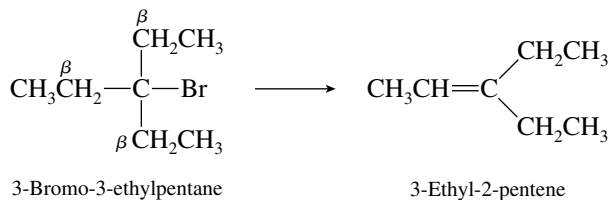
Loss of a proton from the 1,2-dimethylcyclohexyl cation intermediate yields 1,2-dimethylcyclohexene.



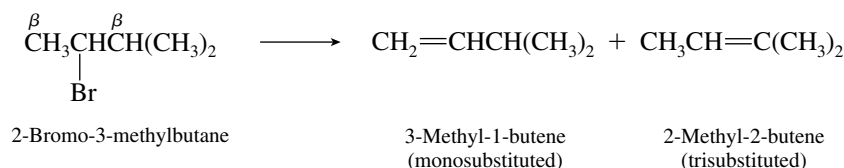
- 5.17 (b) All the hydrogens of *tert*-butyl chloride are equivalent. Loss of any of these hydrogens along with the chlorine substituent yields 2-methylpropene as the only alkene.



- (c) All the β hydrogens of 3-bromo-3-ethylpentane are equivalent, so that β -elimination can give only 3-ethyl-2-pentene.

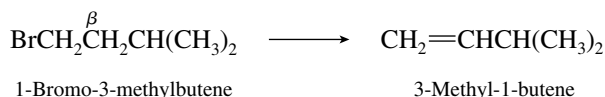


- (d) There are two possible modes of β -elimination from 2-bromo-3-methylbutane. Elimination in one direction provides 3-methyl-1-butene; elimination in the other gives 2-methyl-2-butene.

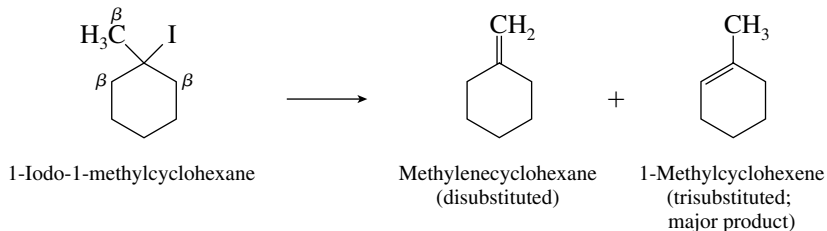


The major product is the more highly substituted alkene, 2-methyl-2-butene. It is the more stable alkene and corresponds to removal of a hydrogen from the carbon that has the fewer hydrogens.

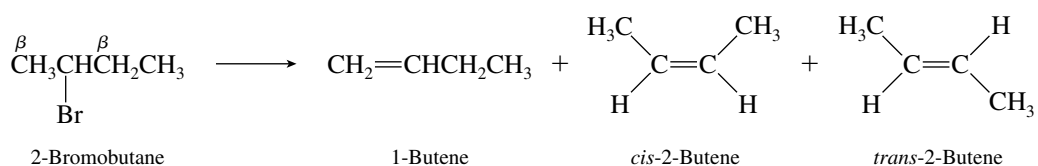
- (e) Regioselectivity is not an issue here, because 3-methyl-1-butene is the only alkene that can be formed by β -elimination from 1-bromo-3-methylbutane.



- (f) Two alkenes may be formed here. The more highly substituted one is 1-methylcyclohexene, and this is predicted to be the major product in accordance with Zaitsev's rule.

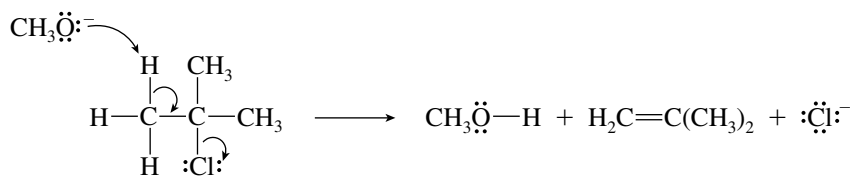


- 5.18** Elimination in 2-bromobutane can take place between C-1 and C-2 or between C-2 and C-3. There are three alkenes capable of being formed: 1-butene and the stereoisomers *cis*-2-butene and *trans*-2-butene.

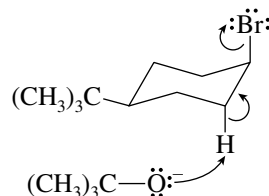


As predicted by Zaitsev's rule, the most stable alkene predominates. The major product is *trans*-2-butene.

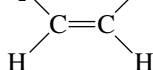
- 5.19** An unshared electron pair of the base methoxide (CH_3O^-) abstracts a proton from carbon. The pair of electrons in this C—H bond becomes the π component of the double bond of the alkene. The pair of electrons in the C—Cl bond becomes an unshared electron pair of chloride ion.



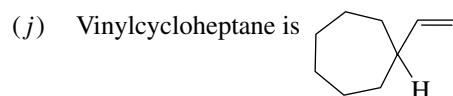
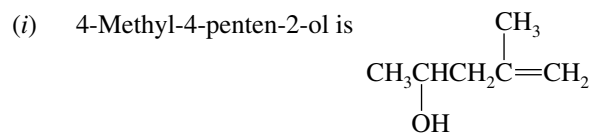
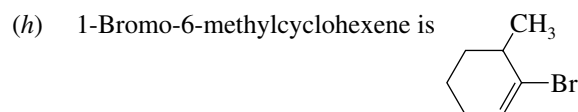
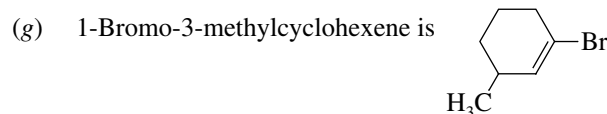
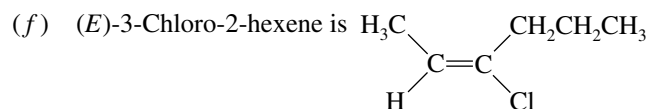
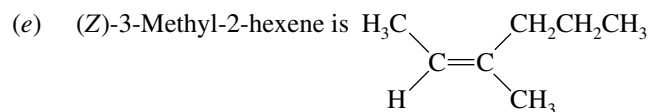
- 5.20** The most stable conformation of *cis*-4-*tert*-butylcyclohexyl bromide has the bromine substituent in an axial orientation. The hydrogen that is removed by the base is an axial proton at C-2. This hydrogen and the bromine are anti periplanar to each other in the most stable conformation.



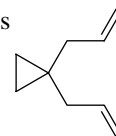
- 5.21** (a) 1-Heptene is $\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CH}_3$.
 (b) 3-Ethyl-2-pentene is $\text{CH}_3\text{CH}=\text{C}(\text{CH}_2\text{CH}_3)_2$.
 (c) *cis*-3-Octene is $\text{CH}_3\text{CH}_2 \text{---} \text{C}=\text{C} \text{---} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



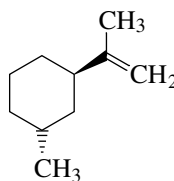
- (d) *trans*-1,4-Dichloro-2-butene is $\text{ClCH}_2 \text{---} \text{C}=\text{C} \text{---} \text{CH}_2\text{Cl}$
-



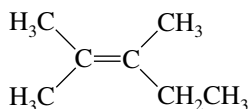
(k) An allyl group is $-\text{CH}_2\text{CH}=\text{CH}_2$. 1,1-Diallylcyclopropane is



(l) An isopropenyl substituent is $-\text{C}(\text{CH}_3)=\text{CH}_2$. *trans*-1-Isopropenyl-3-methylcyclohexane is therefore

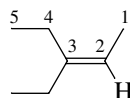


5.22 Alkenes with tetrasubstituted double bonds have four alkyl groups attached to the doubly bonded carbons. There is only one alkene of molecular formula C_7H_{14} that has a tetrasubstituted double bond, 2,3-dimethyl-2-pentene.



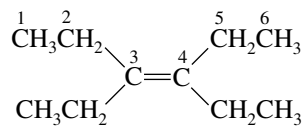
2,3-Dimethyl-2-pentene

5.23 (a) The longest chain that includes the double bond in $(\text{CH}_3\text{CH}_2)_2\text{C}=\text{CHCH}_3$ contains five carbon atoms, and so the parent alkene is a pentene. The numbering scheme that gives the double bond the lowest number is



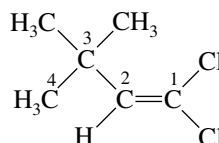
The compound is 3-ethyl-2-pentene.

- (b) Write out the structure in detail, and identify the longest continuous chain that includes the double bond.



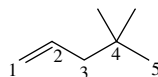
The longest chain contains six carbon atoms, and the double bond is between C-3 and C-4. The compound is named as a derivative of 3-hexene. There are ethyl substituents at C-3 and C-4. The complete name is 3,4-diethyl-3-hexene.

- (c) Write out the structure completely.

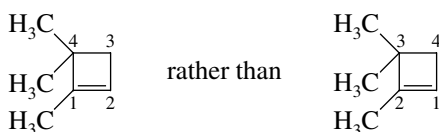


The longest carbon chain contains four carbons. Number the chain so as to give the lowest numbers to the doubly bonded carbons, and list the substituents in alphabetical order. This compound is 1,1-dichloro-3,3-dimethyl-1-butene.

- (d) The longest chain has five carbon atoms, the double bond is at C-1, and there are two methyl substituents. The compound is 4,4-dimethyl-1-pentene.

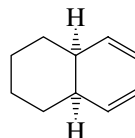


- (e) We number this trimethylcyclobutene derivative so as to provide the lowest number for the substituent at the first point of difference. We therefore number

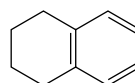


The correct IUPAC name is 1,4,4-trimethylcyclobutene, not 2,3,3-trimethylcyclobutene.

- (f) The cyclohexane ring has a 1,2-*cis* arrangement of vinyl substituents. The compound is *cis*-1,2-divinylcyclohexane.

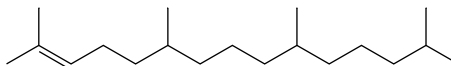


- (g) Name this compound as a derivative of cyclohexene. It is 1,2-divinylcyclohexene.



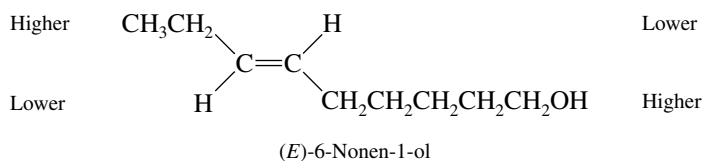
- 5.24 (a) Go to the end of the name, because this tells you how many carbon atoms are present in the longest chain. In the hydrocarbon name 2,6,10,14-tetramethyl-2-pentadecene, the suffix “2-pentadecene” reveals that the longest continuous chain has 15 carbon atoms and that there

is a double bond between C-2 and C-3. The rest of the name provides the information that there are four methyl groups and that they are located at C-2, C-6, C-10, and C-14.

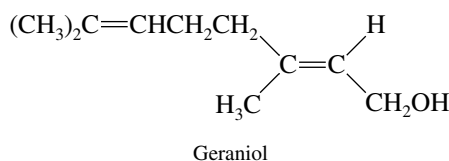


2,6,10,14-Tetramethyl-2-pentadecene

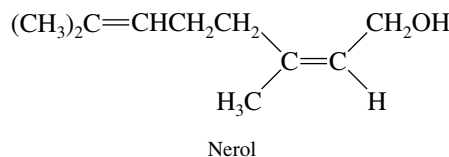
- (b) An allyl group is $\text{CH}_2=\text{CHCH}_2-$. Allyl isothiocyanate is therefore $\text{CH}_2=\text{CHCH}_2\text{N}=\text{C}=\text{S}$.
- 5.25 (a) The *E* configuration means that the higher priority groups are on opposite sides of the double bond.



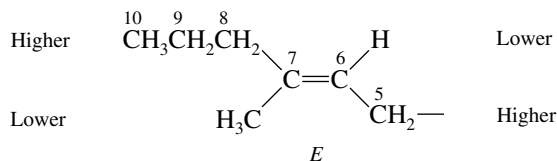
- (b) Geraniol has two double bonds, but only one of them, the one between C-2 and C-3, is capable of stereochemical variation. Of the groups at C-2, CH_2OH is of higher priority than H. At C-3, CH_2CH_2 outranks CH_3 . Higher priority groups are on opposite sides of the double bond in the *E* isomer; hence geraniol has the structure shown.



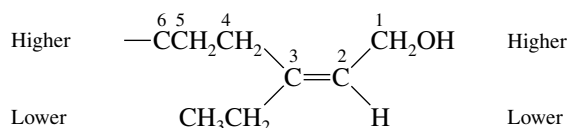
- (c) Since nerol is a stereoisomer of geraniol, it has the same constitution and differs from geraniol only in having the *Z* configuration of the double bond.

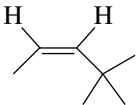
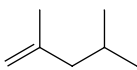
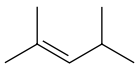


- (d) Beginning at the C-6, C-7 double bond, we see that the propyl group is of higher priority than the methyl group at C-7. Since the C-6, C-7 double bond is *E*, the propyl group must be on the opposite side of the higher priority group at C-6, where the CH_2 fragment has a higher priority than hydrogen. We therefore write for the stereochemistry of the C-6, C-7 double bond as:

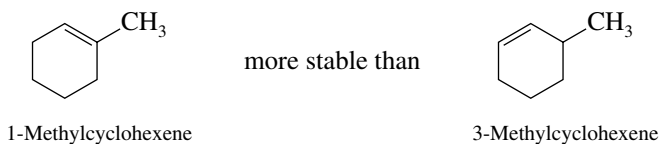


At C-2, CH_2OH is of higher priority than H; and at C-3, $\text{CH}_2\text{CH}_2\text{C}-$ is of higher priority than CH_2CH_3 . The double-bond configuration at C-2 is *Z*. Therefore

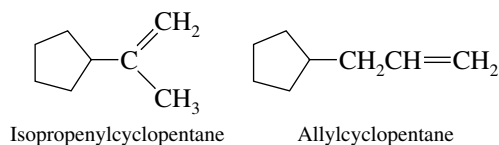


- (d)  (Z)-4,4-Dimethyl-2-pentene; 4650 kJ/mol (1111.4 kcal/mol). Disubstituted double bond, but destabilized by van der Waals strain.
- (b)  2,4-Dimethyl-1-pentene; 4638 kJ/mol (1108.6 kcal/mol). Disubstituted double bond.
- (c)  2,4-Dimethyl-2-pentene; 4632 kJ/mol (1107.1 kcal/mol). Trisubstituted double bond.

- 5.28 (a) 1-Methylcyclohexene is more stable; it contains a **trisubstituted** double bond, whereas 3-methylcyclohexene has only a disubstituted double bond.

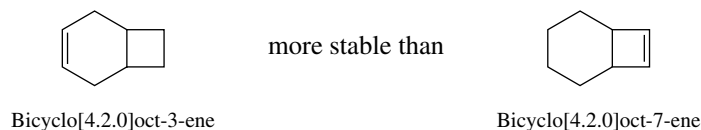


- (b) Both isopropenyl and allyl are three-carbon alkenyl groups: isopropenyl is $\text{CH}_2=\text{C}(\text{CH}_3)-$, allyl is $\text{CH}_2=\text{CHCH}_2-$.

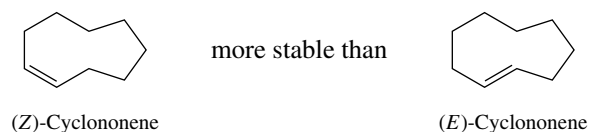


Isopropenylcyclopentane has a disubstituted double bond and so is predicted to be more stable than allylcyclopentane, in which the double bond is monosubstituted.

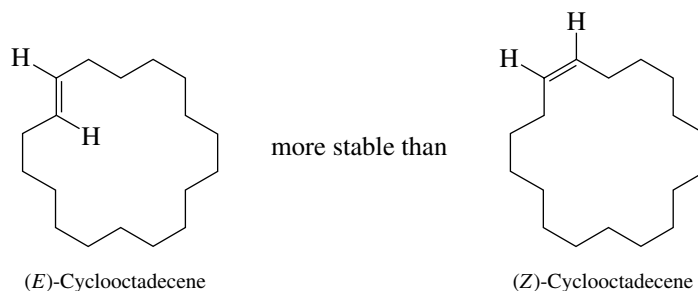
- (c) A double bond in a six-membered ring is less strained than a double bond in a four-membered ring; therefore bicyclo[4.2.0]oct-3-ene is more stable.



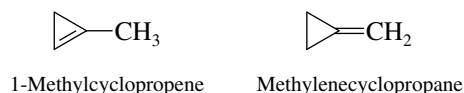
- (d) Cis double bonds are more stable than trans double bonds when the ring is smaller than 11-membered. (Z)-Cyclononene has a cis double bond in a 9-membered ring, and is thus more stable than (E)-cyclononene.



- (e) Trans double bonds are more stable than cis when the ring is large. Here the rings are 18-membered, so that (E)-cyclooctadecene is more stable than (Z)-cyclooctadecene.

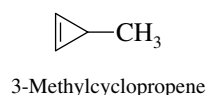


- 5.29 (a) Carbon atoms that are involved in double bonds are sp^2 -hybridized, with ideal bond angles of 120° . Incorporating an sp^2 -hybridized carbon into a three-membered ring leads to more angle strain than incorporation of an sp^3 -hybridized carbon. 1-Methylcyclopropene has two sp^2 -hybridized carbons in a three-membered ring and so has substantially more angle strain than methylenecyclopropane.



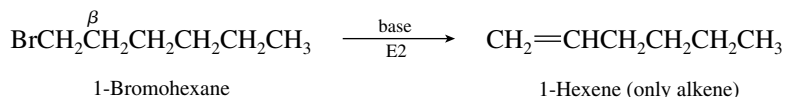
The higher degree of substitution at the double bond in 1-methylcyclopropene is not sufficient to offset the increased angle strain, and so 1-methylcyclopropene is less stable than methylenecyclopropane.

- (b) 3-Methylcyclopropene has a disubstituted double bond and two sp^2 -hybridized carbons in its three-membered ring. It is the least stable of the isomers.

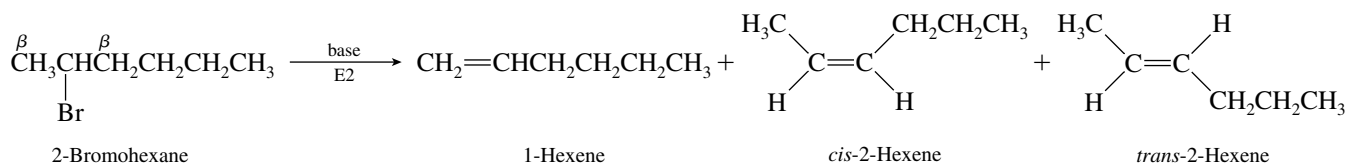


- 5.30 In all parts of this exercise, write the structure of the alkyl halide in sufficient detail to identify the carbon that bears the halogen and the β -carbon atoms that bear at least one hydrogen. These are the carbons that become doubly bonded in the alkene product.

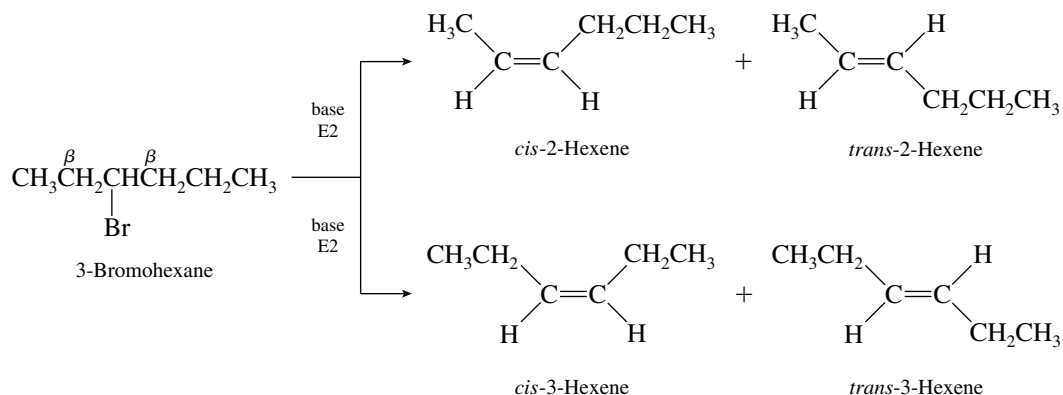
- (a) 1-Bromohexane can give only 1-hexene under conditions of E2 elimination.



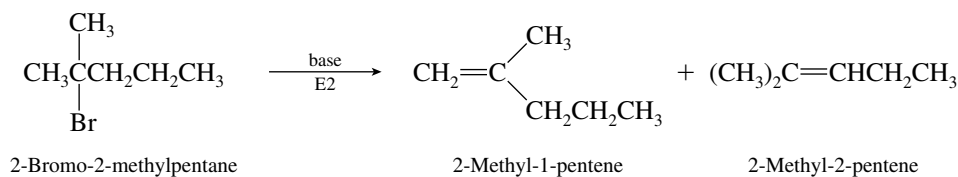
- (b) 2-Bromohexane can give both 1-hexene and 2-hexene on dehydrobromination. The 2-hexene fraction is a mixture of cis and trans stereoisomers.



- (c) Both a cis–trans pair of 2-hexenes and a cis–trans pair of 3-hexenes are capable of being formed from 3-bromohexane.

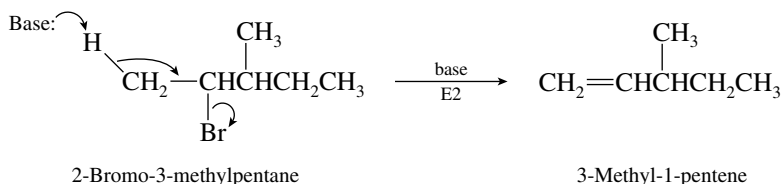


- (d) Dehydrobromination of 2-bromo-2-methylpentane can involve one of the hydrogens of either a methyl group (C-1) or a methylene group (C-3).

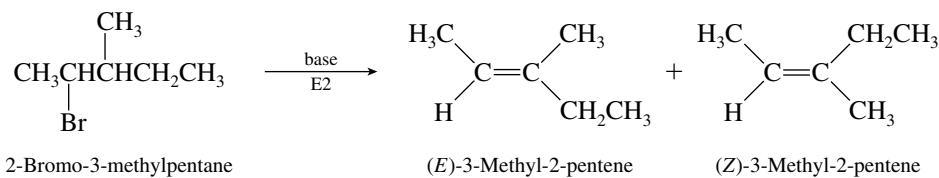


Neither alkene is capable of existing in stereoisomeric forms, and so these two are the only products of E2 elimination.

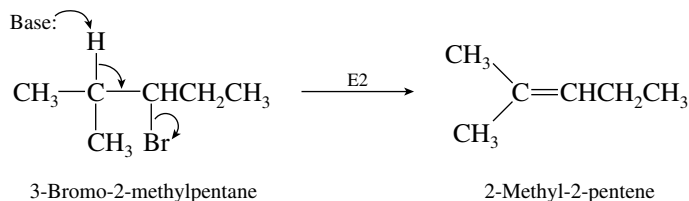
- (e) 2-Bromo-3-methylpentane can undergo dehydrohalogenation by loss of a proton from either C-1 or C-3. Loss of a proton from C-1 gives 3-methyl-1-pentene.



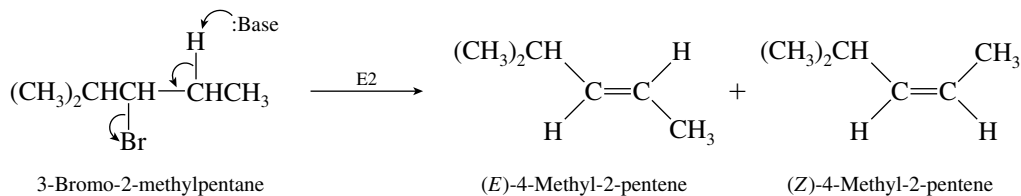
Loss of a proton from C-3 gives a mixture of (*E*)- and (*Z*)-3-methyl-2-pentene.



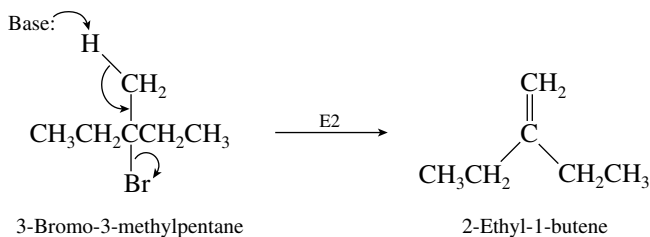
- (f) Three alkenes are possible from 3-bromo-2-methylpentane. Loss of the C-2 proton gives 2-methyl-2-pentene.



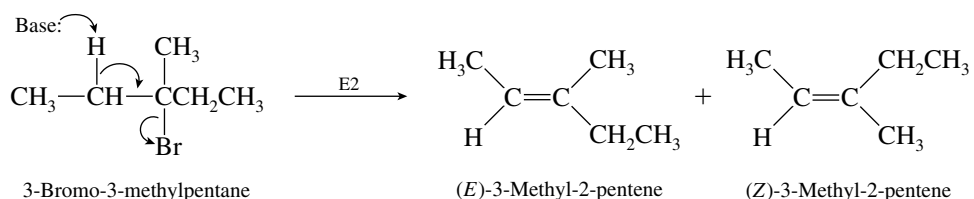
Abstraction of a proton from C-4 can yield either (*E*)- or (*Z*)-4-methyl-2-pentene.



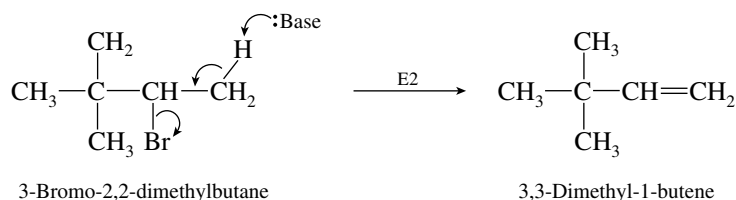
- (g) Proton abstraction from the C-3 methyl group of 3-bromo-3-methylpentane yields 2-ethyl-1-butene.



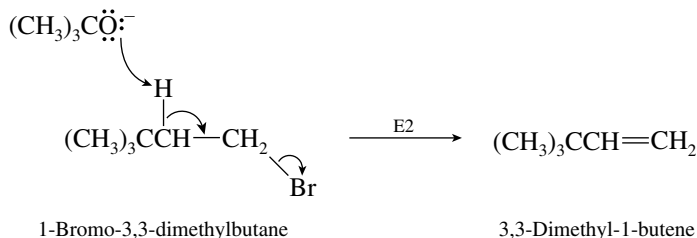
Stereoisomeric 3-methyl-2-pentenes are formed by proton abstraction from C-2.



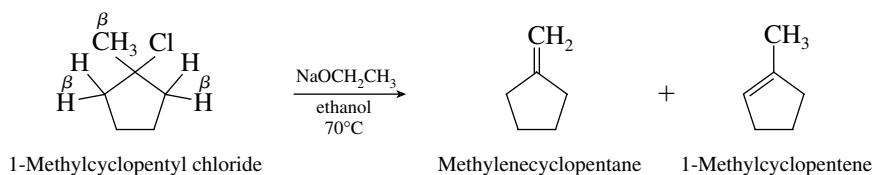
- (h) Only 3,3-dimethyl-1-butene may be formed under conditions of E2 elimination from 3-bromo-2,2-dimethylbutane.



- 5.31 (a) The reaction that takes place with 1-bromo-3,3-dimethylbutane is an E2 elimination involving loss of the bromine at C-1 and abstraction of the proton at C-2 by the strong base potassium *tert*-butoxide, yielding a single alkene.

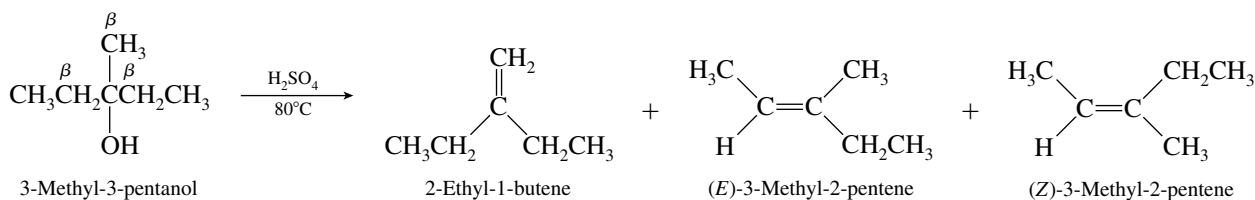


- (b) Two alkenes are capable of being formed in this β -elimination reaction.



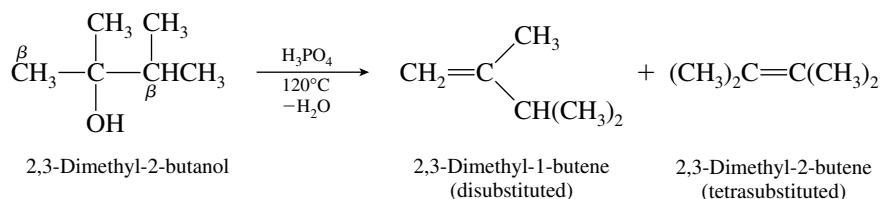
The more highly substituted alkene is 1-methylcyclopentene; it is the major product of this reaction. According to Zaitsev's rule, the major alkene is formed by proton removal from the β carbon that has the fewest hydrogens.

- (c) Acid-catalyzed dehydration of 3-methyl-3-pentanol can lead either to 2-ethyl-1-butene or to a mixture of (*E*)- and (*Z*)-3-methyl-2-pentene.



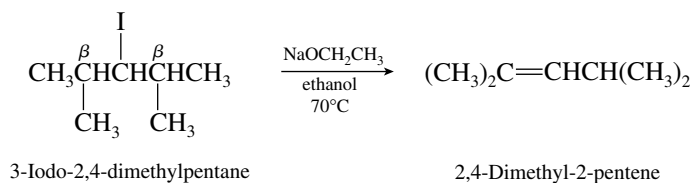
The major product is a mixture of the trisubstituted alkenes, (*E*)- and (*Z*)-3-methyl-2-pentene. Of these two stereoisomers the *E* isomer is slightly more stable and is expected to predominate.

- (d) Acid-catalyzed dehydration of 2,3-dimethyl-2-butanol can proceed in either of two directions.

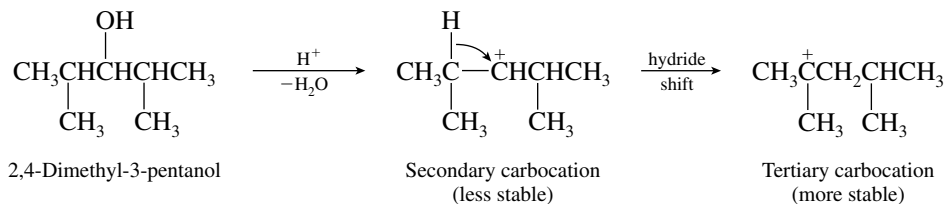


The major alkene is the one with the more highly substituted double bond, 2,3-dimethyl-2-butene. Its formation corresponds to Zaitsev's rule in that a proton is lost from the β carbon that has the fewest hydrogens.

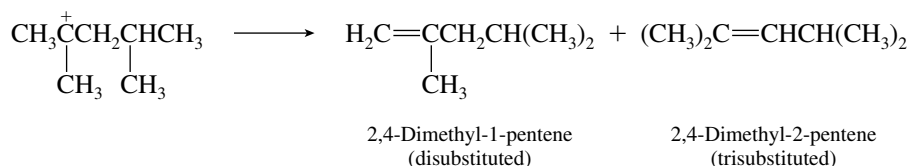
- (e) Only a single alkene is capable of being formed on E2 elimination from this alkyl iodide. Stereoisomeric alkenes are not possible, and because all the β hydrogens are equivalent, regioisomers cannot be formed either.



- (f) Despite the structural similarity of this alcohol to the alkyl halide in the preceding part of this problem, its dehydration is more complicated. The initially formed carbocation is secondary and can rearrange to a more stable tertiary carbocation by a hydride shift.



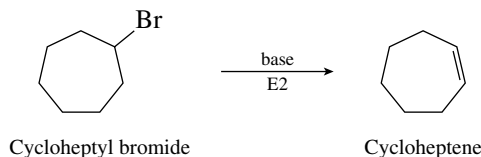
The tertiary carbocation, once formed, can give either 2,4-dimethyl-1-pentene or 2,4-dimethyl-2-pentene by loss of a proton.



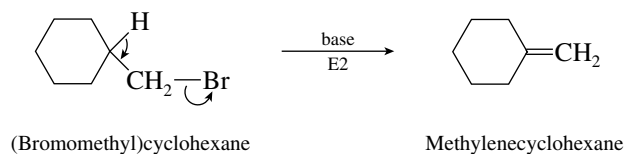
The proton is lost from the methylene group in preference to the methyl group. The major alkene is the more highly substituted one, 2,4-dimethyl-2-pentene.

- 5.32** In all parts of this problem you need to reason backward from an alkene to an alkyl bromide of molecular formula $\text{C}_7\text{H}_{13}\text{Br}$ that gives *only* the desired alkene under E2 elimination conditions. Recall that the carbon-carbon double bond is formed by loss of a proton from one of the carbons that becomes doubly bonded and a bromine from the other.

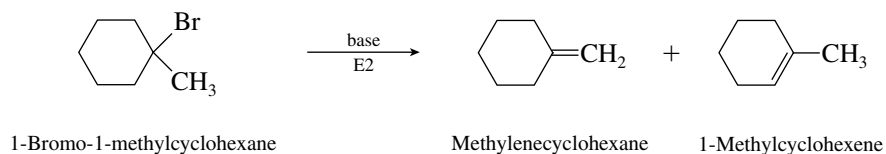
- (a) Cycloheptene is the only alkene formed by an E2 elimination reaction of cycloheptyl bromide.



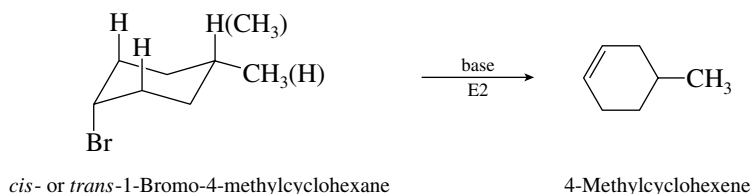
- (b) (Bromomethyl)cyclohexane is the correct answer. It gives methylenecyclohexane as the *only* alkene under E2 conditions.



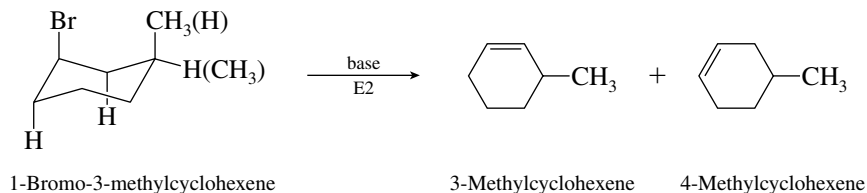
1-Bromo-1-methylcyclohexane is not correct. It gives a mixture of 1-methylcyclohexene and methylenecyclohexane on elimination.



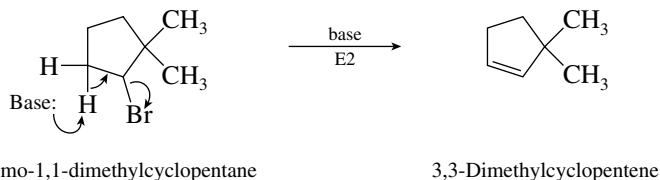
- (c) In order for 4-methylcyclohexene to be the only alkene, the starting alkyl bromide must be 1-bromo-4-methylcyclohexane. Either the *cis* or the *trans* isomer may be used, although the *cis* will react more readily, as the more stable conformation (equatorial methyl) has an axial bromine.



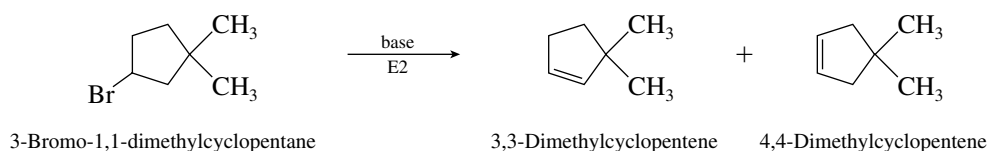
1-Bromo-3-methylcyclohexane is incorrect; its dehydrobromination yields a mixture of 3-methylcyclohexene and 4-methylcyclohexene.



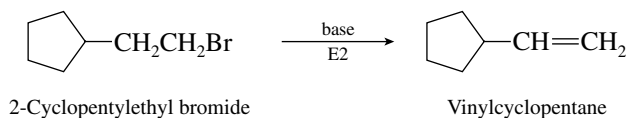
- (d) The bromine must be at C-2 in the starting alkyl bromide for a single alkene to be formed on E2 elimination.



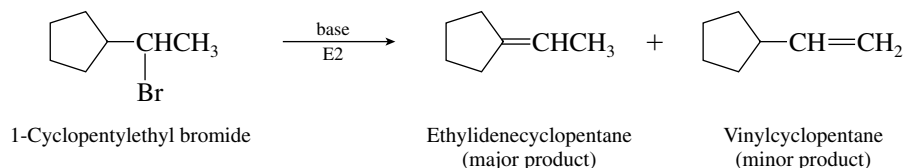
If the bromine substituent were at C-3, a mixture of 3,3-dimethyl- and 4,4-dimethylcyclopentene would be formed.



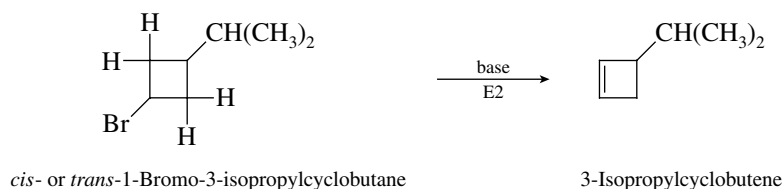
- (e) The alkyl bromide must be primary in order for the desired alkene to be the only product of E2 elimination.



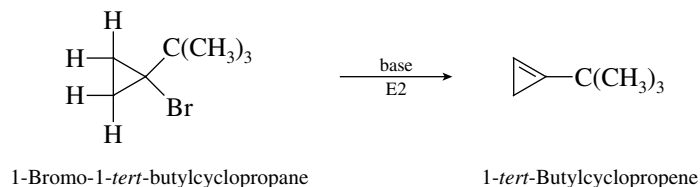
If 1-cyclopentylethyl bromide were used, a mixture of regioisomeric alkenes would be formed, with the desired vinylcyclopentane being the minor component of the mixture.



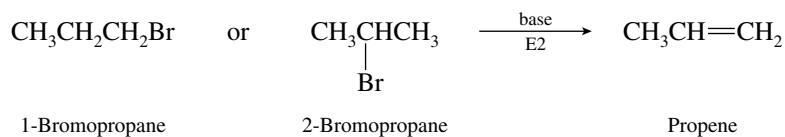
- (f) Either *cis*- or *trans*-1-bromo-3-isopropylcyclobutane would be appropriate here.



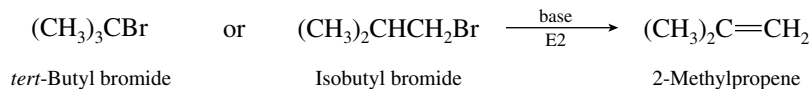
- (g) The desired alkene is the exclusive product formed on E2 elimination from 1-bromo-1-*tert*-butylcyclopropane.



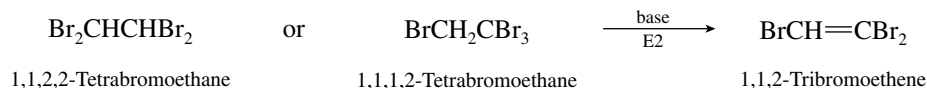
- 5.33 (a) Both 1-bromopropane and 2-bromopropane yield propene as the exclusive product of E2 elimination.



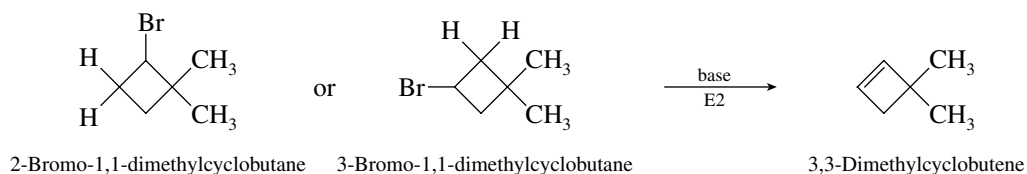
- (b) Isobutene is formed on dehydrobromination of either *tert*-butyl bromide or isobutyl bromide.



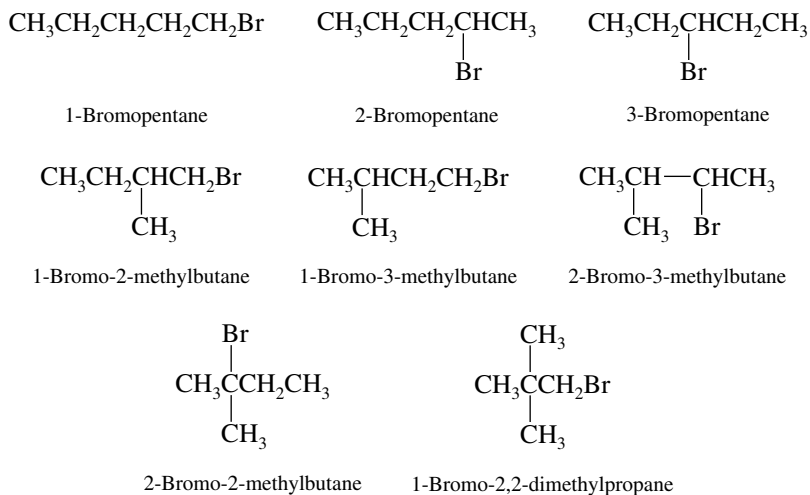
- (c) A tetrabromoalkane is required as the starting material to form a tribromoalkene under E2 elimination conditions. Either 1,1,2,2-tetrabromoethane or 1,1,1,2-tetrabromoethane is satisfactory.



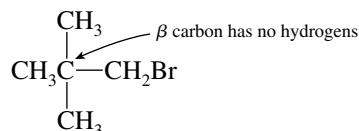
(d) The bromine substituent may be at either C-2 or C-3.



5.34 (a) The isomeric alkyl bromides having the molecular formula $C_5H_{11}Br$ are:

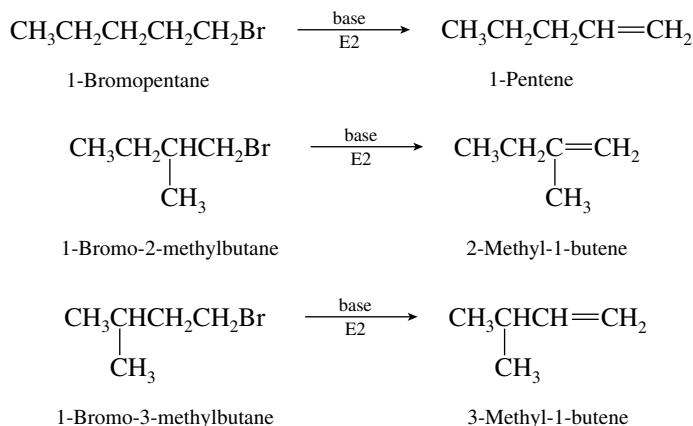


- (b) The order of reactivity toward E1 elimination parallels carbocation stability and is tertiary > secondary > primary. The tertiary bromide 2-bromo-2-methylbutane will undergo E1 elimination at the fastest rate.
- (c) 1-Bromo-2,2-dimethylpropane has no hydrogens on the β carbon and so cannot form an alkene by an E2 process.

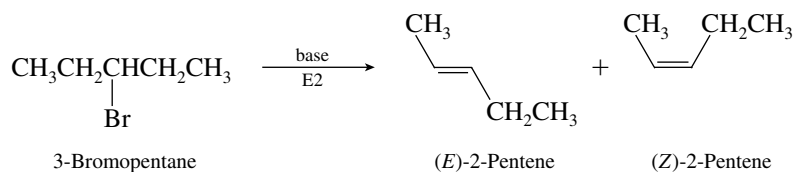


The only available pathway is E1 with rearrangement.

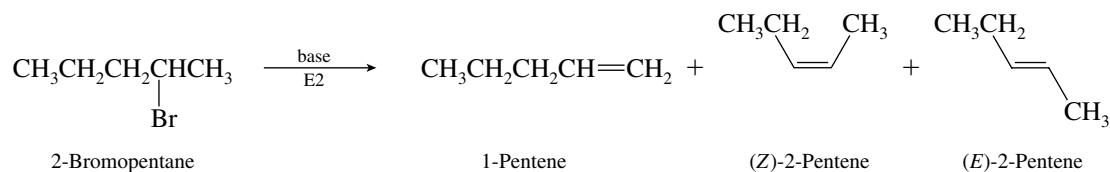
(d) Only the primary bromides will give a single alkene on E2 elimination.



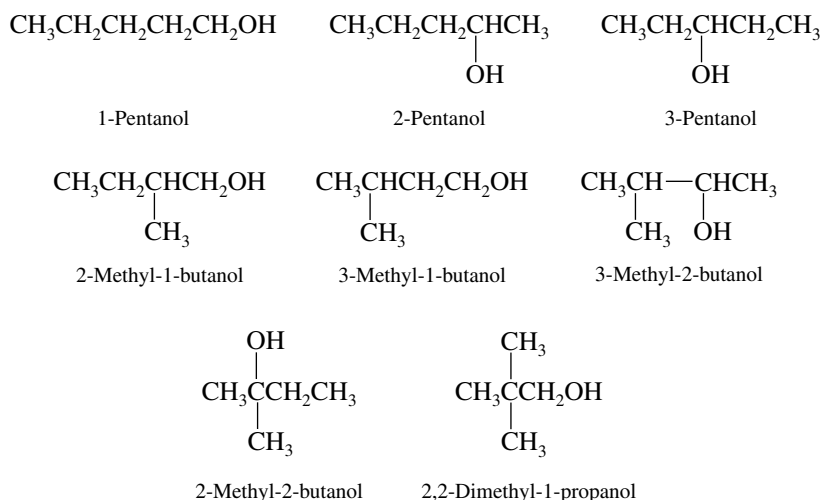
(e) Elimination in 3-bromopentane will give the stereoisomers (*E*)- and (*Z*)-2-pentene.



(f) Three alkenes can be formed from 2-bromopentane.

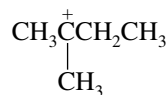


5.35 (a) The isomeric $\text{C}_5\text{H}_{12}\text{O}$ alcohols are:



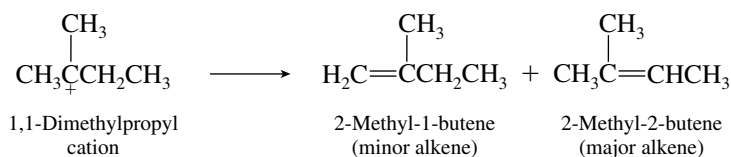
(b) The order of reactivity in alcohol dehydration parallels carbocation stability and is tertiary > secondary > primary. The only tertiary alcohol in the group is 2-methyl-2-butanol. It will dehydrate fastest.

(c) The most stable C_5H_{11} carbocation is the tertiary carbocation.

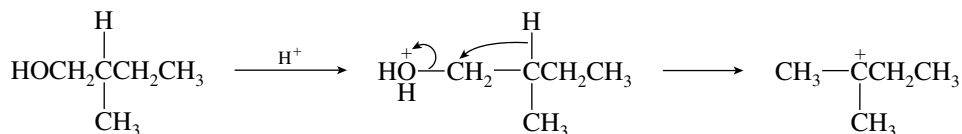
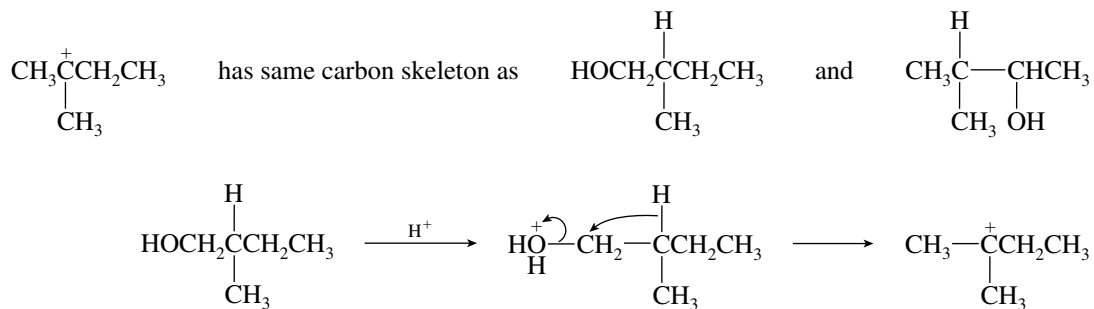


1,1-Dimethylpropyl cation

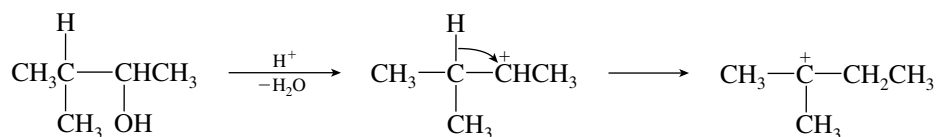
(d) A proton may be lost from C-1 or C-3:



- (e) For the 1,1-dimethylpropyl cation to be formed by a process involving a hydride shift, the starting alcohol must have the same carbon skeleton as the 1,1-dimethylpropyl cation.

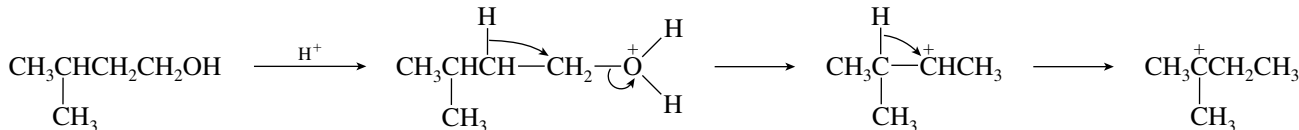


2-Methyl-1-butanol



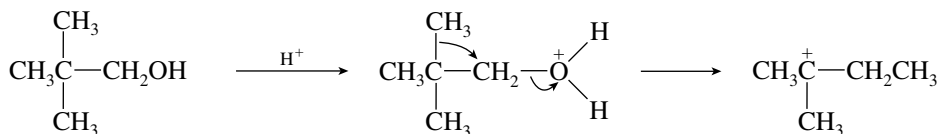
3-Methyl-2-butanol

Although the same carbon skeleton is necessary, it alone is not sufficient; the alcohol must also have its hydroxyl group on the carbon atom adjacent to the carbon that bears the migrating hydrogen. Thus, 3-methyl-1-butanol cannot form a tertiary carbocation by a single hydride shift. It requires two sequential hydride shifts.



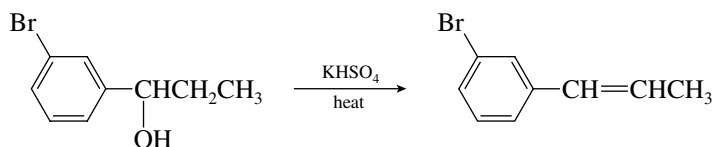
3-Methyl-1-butanol

- (f) 2,2-Dimethyl-1-propanol can yield a tertiary carbocation by a process involving a methyl shift.



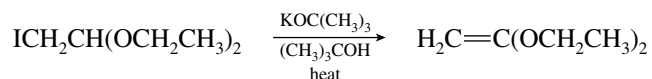
2,2-Dimethyl-1-propanol

- 5.36** (a) Heating an alcohol in the presence of an acid catalyst (KHSO_4) leads to dehydration with formation of an alkene. In this alcohol, elimination can occur in only one direction to give a mixture of cis and trans alkenes.

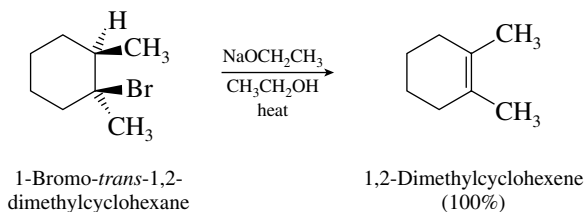


Cis-trans mixture

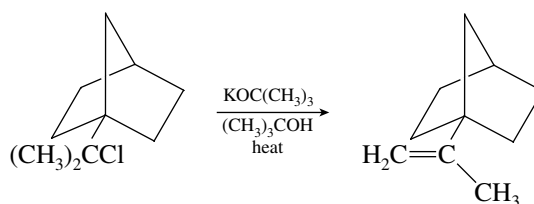
- (b) Alkyl halides undergo E2 elimination on being heated with potassium *tert*-butoxide.



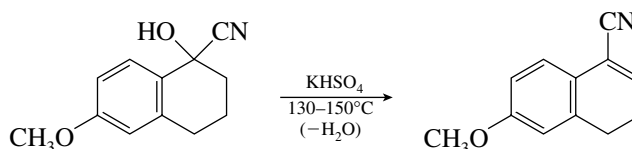
- (c) The exclusive product of this reaction is 1,2-dimethylcyclohexene.



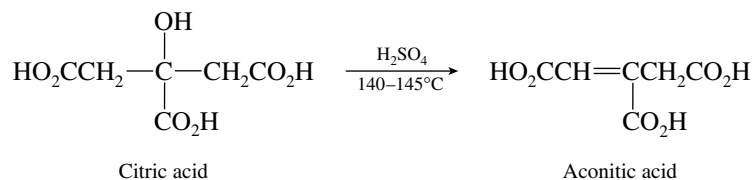
- (d) Elimination can occur only in one direction, to give the alkene shown.



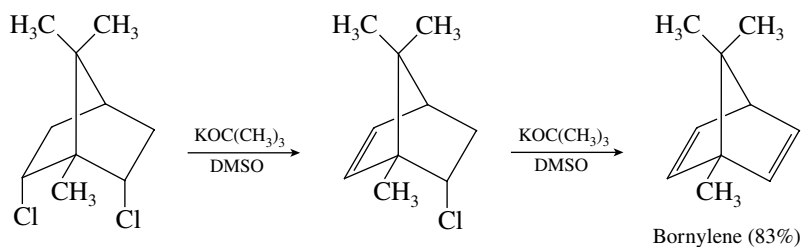
- (e) The reaction is a conventional one of alcohol dehydration and proceeds as written in 76–78% yield.



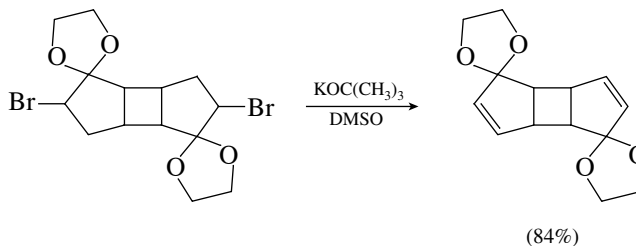
- (f) Dehydration of citric acid occurs, giving aconitic acid.



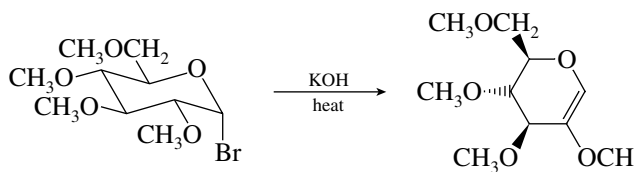
- (g) Sequential double dehydrohalogenation gives the diene.



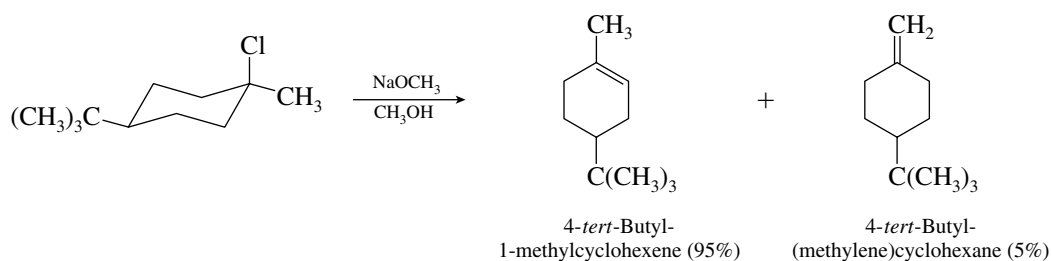
- (h) This example has been reported in the chemical literature, and in spite of the complexity of the starting material, elimination proceeds in the usual way.



- (i) Again, we have a fairly complicated substrate, but notice that it is well disposed toward E2 elimination of the axial bromine.

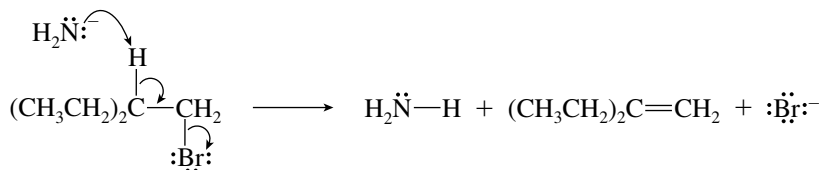


- (j) In the most stable conformation of this compound, chlorine occupies an axial site, and so it is ideally situated to undergo an E2 elimination reaction by way of an anti arrangement in the transition state.

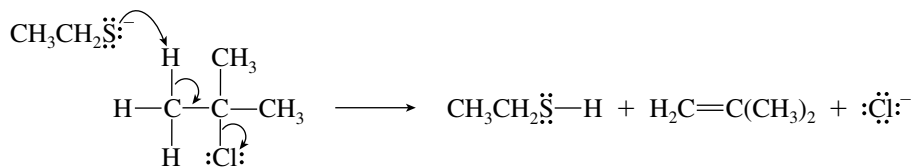


The minor product is the less highly substituted isomer, in which the double bond is exocyclic to the ring.

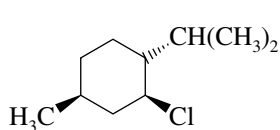
- 5.37** First identify the base as the amide ion (H_2N^-) portion of potassium amide (KNH_2). Amide ion is a strong base and uses an unshared electron pair to abstract a proton from β carbon of the alkyl halide. The pair of electrons in the $\text{C}-\text{H}$ bond becomes the π component of the double bond as the $\text{C}-\text{Br}$ bond breaks. The electrons in the $\text{C}-\text{Br}$ bond become an unshared electron pair of bromide ion.



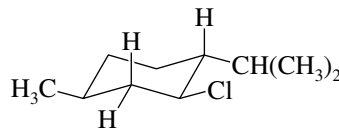
- 5.38** The problem states that the reaction is first order in $(\text{CH}_3)_3\text{CCl}$ (*tert*-butyl chloride) and first order in $\text{NaSCH}_2\text{CH}_3$ (sodium ethanethiolate). It therefore exhibits the kinetic behavior (overall second order) of a reaction that proceeds by the E2 mechanism. The base that abstracts the proton from carbon is the anion $\text{CH}_3\text{CH}_2\text{S}^-$.



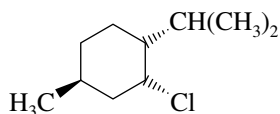
- 5.39** The two starting materials are stereoisomers of each other, and so it is reasonable to begin by examining each one in more stereochemical detail. First, write the most stable conformation of each isomer, keeping in mind that isopropyl is the bulkiest of the three substituents and has the greatest preference for an equatorial orientation.



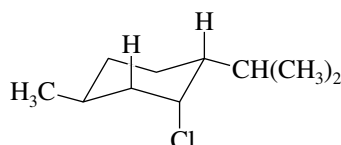
Menthyl chloride



Most stable conformation of menthyl chloride:
none of the three β protons is anti to chlorine



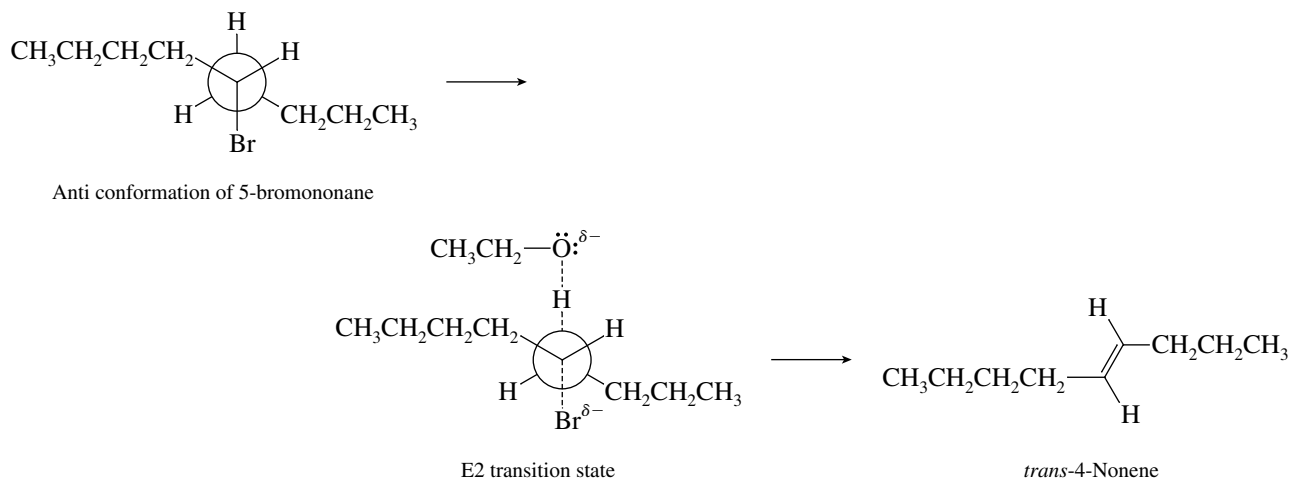
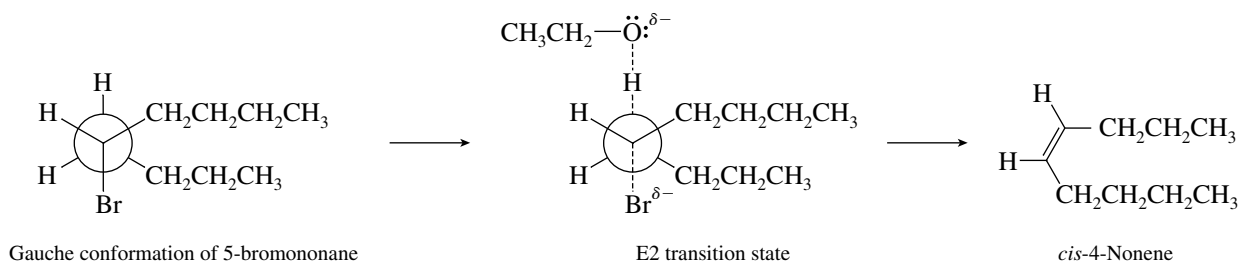
Neomenthyl chloride



Most stable conformation of neomenthyl chloride:
each β carbon has a proton that is anti to chlorine

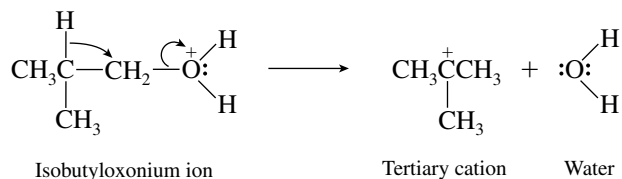
The anti periplanar relationship of halide and proton can be achieved only when the chlorine is axial; this corresponds to the most stable conformation of neomenthyl chloride. Menthyl chloride, on the other hand, must undergo appreciable distortion of its ring to achieve an anti periplanar Cl—C—C—H geometry. Strain increases substantially in going to the transition state for E2 elimination in menthyl chloride but not in neomenthyl chloride. Neomenthyl chloride undergoes E2 elimination at the faster rate.

- 5.40** The proton that is removed by the base must be anti to bromine. Thus, the alkyl groups must be gauche to one another in the conformation that leads to *cis*-4-nonene and anti to one another in the one that leads to *trans*-4-nonene.

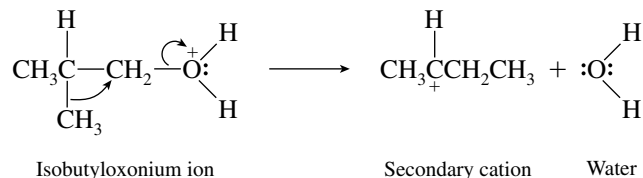


The alkyl groups move closer together (van der Waals strain increases) as the transition state for formation of *cis*-4-nonene is approached. No comparable increase in strain is involved in going to the transition state for formation of the *trans* isomer.

- 5.41 Begin by writing chemical equations for the processes specified in the problem. First consider rearrangement by way of a hydride shift:



Rearrangement by way of a methyl group shift is as follows:



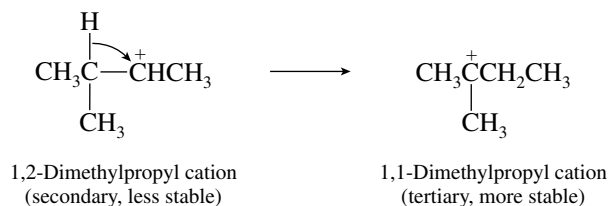
A hydride shift gives a tertiary carbocation; a methyl migration gives a secondary carbocation. It is reasonable to expect that rearrangement will occur so as to produce the more stable of these two carbocations because the transition state has carbocation character at the carbon that bears the migrating group. We predict that rearrangement proceeds by a hydride shift rather than a methyl shift, since the group that remains behind in this process stabilizes the carbocation better.

- 5.42 Rearrangement proceeds by migration of a hydrogen or an alkyl group from the carbon atom adjacent to the positively charged carbon.

- (a) A propyl cation is primary and rearranges to an isopropyl cation, which is secondary, by migration of a hydrogen with its pair of electrons.

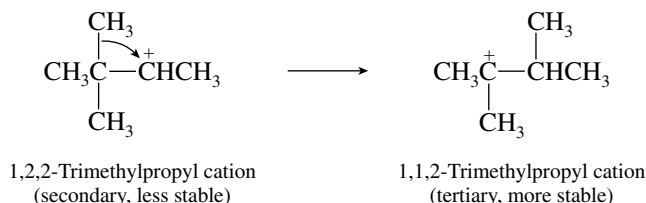


- (b) A hydride shift transforms the secondary carbocation to a tertiary one.

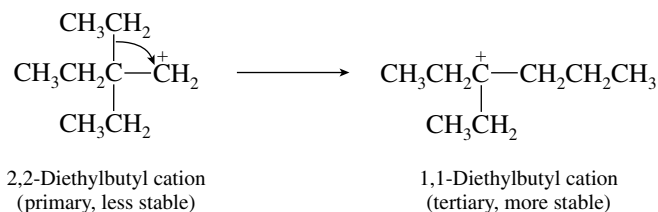


This hydride shift occurs in preference to methyl migration, which would produce the same secondary carbocation. (Verify this by writing appropriate structural formulas.)

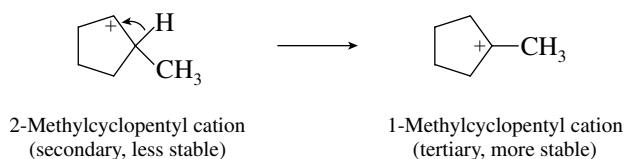
- (c) Migration of a methyl group converts this secondary carbocation to a tertiary one.



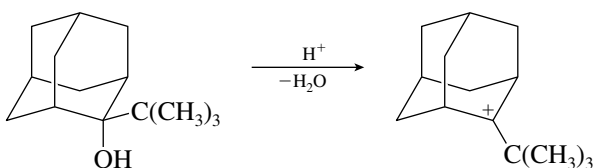
- (d) The group that shifts in this case is the entire ethyl group.



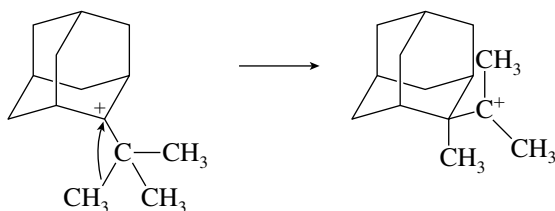
- (e) Migration of a hydride from the ring carbon that bears the methyl group produces a tertiary carbocation.



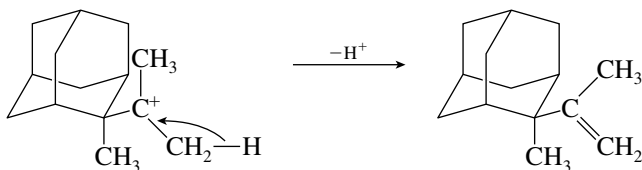
- 5.43 (a) Note that the starting material is an alcohol and that it is treated with an acid. The product is an alkene but its carbon skeleton is different from that of the starting alcohol. The reaction is one of alcohol dehydration accompanied by rearrangement at the carbocation stage. Begin by writing the step in which the alcohol is converted to a carbocation.



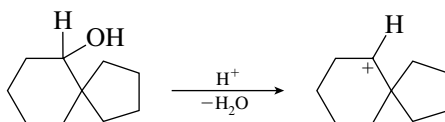
The carbocation is tertiary and relatively stable. Migration of a methyl group from the *tert*-butyl substituent, however, converts it to an isomeric carbocation, which is also tertiary.



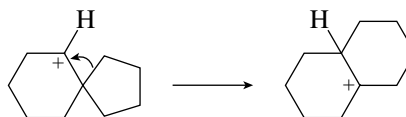
Loss of a proton from this carbocation gives the observed product.



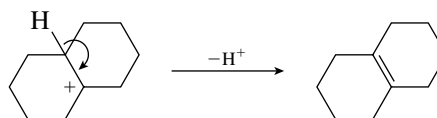
- (b) Here also we have an alcohol dehydration reaction accompanied by rearrangement. The initially formed carbocation is secondary.



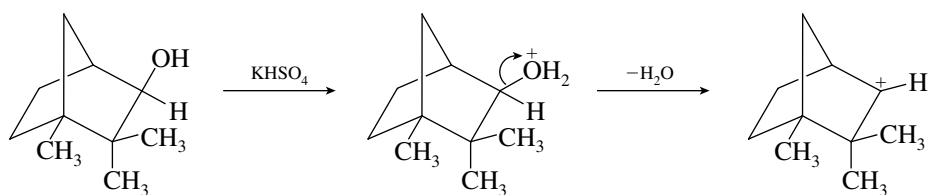
This cation can rearrange to a tertiary carbocation by an alkyl group shift.



Loss of a proton from the tertiary carbocation gives the observed alkene.



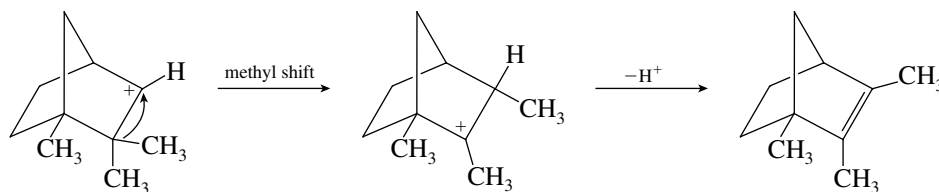
- (c) The reaction begins as a normal alcohol dehydration in which the hydroxyl group is protonated by the acid catalyst and then loses water from the oxonium ion to give a carbocation.



4-Methylcamphenilol

Secondary carbocation

We see that the final product, 1-methylsantene, has a rearranged carbon skeleton corresponding to a methyl shift, and so we consider the rearrangement of the initially formed secondary carbocation to a tertiary ion.

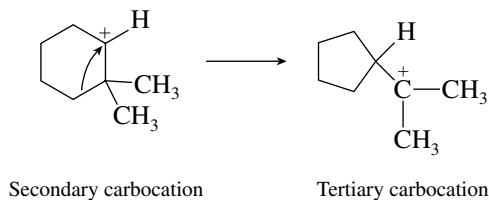


Tertiary carbocation

1-Methylsantene

Deprotonation of the tertiary carbocation yields 1-methylsantene.

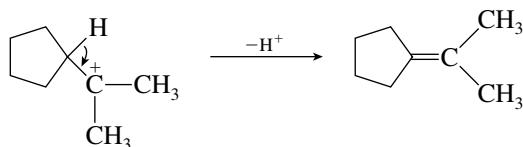
- 5.44 The secondary carbocation can, as we have seen, rearrange by a methyl shift (Problem 5.16). It can also rearrange by migration of one of the ring bonds.



Secondary carbocation

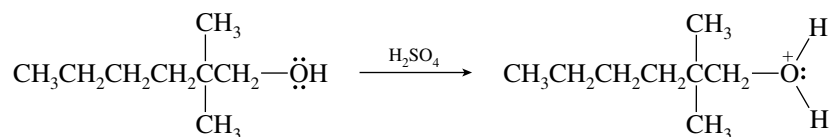
Tertiary carbocation

The tertiary carbocation formed by this rearrangement can lose a proton to give the observed byproduct.

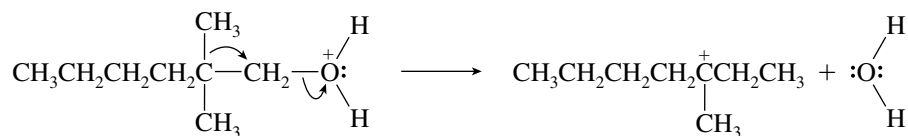


Isopropylidenecyclopentane

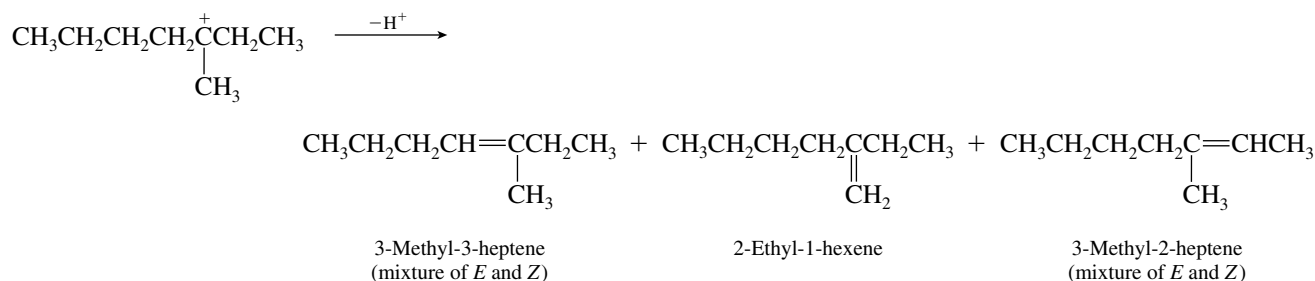
- 5.45 Let's do both part (a) and part (b) together by reasoning mechanistically. The first step in any acid-catalyzed alcohol dehydration is proton transfer to the OH group.



But notice that because this alcohol does not have any hydrogens on its β carbon, it cannot dehydrate directly. Any alkenes that are formed must arise by rearrangement processes. Consider, for example, migration of either of the two equivalent methyl groups at C-2.

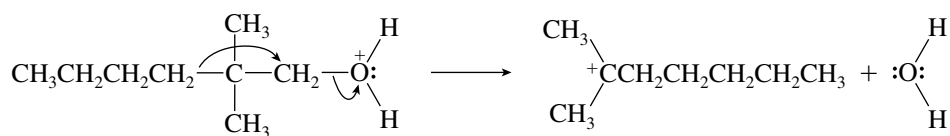


The resulting carbocation can lose a proton in three different directions.

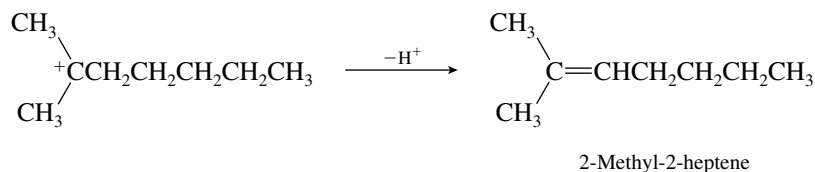


The alkene mixture shown in the preceding equation constitutes part of the answer to part (b). None of the alkenes arising from methyl migration is 2-methyl-2-heptene, the answer to part (a), however.

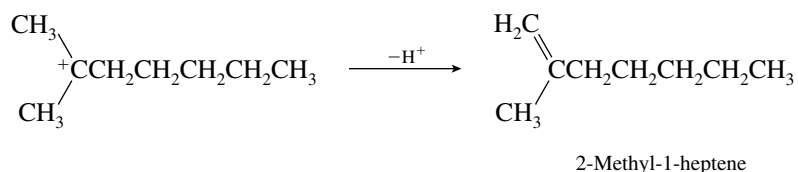
What other group can migrate? The other group attached to the β carbon is a butyl group. Consider its migration.



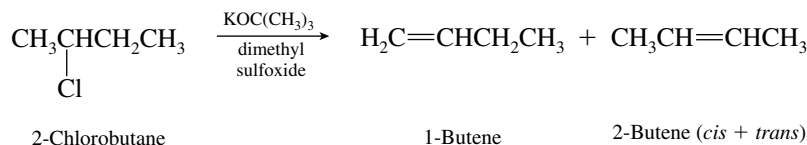
Loss of a proton from the carbocation gives the alkene in part (a).



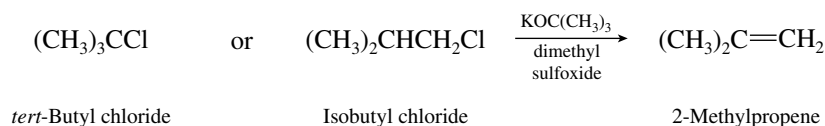
A proton can also be lost from one of the methyl groups to give 2-methyl-1-heptene. This is the last alkene constituting the answer to part (b).



- 5.46 Only two alkanes have the molecular formula C_4H_{10} : butane and isobutane (2-methylpropane)—both of which give two monochlorides on free-radical chlorination. However, dehydrochlorination of one of the monochlorides derived from butane yields a mixture of alkenes.

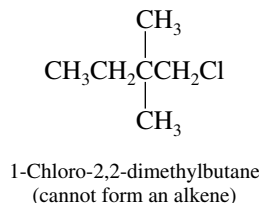


Both monochlorides derived from 2-methylpropane yield only 2-methylpropene under conditions of E2 elimination.

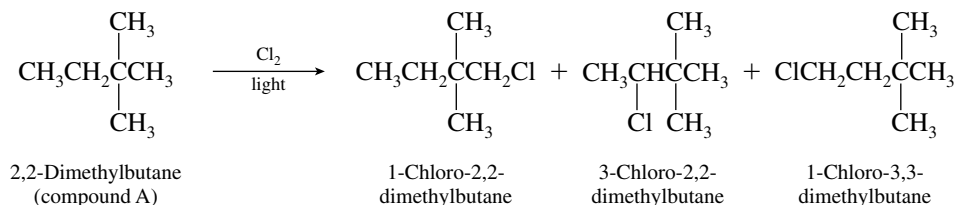


Compound A is therefore 2-methylpropane, the two alkyl chlorides are *tert*-butyl chloride and isobutyl chloride, and alkene B is 2-methylpropene.

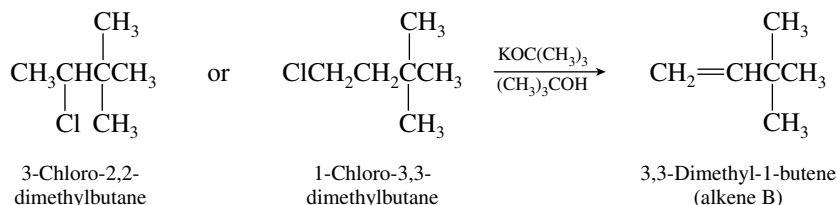
- 5.47 The key to this problem is the fact that one of the alkyl chlorides of molecular formula $C_6H_{13}Cl$ does not undergo E2 elimination. It must therefore have a structure in which the carbon atom that is β to the chlorine bears no hydrogens. This $C_6H_{13}Cl$ isomer is 1-chloro-2,2-dimethylbutane.



Identifying this monochloride derivative gives us the carbon skeleton. The starting alkane (compound A) must be 2,2-dimethylbutane. Its free-radical halogenation gives three different monochlorides:



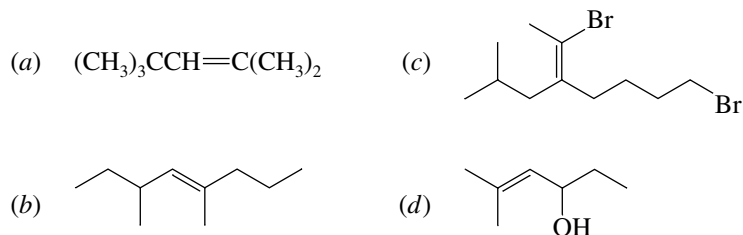
Both 3-chloro-2,2-dimethylbutane and 1-chloro-3,3-dimethylbutane give only 3,3-dimethyl-1-butene on E2 elimination.



SELF-TEST

PART A

A-1. Write the correct IUPAC name for each of the following:



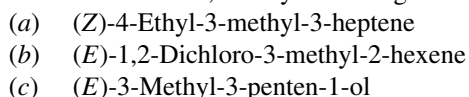
A-2. Each of the following is an incorrect name for an alkene. Write the structure and give the correct name for each.



A-3. (a) Write the structures of all the alkenes of molecular formula C_5H_{10} .
 (b) Which isomer is the most stable?
 (c) Which isomers are the least stable?
 (d) Which isomers can exist as a pair of stereoisomers?

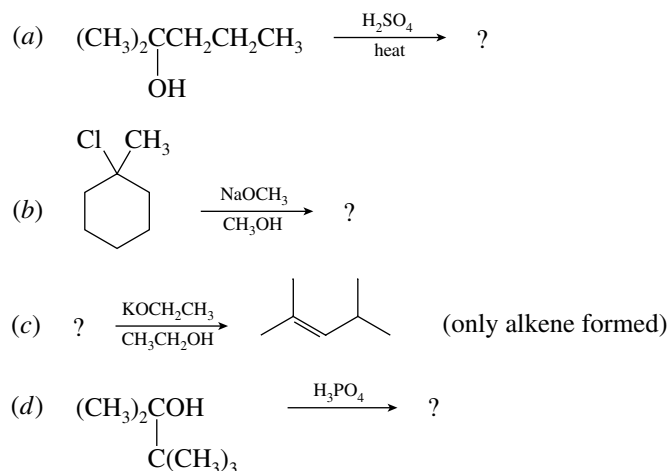
A-4. How many carbon atoms are sp^2 -hybridized in 2-methyl-2-pentene? How many are sp^3 -hybridized? How many σ bonds are of the sp^2 - sp^3 type?

A-5. Write the structure, clearly indicating the stereochemistry, of each of the following:



A-6. Write structural formulas for two alkenes of molecular formula C_7H_{14} that are stereoisomers of each other and have a trisubstituted double bond. Give systematic names for each.

A-7. Write structural formulas for the reactant or product(s) omitted from each of the following. If more than one product is formed, indicate the major one.

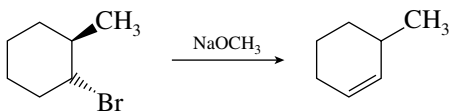


A-8. Write the structure of the $\text{C}_6\text{H}_{13}\text{Br}$ isomer that is *not* capable of undergoing E2 elimination.

A-9. Write a stepwise mechanism for the formation of 2-methyl-2-butene from the dehydration of 2-methyl-2-butanol is sulfuric acid.

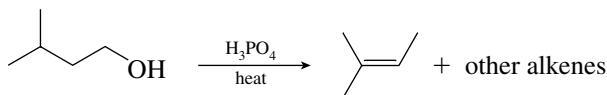
A-10. Draw the structures of all the alkenes, including stereoisomers, that can be formed from the E2 elimination of 3-bromo-2,3-dimethylpentane with sodium ethoxide ($\text{NaOCH}_2\text{CH}_3$) in ethanol. Which of these would you expect to be the major product?

- A-11.** Using curved arrows and perspective drawings (of chair cyclohexanes), explain the formation of the indicated product from the following reaction:



- A-12.** Compare the relative rate of reaction of *cis*- and *trans*-1-chloro-3-isopropylcyclohexane with sodium methoxide in methanol by the E2 mechanism.

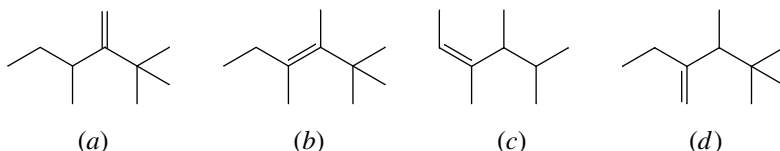
- A-13.** Outline a mechanism for the following reaction:



- A-14.** Compound A, on reaction with bromine in the presence of light, gave as the major product compound B ($\text{C}_9\text{H}_{19}\text{Br}$). Reaction of B with sodium ethoxide in ethanol gave 3-ethyl-4,4-dimethyl-2-pentene as the only alkene. Identify compounds A and B.

PART B

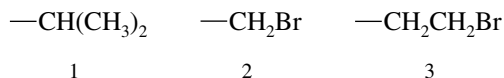
- B-1.** Which one of the alkenes shown below has the *Z* configuration of its double bond?



- B-2.** Carbon–carbon double bonds do not undergo rotation as do carbon–carbon single bonds. The reason is that

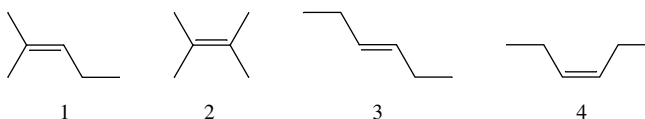
- The double bond is much stronger and thus more difficult to rotate
- Overlap of the sp^2 orbitals of the carbon–carbon σ bond would be lost
- Overlap of the p orbitals of the carbon–carbon π bond would be lost
- The shorter bond length of the double bond makes it more difficult for the attached groups to pass one another
- The statement is incorrect—rotation around double bonds does occur.

- B-3.** Rank the following substituent groups in order of decreasing priority according to the Cahn–Ingold–Prelog system:



- (a) $2 > 3 > 1$ (b) $1 > 3 > 2$ (c) $3 > 1 > 2$ (d) $2 > 1 > 3$

- B-4.** The heats of combustion for the four C_6H_{12} isomers shown are (not necessarily in order): 955.3, 953.6, 950.6, and 949.7 (all in kilocalories per mole). Which of these values is most likely the heat of combustion of isomer 1?

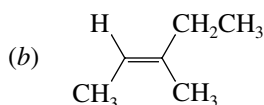
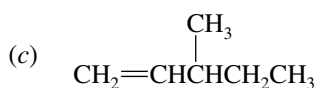
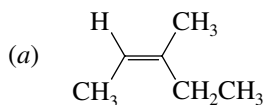
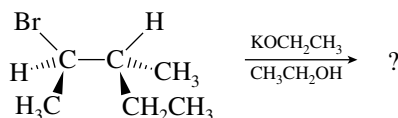


- (a) 955.3 kcal/mol (c) 950.6 kcal/mol
(b) 953.6 kcal/mol (d) 949.7 kcal/mol

1. Dehydration
2. E2 mechanism
3. Carbon skeleton migration
4. Most stable carbocation forms
5. Single-step reaction

(a) 1, 3 (b) 1, 2, 3 (c) 1, 2, 5 (d) 1, 3, 4

B-11. Select the formula or statement representing the major product(s) of the following reaction:

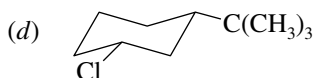
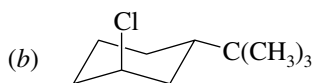
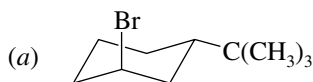


(d) Both (a) and (b) form in approximately equal amounts.

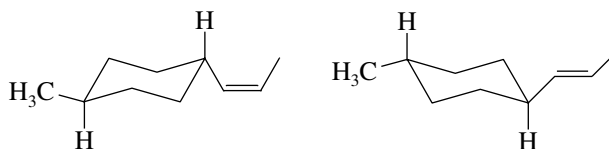
B-12. Which one of the following statements concerning E2 reactions of alkyl halides is true?

- The rate of an E2 reaction depends only on the concentration of the alkyl halide.
- The rate of an E2 reaction depends only on the concentration of the base.
- The C—H bond and the C—X (X = halogen) bond are broken in the same step.
- Alkyl chlorides generally react faster than alkyl bromides.

B-13. Which alkyl halide undergoes E2 elimination at the fastest rate?



B-14. What is the relationship between the pair of compounds shown?



- Identical: superimposable without bond rotations
- Conformations
- Stereoisomers
- Constitutional isomers

B-15. Which one of the following will give 2-methyl-1-butene as the *only* alkene on treatment with $\text{KOC}(\text{CH}_3)_3$ in dimethyl sulfoxide?

- 1-Bromo-2-methylbutane
- 2-Methyl-1-butanol
- 2-Bromo-2-methylbutane
- 2-Methyl-2-butanol