Montogue

Quiz CH201

Organic Chemistry

Nucleophilic Substitution and Elimination

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PROBLEMS

Problem 1

The following substitution reaction exhibits second-order kinetics, and is therefore presumed to occur via an S_N2 process:

What happens to the reaction rate if the concentration of 1-iodopropane is doubled and the concentration of sodium hydroxide is tripled?

Problem 2

Consider the reaction of I^- with CH_3CH_2Cl. The rate constant for the reaction at 60°C is 5×10^{-5} L mol^{-1} s^{-1}.

2.1. Would you expect the reaction to be S_N1 or S_N2?

2.2. With $[I^-]$ = 0.1 mol L^{-1} and $[CH_3CH_2Cl]$ = 0.1 mol L^{-1}, what is the reaction rate?

2.3. With $[I^-]$ = 0.24 mol L^{-1} and $[CH_3CH_2Cl]$ = 0.32 mol L^{-1}, what is the reaction rate?

Problem 3 (Klein, 2017, w/ permission)

Draw the product of each of the following S_N2 reactions.

3.1. (*S*)-2-chloropentane and NaSH

3.2. (*R*)-3-iodohexane and NaCl

3.3. (*R*)-2-bromohexane and NaCN

3.4. 1-bromoheptane and NaOH

Problem 4

For each pair, predict the stronger nucleophile in a S_N2 reaction (using an alcohol as solvent). Explain your prediction.

4.1. $(CH_3CH_2)_3N$ or $(CH_3CH_2)_2NH$

4.2. $(CH_3)_2O$ or $(CH_3)_2S$

4.3. NH_3 or PH_3

4.4. CH_3S^- or H_2S

4.5. $(CH_3)_3N$ or $(CH_3)_2O$

4.6. CH_3COO^- or CF_3COO^-

4.7. $(CH_3)_2CHO^-$ or $CH_3CH_2CH_2O^-$

4.8. I^- or Cl^-

Problem 5

Which reaction in each of the following pairs would you expect to be faster?

5.1. The S_N2 displacement by I^- on $CHCl_3$ or on CH_3OTos.

5.2. The S_N2 displacement by $CH_3CO_2^-$ on bromoethane or on bromocycloethane.

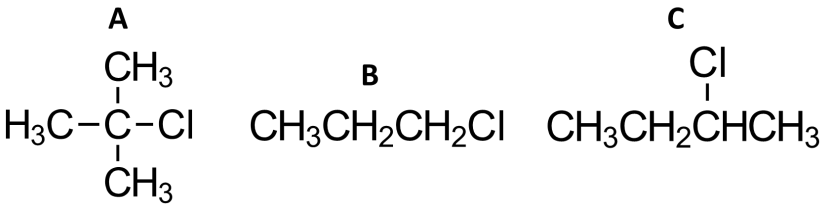
5.3. The S_N2 displacement on 2-bromopropane by $CH_3CH_2O^-$ or by CN^-.

5.4. The S_N2 displacement by $HC\equiv C^-$ on bromomethane in benzene or in acetonitrile.

▶ Problem 6 (McMurry, 2008, w/ permission)

Order each of the following sets of compounds with respect to S_N2 reactivity.

6.1.



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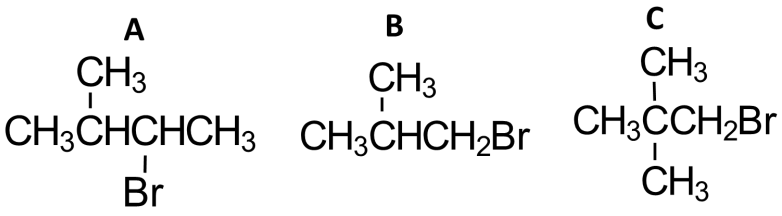

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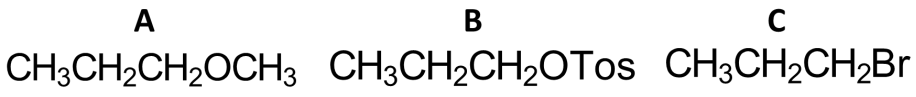
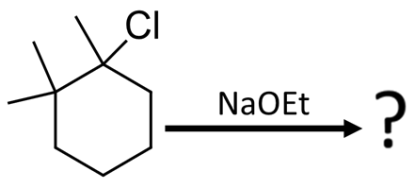


▶ Problem 7

Predict the product(s) of the following E2 elimination reactions.

7.1.



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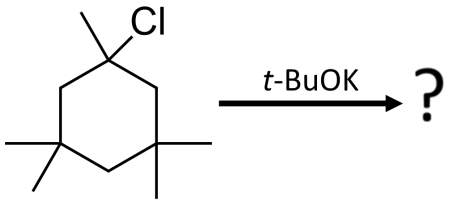
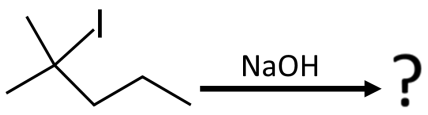


7.3.



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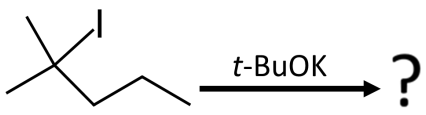

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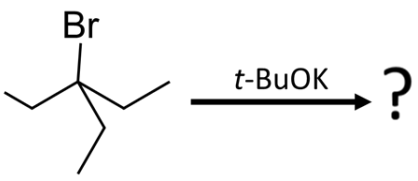

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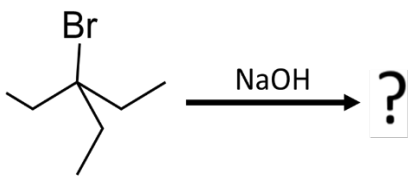
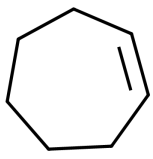


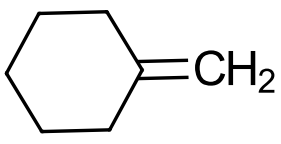
▶ Problem 8 (Carey, 2008, w/ permission)

Find the compound of molecular formula $C_7H_{13}Br$ that gives the alkenes shown as the **exclusive** product of E2 elimination.

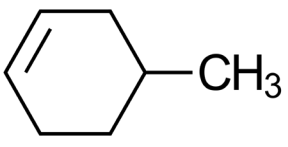
8.1.



8.2.



8.3.



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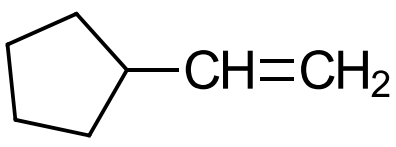

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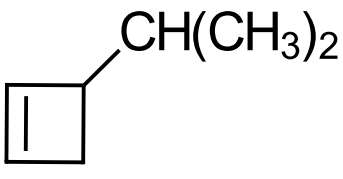

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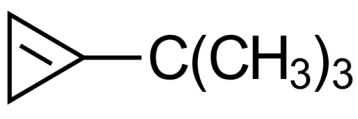
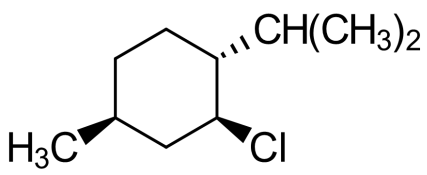
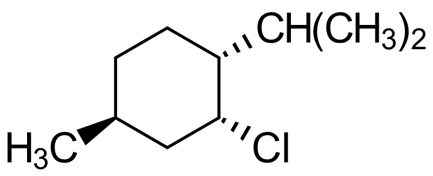


▶ Problem 9 (Carey, 2008, w/ permission)

Menthyl chloride and neomenthyl chloride have the structures shown. One of these stereoisomers undergoes elimination on treatment with sodium ethoxide in ethanol much more readily than the other. Which reacts faster, menthyl chloride or neomenthyl chloride? Why?



Menthyl chloride

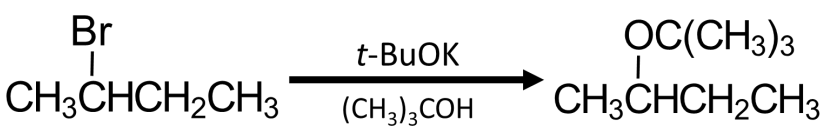


Neomenthyl chloride

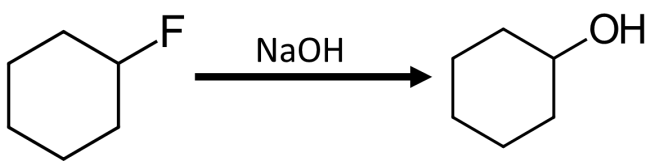
▶ Problem 10 (McMurry, 2008, w/ permission)

The reactions shown below are unlikely to occur as written. Tell what is wrong with each, and predict the actual product.

10.1.



10.2.



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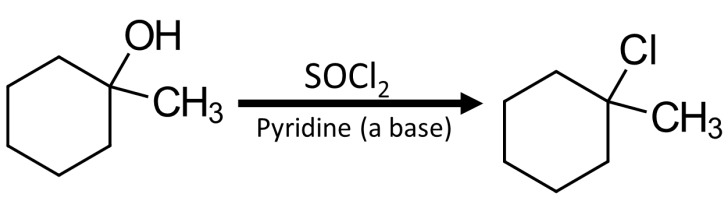
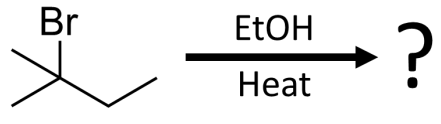


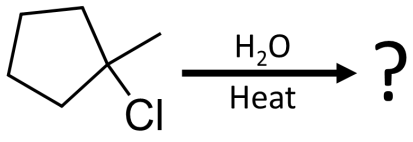
▶ Problem 11 (Klein, 2017, w/ permission)

Draw all of the expected products for each of the following solvolysis reactions.

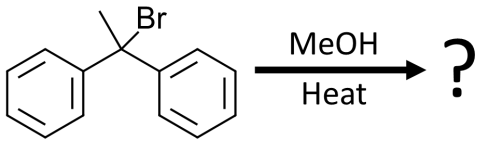
11.1.



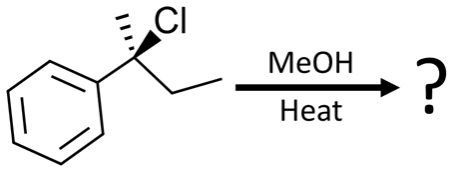
11.2.



11.3.



11.4.

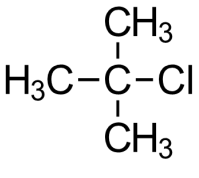


▶ Problem 12 (McMurry, 2008, w/ permission)

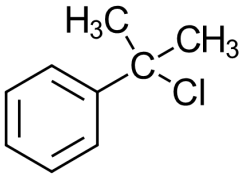
Order each of the following sets of compounds with respect to S_N1 reactivity.

12.1.

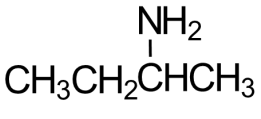
A



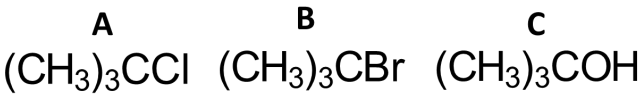
B



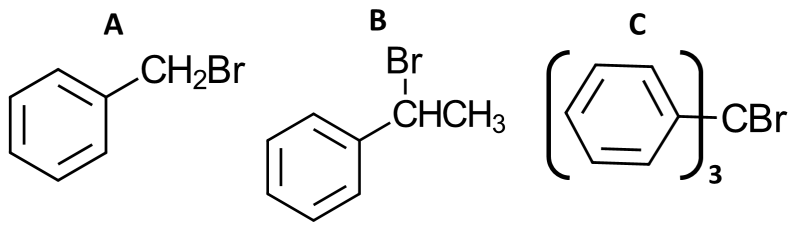
C



12.2.

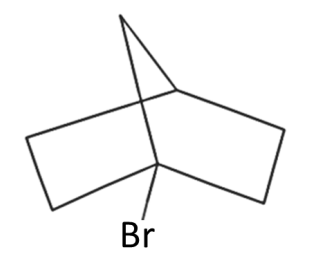


12.3.



▶ **Problem 13** (Solomons *et al.*, 2014)

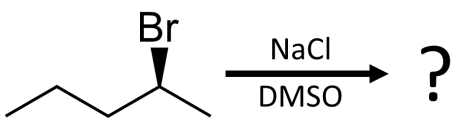
1-Bromo[2.2.1]bicycloheptane is unreactive toward both S_N2 and S_N1 reactions. Referring to the structure of this molecule, answer: what barriers are there to substitution of 1-bromo[2.2.1]bicycloheptane by both S_N2 and S_N1 reaction mechanisms?



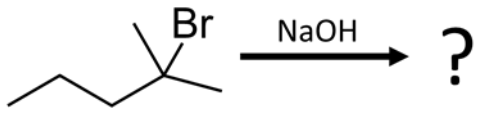
▶ **Problem 14** (Klein, 2017, w/ permission)

Identify the major and minor product(s) expected for each of the following reactions.

14.1.



14.2.



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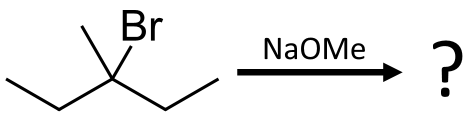

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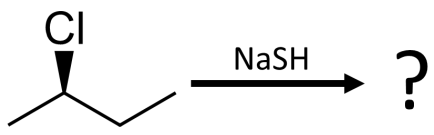

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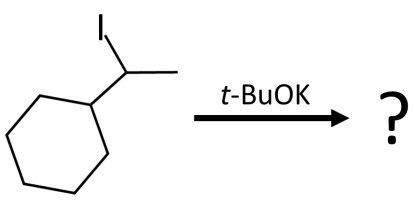

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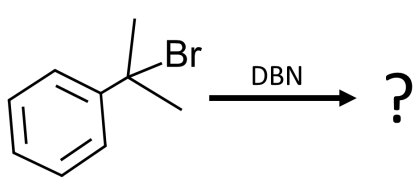

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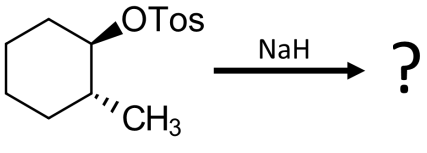

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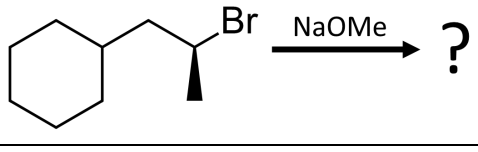
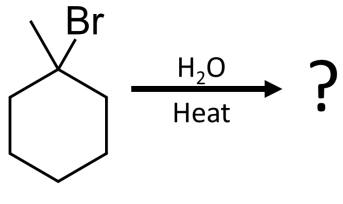
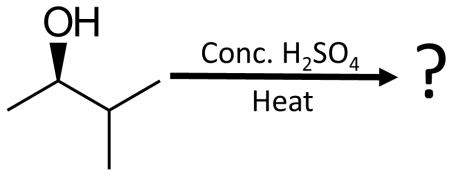


14.9.



14.10.



▶ **Problem 15** (Carey, 2008, w/ permission)

List all the isomeric alkyl bromides having the molecular formula $C_5H_{11}Br$.

15.1. Which one undergoes E1 elimination at the fastest rate?

15.2. Which one is incapable of reacting by the E2 mechanism?

15.3. Which ones can yield only a single alkene on E2 elimination?
15.4. For which isomer does E2 elimination give two alkenes that are not constitutional isomers?
15.5. Which one yields the most complex mixture of alkenes on E2 elimination?

▶ Problem 16 (Klein, 2017, w/ permission)

Compound A and compound B are constitutional isomers with the molecular formula C_4H_9Cl. Treatment of compound A with sodium methoxide gives *trans*-2-butene as the major product, while treatment of compound B with sodium methoxide gives a different disubstituted alkene as the major product.
16.1. Draw the structure of compound A.
16.2. Draw the structure of compound B.

▶ Problem 17 (Carey, 2008, w/ permission)

Compound A (C_4H_{10}) gives two different monochlorides on photochemical chlorination. Treatment of either of these monochlorides with potassium *tert*-butoxide in dimethyl sulfoxide gives the same alkene B (C_4H_8) as the only product. What are the structures of compound A, the two monochlorides, and alkene B?

▶ Problem 18 (Carey, 2008, w/ permission)

Compound A (C_6H_{14}) gives three different monochlorides on photochemical chlorination. One of these monochlorides is inert to E2 elimination. The other two monochlorides yield the same alkene B (C_6H_{12}) on being heated with potassium *tert*-butoxide in *tert*-butyl alcohol. Identify compound A, the three monochlorides, and alkene B.

▶ Problem 19 (Solomons *et al.*, 2014)

The reaction of chloroethane with water *in the gas phase* to produce ethanol and hydrogen chloride has ΔH^o = + 26.6 kJ mol^{-1} and ΔS^o = +4.81 J K^{-1} mol^{-1} at 25°C.
19.1. Which of these terms, if either, favors the reaction going to completion?
19.2. Calculate ΔG^o for the reaction.
19.3. Calculate the equilibrium constant for the reaction.
19.4. In aqueous solution the equilibrium constant is very much larger than the one you just calculated. How can you account for this fact?

SOLUTIONS

P.1 ➡ *Solution*

The rate of a S_N2 reaction is linearly dependent on the concentrations of each reactant (second order overall). Doubling the concentration of 1-iodopropane and tripling the concentration of sodium hydroxide will cause the reaction rate to become 2 × 3 = 6 times faster.

P.2 ➡ *Solution*

2.1: The reaction is S_N2 because the substrate is a I^- halide.
2.2: Since the reaction is S_N2, the reaction rate is given by

$$\text{Rate} = k\left[\text{I}^-\right]\left[\text{CH}_3\text{CH}_2\text{Cl}\right]$$

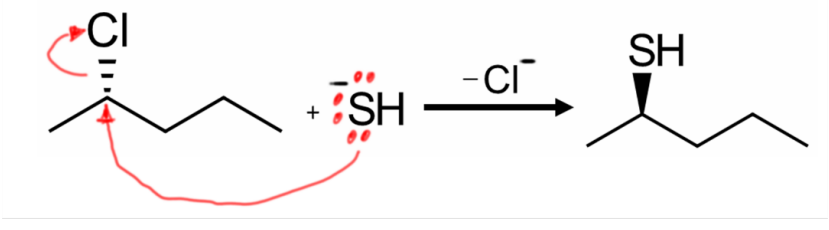
$$\therefore \text{Rate} = \left(5\times10^{-5}\right)\times0.1\times0.1 = \boxed{5\times10^{-7}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}$$

2.3: The reaction rate, in this case, is given by

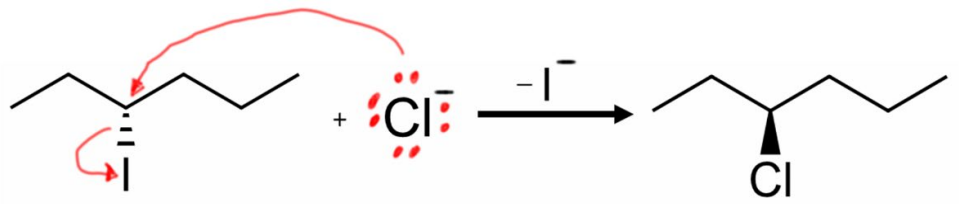
$$\text{Rate} = \left(5\times10^{-5}\right)\times0.24\times0.32 = \boxed{3.84\times10^{-6}\ \text{mol}\,\text{L}^{-1}\,\text{s}^{-1}}$$

P.3 ➡ *Solution*

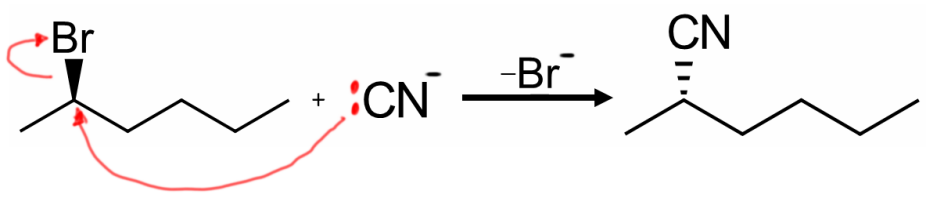
3.1: The substrate is (*S*)-2-chloropentane, and the nucleophile is HS^-. Chloride is ejected as a leaving group, with inversion of configuration. The product is (*R*)-2-pentanethiol.



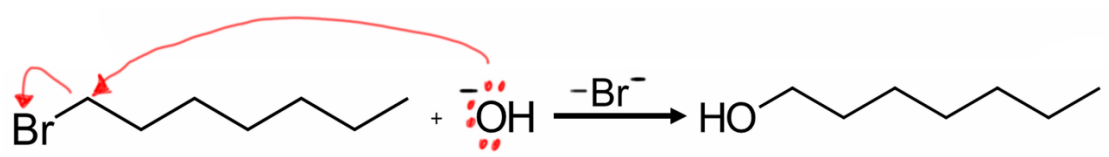
3.2: The substrate is (*R*)-3-iodohexane, and the nucleophile is Cl^-. Iodine is ejected as a leaving group, with inversion of configuration. The product is (*S*)-3-chlorohexane.



3.3: The substrate is (*R*)-2-bromohexane, and the nucleophile is CN^-. Bromide is ejected as a leaving group, with inversion of configuration. The product is (*S*)-2-methylhexanenitrile.



3.4: The substrate is 1-bromoheptane, and the nucleophile is OH^-. Bromide is ejected as a leaving group. There is no inversion of configuration in this case because there is no chiral center. The product is heptanol.



P.4 ➡ *Solution*

4.1: $(CH_3CH_2)_2NH$ is a better nucleophile because it is less sterically hindered.

4.2: $(CH_3)_2S$ is a better nucleophile because it is larger, more polarizable than O.

4.3: Phosphine is a better nucleophile because P is larger, more polarizable than N.

4.4: CH_3S^- is a better nucleophile because anions are better nucleophiles than neutral molecules of the same element.

4.5: $(CH_3)_3N$ is a better nucleophile because N is slightly less electronegative than O and hence is easier to donate electrons.

4.6: CH_3COO^- is a better nucleophile because it is more basic, with electrons less delocalized than in CF_3COO^- because of the inductive effect of F substituents.

4.7: $CH_3CH_2CH_2O^-$ is a better nucleophile because it features less branching, and hence less steric hindrance.

4.8: I^- is a better nucleophile because it is larger and more polarizable than Cl^-.

P.5 ➡ *Solution*

5.1: The difference on this pair of reactions concerns the leaving group. Since ^-OTos is a better leaving group than Cl^- - the best leaving groups are those that are most stable, that is, those that are the conjugate bases of strong acids - S_N2 displacement by iodide on CH_3OTos proceeds faster.

5.2: The substrates on these two reactions are different. Bromoethane is a primary bromoalkane, and bromocyclohexane is a secondary bromoalkane. Since S_N2 reactions proceed faster at primary than secondary carbon atoms, S_N2 displacement on bromoethane is a faster reaction.

5.3: Ethoxide ion and cyanide ion are different nucleophiles. Since CN^- is more reactive than $CH_3CH_2CO^-$ in S_N2 reactions, S_N2 displacement on 2-bromopropane by CN^- proceeds at a faster rate.

5.4: The solvent in each reaction is different. The S_N2 reaction on bromoethane in polar, aprotic acetonitrile proceeds faster than the reaction in nonpolar benzene.

P.6 ➡ *Solution*

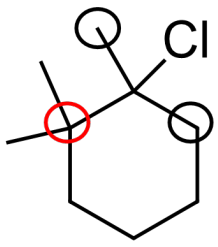
6.1: A primary substrate is more reactive than a secondary substrate, which in turn is more reactive than a tertiary substrate. The correct order, from least reactive to most reactive, is **A** < **C** < **B**.

6.2: The less sterically hindered a substrate, the more reactive it is. The correct order, from least reactive to most reactive, is **C** < **A** < **B**.

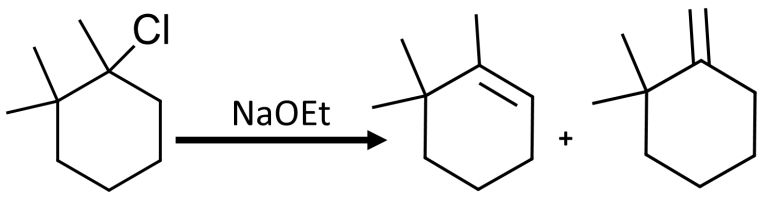
6.3: The greater the extent of charge stabilization of the leaving group, the lower the energy of the transition state and the more rapid the reaction. The groups that best stabilize a negative charge are also the weakest bases. As a result, $TosO^-$ is a more reactive leaving group than Br^-, which in turn is more reactive than OCH_3^-. The correct order, from least reactive to most reactive, is **A** < **C** < **B**.

P.7 ➡ *Solution*

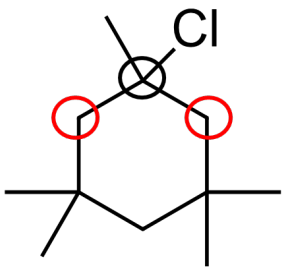
7.1: The starting molecule has three β positions, but one of them (highlighted in red) does not bear protons.



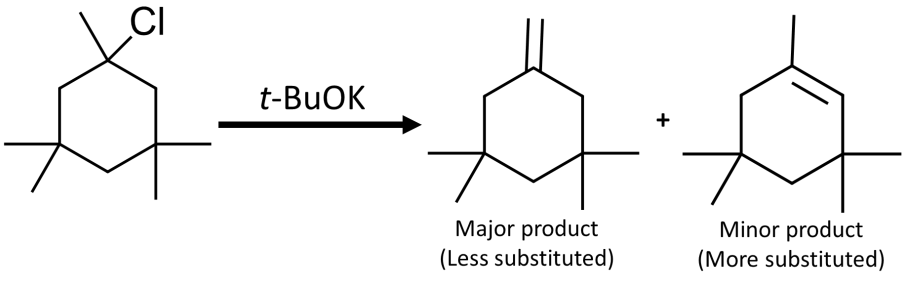
Since there are two β positions bearing protons, there are two possible elimination products. Since the base (ethoxide) is not sterically hindered, we expect that the major product will be the more-substituted alkene, and the minor product will be the less-substituted alkene. The major product is 1,6,6-trimethylcyclohexene.



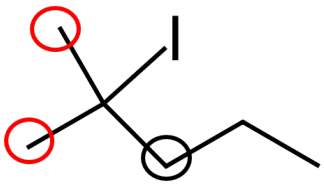
7.2: The starting molecule has three β positions that bear protons, but two of them (highlighted in red) are identical.



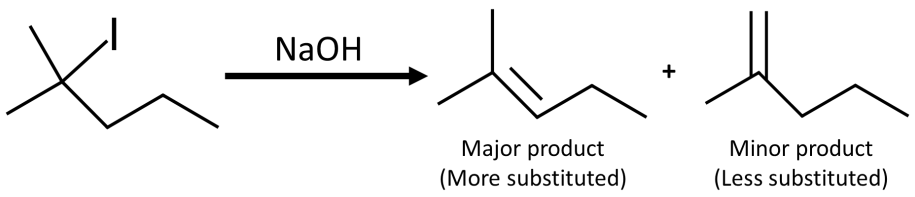
Thus, there are only two unique β positions, giving rise to two possible elimination products, shown below. Since the base (*tert*-butoxide) is sterically hindered, we expect that the major product will be the less-substituted alkene, and the minor product will be the more-substituted alkene. The major product is 1,1,3,3-tetramethyl-5-methylenecyclohexane.



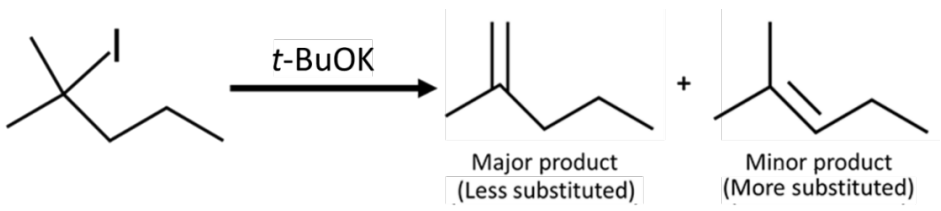
7.3: The starting molecule has three β positions that bear protons, but two of them (highlighted in red) are identical.



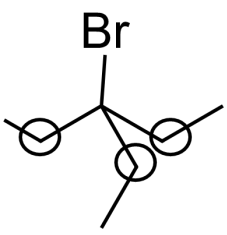
Thus, there are only two unique β positions, giving rise to two possible elimination products, shown below. Since the base (hydroxide) is not sterically hindered, we expect that the major product will be the more-substituted alkene, and the minor product will be the less-substituted alkene. The major product is 2-methyl-2-pentene.



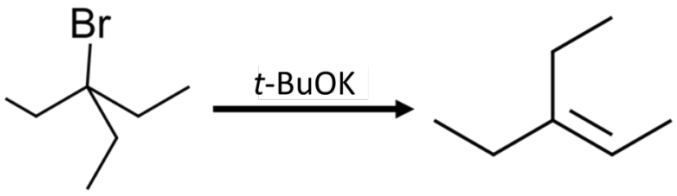
7.4: As mentioned in the solution to the previous problem, the starting molecule has only two unique β positions, giving rise to two possible elimination products. Since the base (*tert*-butoxide) in this case is sterically hindered, we expect that the major product will be the *less*-substituted alkene, 2-methyl-1-pentene.



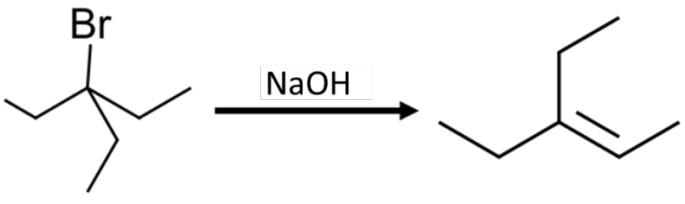
7.5: The starting molecule has three β positions that bear protons.



In this case, all three β positions are identical, so removing a proton from any one of these positions will lead to the same product. As such, there is only one possible elimination product, namely 3-ethyl-2-pentene.

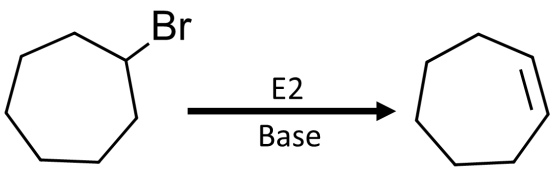


7.6: As mentioned in the solution to the previous problem, all three β positions are identical, so only one elimination product (3-ethyl-2-pentene) is possible, regardless of the base used.

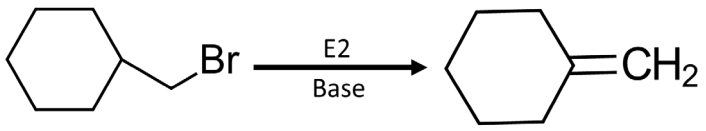


P.8 ➡ *Solution*

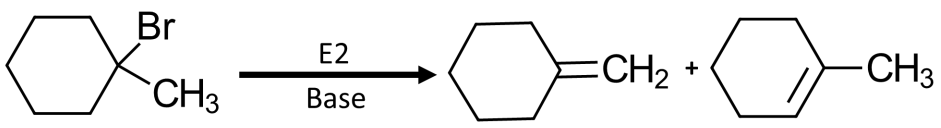
8.1: Cycloheptene is the only alkene formed by an E2 elimination reaction of cycloheptyl bromide.



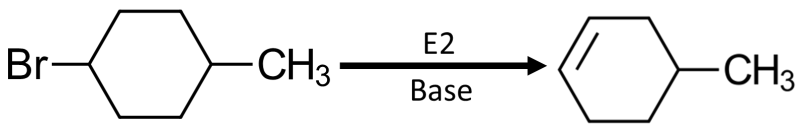
8.2: Methylenecyclohexane is the only alkene formed by an E2 elimination reaction of methylenecyclohexane.



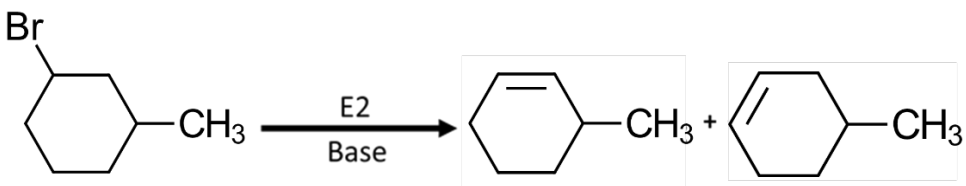
1-Bromo-1-methylcyclohexane is not a correct choice of reactant, as it would yield a mixture of methylenecyclohexane and 1-methylcyclohexene on elimination.



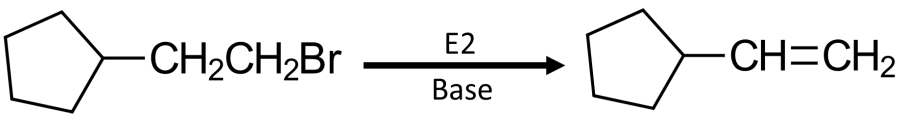
8.3: In order for 4-methylcyclohexane to be the only alkene, the starting alkyl bromide must be 1-bromo-4-methylcyclohexane. Either the *cis* or the *trans* isomer may be used, but the *cis* one will react more rapidly because the more stable conformation (equatorial methyl) has an axial bromine.



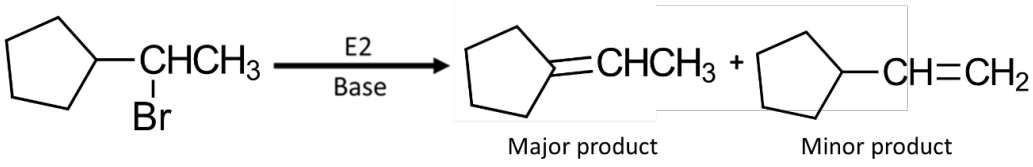
1-Bromo-3-methylcyclohexane is not the correct choice of reactant, as it would yield a mixture of 3-methylcyclohexene and 4-methylcyclohexene on elimination.



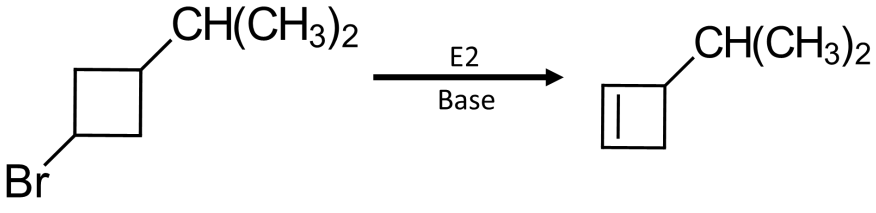
8.4: The following alkyl bromide, 2-cyclopentylethyl bromide, should yield vinylcyclopentane as the sole product upon E2 elimination.



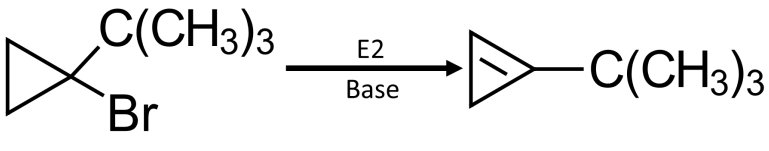
If 1-cyclopentylethyl bromide were used, a mixture of regioisomeric alkenes would be formed, with the desired vinylcyclopentane being the minor component of the mixture.



8.5: This cyclic alkene can be obtained by E2 elimination of *cis*- or *trans*-1-bromo-3-isopropylcyclobutane.



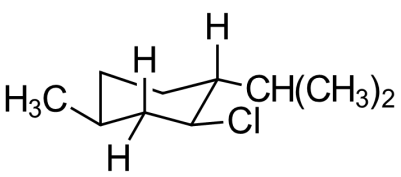
8.6: This cyclic alkene can be obtained by E2 elimination of 1-bromo-1-*tert*-butylcyclopropane.



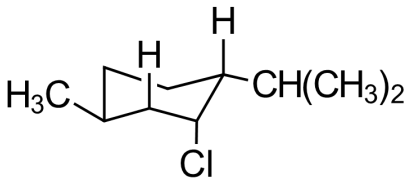
P.9 ➡ *Solution*

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. Notice that in the most stable configuration of menthyl chloride, none of the three β protons is *anti* to

chlorine. In the most stable conformation of neomenthyl chloride, each β carbon has a proton that is *anti* to chlorine.



Most stable conformation of menthyl chloride



Most stable conformation of neomenthyl chloride

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.

P.10 ➡ *Solution*

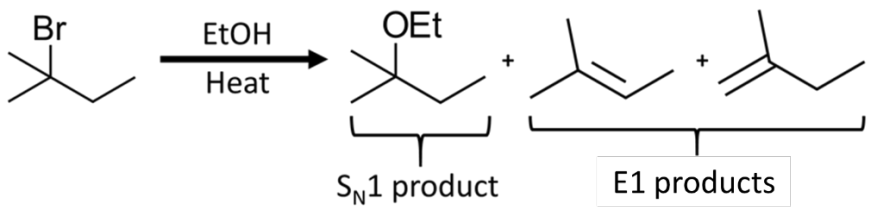
10.1: Substitution does not take place with secondary alkyl halides when a strong, bulky base is used. Elimination occurs instead and yields $H_2C{=}CHCH_2CH_3$ and $CH_3CH{=}CHCH_3$.

10.2: Fluoroalkanes do not undergo S_N2 reactions because F^- is a poor leaving group.

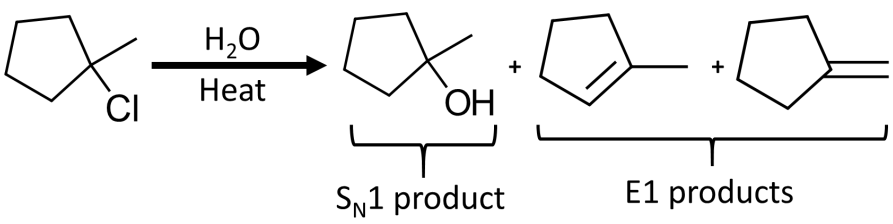
10.3: $SOCl_2$ in pyridine converts primary and secondary alcohols to chlorides by an S_N2 mechanism. 1-Methyl-2-cyclohexanol is a tertiary alcohol and does not undergo S_N2 substitution. Instead, E2 elimination occurs to give 1-methylcyclohexene.

P.11 ➡ *Solution*

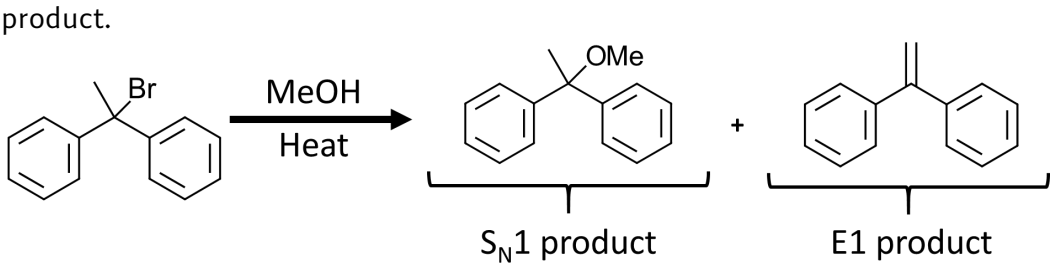
11.1: Solvolysis is expected to afford S_N1 and E1 products. In the S_N1 product, an ethoxy group (OEt) has replaced bromide. There are two E1 products (two regiochemical outcomes), although the disubstituted alkene is expected to be a minor product.



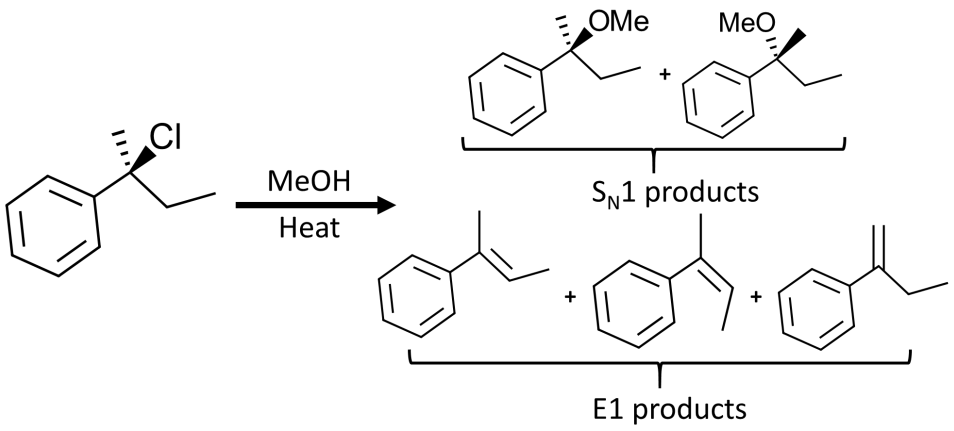
11.2: As mentioned in the solution to the previous problem, solvolysis yields S_N1 and E1 products. In the S_N1 product, a hydroxyl group has replaced chloride. There are two E1 products (two regiochemical outcomes), although the disubstituted alkene is expected to be a minor product.



11.3: As in a typical solvolysis reaction, there should be S_N1 and E1 products. In the S_N1 product, a methoxy group (OMe) has replaced bromide. In this case, there is only one E1 product, as there is only one regiochemical outcome, although the ensuing disubstituted alkene should be only a minor product.



11.4: In this case, the α position is a chiral center, so we expect S_N1 substitution to yield a pair of enantiomers, with a small preference for the inverted product as a result of ion pairs. Further, E1 elimination should yield three products, as shown below.



P.12 ➡ *Solution*

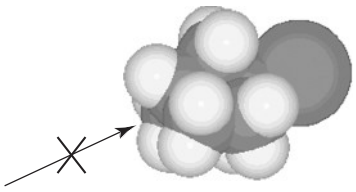
12.1: Molecule A has three methyl groups attached to the α carbon and hence should yield a stable carbocation before undergoing S_N1 substitution. Molecule B has an aromatic ring attached to the α carbon, and hence should produce an even more stable carbocation. The least reactive molecule is compound C. The correct order, from least reactive to most reactive, is **C** < **A** < **B**.

12.2: As mentioned in Problem 6, the starting molecules with the α carbon attached to the weakest bases make for the most reactive substrates. The correct order, from least reactive to most reactive, is **C** < **A** < **B**.

12.3: Starting molecule A has the α carbon bonded to an aromatic ring and hence should yield a relatively stable carbocation when undergoing S_N1 substitution. Molecule B has the α carbon attached not only to an aromatic ring but also to a methyl group, and therefore should produce a more stable carbocation than substrate A. Molecule C has the α carbon linked to three aromatic rings, which makes it more reactive than both A and B. The correct order, from least reactive to most reactive, is **A** < **B** < **C**.

P.13 ➡ *Solution*

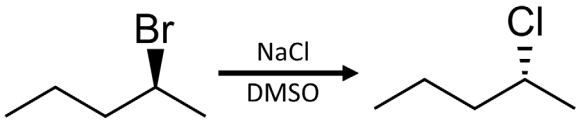
Regarding the S_N2 reaction, there is extreme steric hindrance for attack by the nucleophile from the back side with respect to the leaving group due to atoms on the other side of the rigid ring structure, as the following model shows.



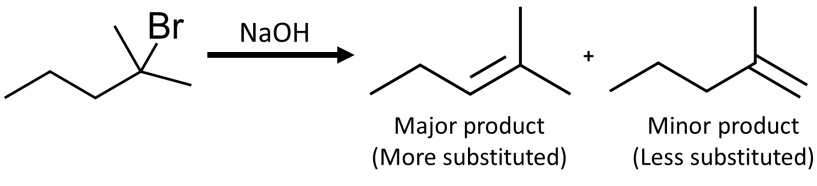
For the S_N1 reaction, formation of a carbocation would require that the bridgehead carbon approach trigonal planar geometry, which would lead to a carbocation of extremely high energy due to the geometric constraints of the bicyclic ring.

P.14 ➡ *Solution*

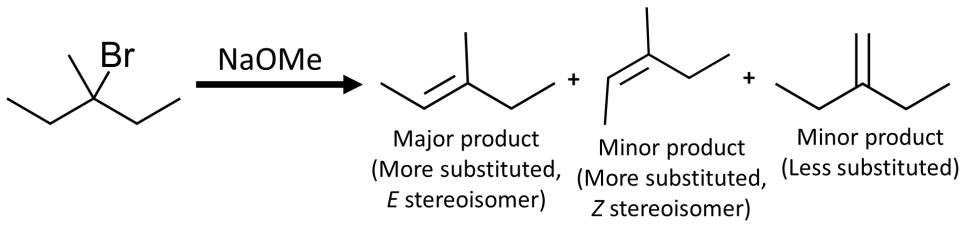
14.1: The reagent is chloride, which is a nucleophile, so we expect a substitution reaction. The substrate is secondary and the solvent (dimethyl sulfoxide) is polar aprotic, indicating an S_N2 reaction. As such, we expect inversion of configuration, as shown.



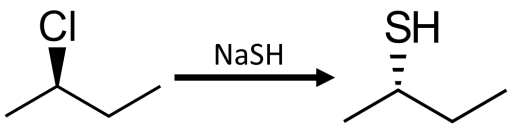
14.2: The reagent is hydroxide, which is both a strong base and a strong nucleophile. The substrate is tertiary, so we expect an E2 process. There are three β positions, but two of them are identical, so there are two possible regiochemical outcomes. The more-substituted alkene is the major product, as shown. The products are not stereoisomeric, so stereochemistry is not a consideration.



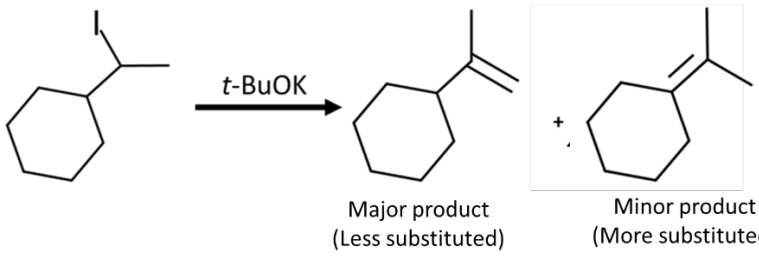
14.3: The reagent is methoxide, which is both a strong base and a strong nucleophile. The substrate is tertiary, so we expect an E2 process. The substrate has three β positions that bear protons, but two of them are identical, giving rise to two regiochemical outcomes. Since the base (methoxide) is not sterically hindered, we expect that the major product will be the more-substituted alkene – in this case, the *E* isomer, because the process is stereoselective. The minor products are the *Z* isomer and the less-substituted alkene.



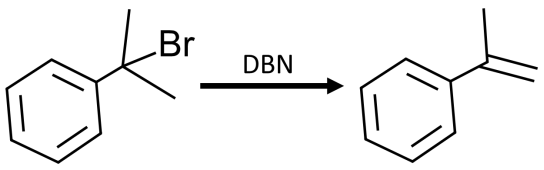
14.4: The reagent is HS^-, which is a strong nucleophile, and the substrate is secondary, so we expect an S_N2 process, with inversion of configuration.



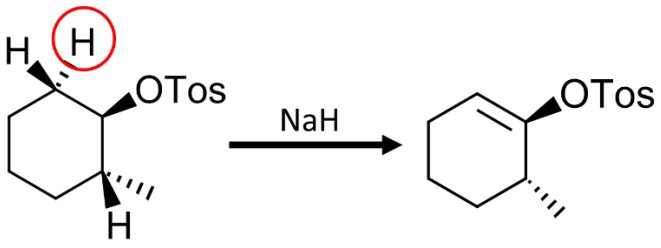
14.5: The reagent is *tert*-butoxide, which is a strong, sterically hindered base. The substrate is tertiary, so we expect an E2 process. There are three β positions, but two of them are identical, so there are two possible regiochemical outcomes. Since the base is sterically hindered, we expect that the less-substituted alkene will be the major product, as shown. The products are not stereoisomeric, so stereochemistry is not a consideration.



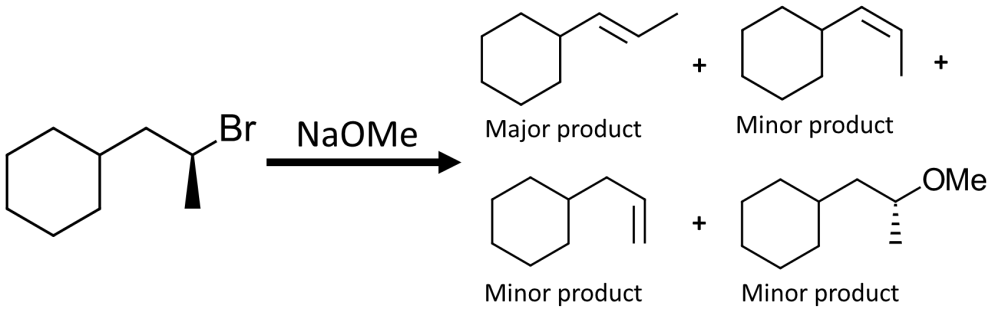
14.6: The reagent is DBN, which is a strong base. The substrate is tertiary, so we expect an E2 process. There are two β positions bearing protons, and both of these positions are identical, so there is only one possible regiochemical outcome. The product is not stereoisomeric, so stereochemistry is not a consideration.



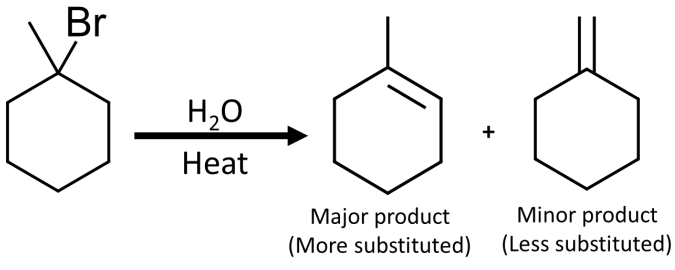
14.7: The reagent is hydride (H^-), which is a strong base (not a nucleophile), so we expect an E2 process (no S_N2). For substituted cyclohexanes, an E2 reaction occurs via a conformation in which the leaving group and the β proton are antiperiplanar to one another (one must be on a wedge and the other must be on a dash). The leaving group (OTos) is on a wedge. Therefore, we are looking for a β proton that is on a dash. There is only one such group in this starting molecule, as highlighted below, giving rise to only one elimination product.



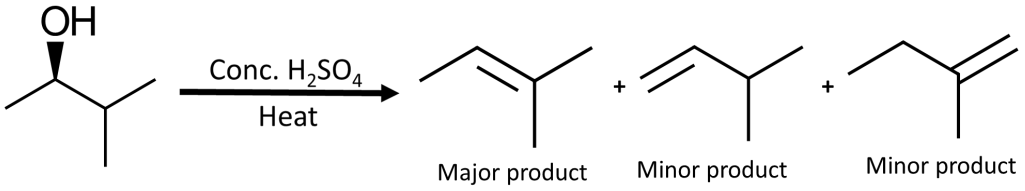
14.8: The reagent is methoxide, which is both a strong base and a strong nucleophile. The substrate is secondary, so we expect both E2 and S_N2 reactions, although E2 will predominate. Accordingly, the major product is the more substituted alkene, with the *trans* stereoisomer favored over the *cis* stereoisomer. The minor products include the *cis* isomer, the less-substituted alkene, and the S_N2 substitution product.



14.9: The reagent is water, which is both a weak base and a weak nucleophile. The substrate is tertiary, so we expect E1 and S_N1 processes. One of the alkene products is trisubstituted, so we expect the E1 pathway to predominate. For the E1 pathway, two regiochemical outcomes are possible. The base is not sterically hindered, so the more-substituted alkene is the major product, as shown.

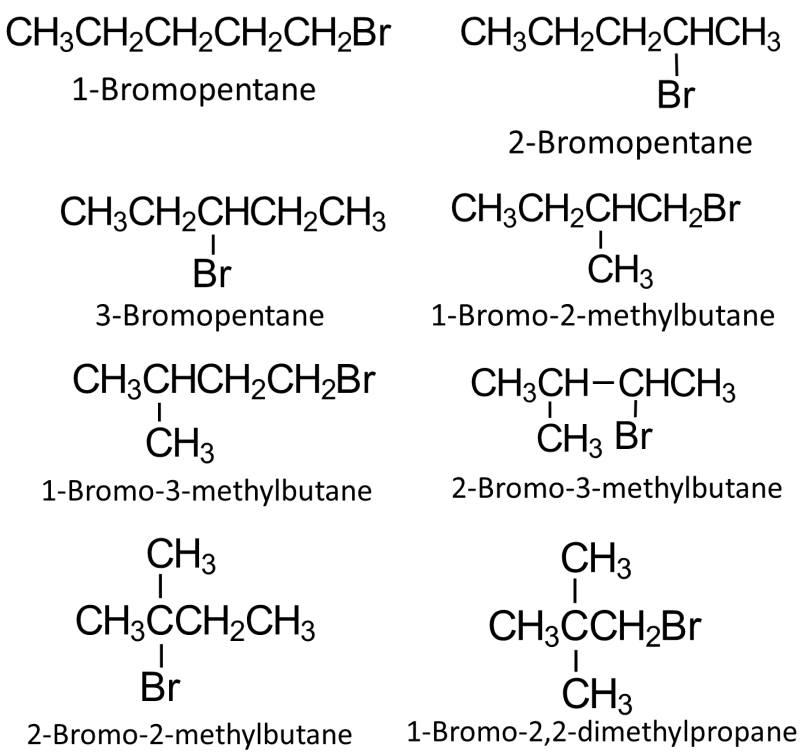


14.10: This process involves an alcohol instead of an alkyl halide, which is the main type of compound studied in this quiz, but the reaction in question – an E1 elimination – nonetheless falls within the scope of the present material. There are two different β positions that bear protons, so there are two possible regiochemical outcomes. The more-substituted alkene is the major product, and the less-substituted alkene is a minor product. Another minor product can result if the initially formed secondary carbocation undergoes a rearrangement to give a tertiary carbocation, followed by deprotonation to give a disubstituted alkene, as shown.



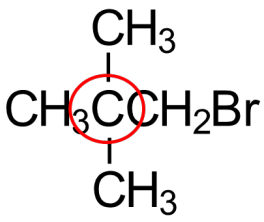
P.15 ➡ *Solution*

15.1: The isomers with formula $C_5H_{11}Br$ are listed below.

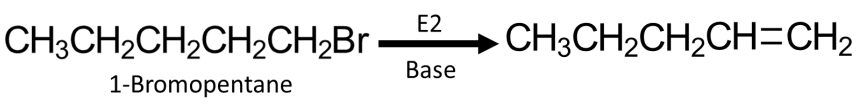


The order of reactivity toward E1 elimination parallels carbocation stability and is *tertiary* > *secondary* > *primary*. Among the isomers listed, the bromide 2-bromo-2-methylbutane has a tertiary α carbon and should undergo E1 elimination at the fastest rate.

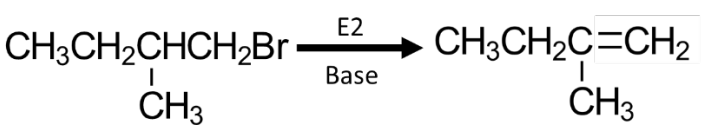
15.2: As highlighted below, 1-bromo-2,2-dimethylpropane has no hydrogens on the β carbon and so cannot form an alkene by an E2 process. The only available pathway is E1 with rearrangement.



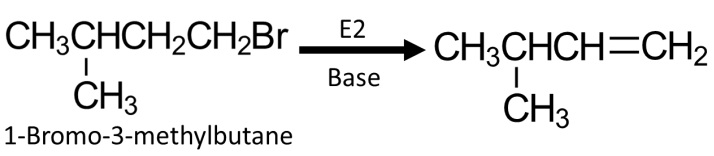
15.3: The three primary bromides yield a single alkene upon undergoing E2 elimination.



1-Bromopentane

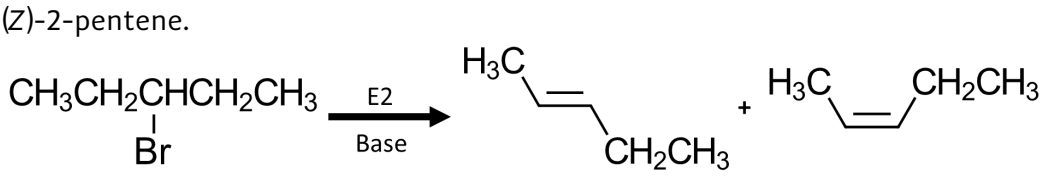


1-Bromo-2-methylbutane



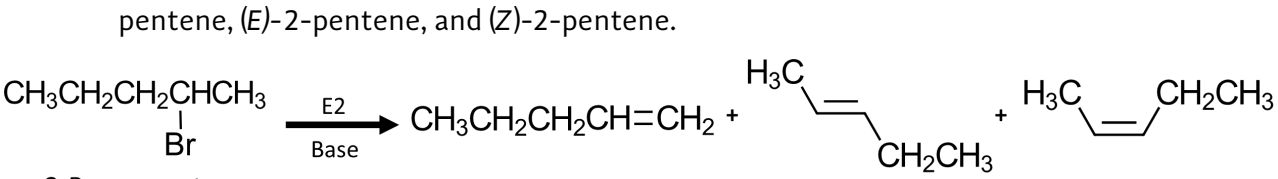
1-Bromo-3-methylbutane

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



3-Bromopentane

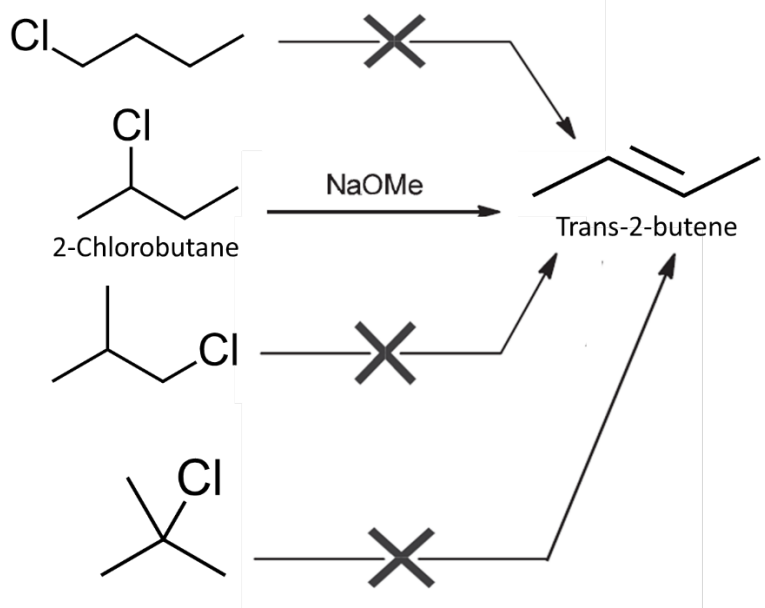
15.5: Three alkenes can be formed from 2-bromopentane, namely 1-pentene, (*E*)-2-pentene, and (*Z*)-2-pentene.



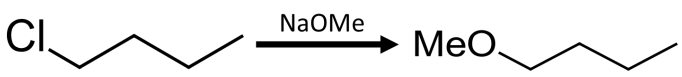
2-Bromopentane

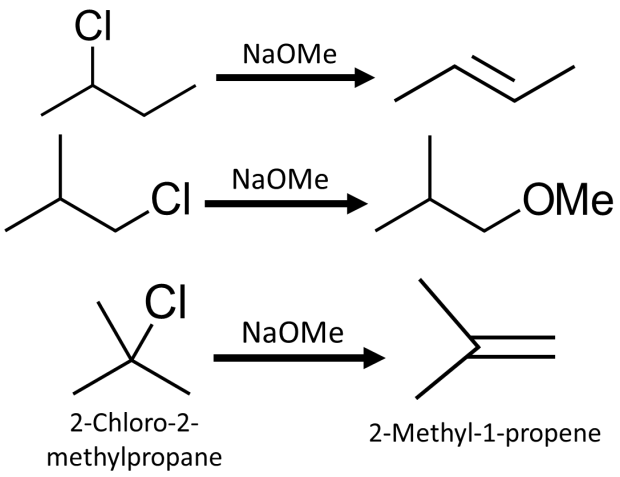
P.16 ➡ *Solution*

16.1: There are four aliphatic constitutional isomers with the molecular formula C_4H_9Cl, all of which are shown below. Only one of them, 2-chlorobutane, yields the desired product when treated with methoxide.



16.2: We saw in the solution to Problem 16.1 that there are four constitutional isomers with molecular formula C_4H_9Cl. Let's consider the major product that is expected when each of these isomers is treated with methoxide. Notice that only one of these cases produces different products, and only one of them, namely 2-chloro-2-methylpropane, yields a disubstituted alkene different from *trans*-2-butene.



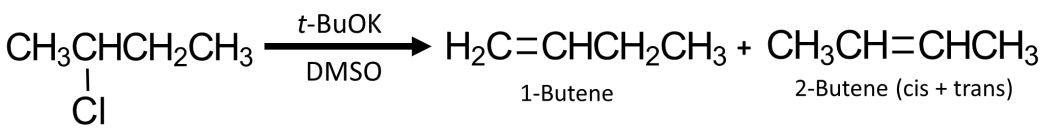


2-Chloro-2-methylpropane

2-Methyl-1-propene

P.17 ➡ *Solution*

Only two alkanes have the molecular formula C_4H_{10}: butane and isobutane (2-methylpropane). However, dechlorination of one of the monochlorides derived from butane yields a mixture of two alkenes.

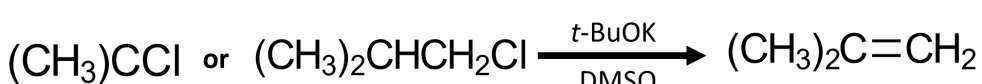


2-Chlorobutane

1-Butene

2-Butene (cis + trans)

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



Tert-butyl chloride

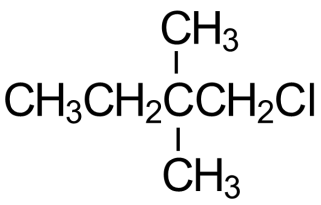
Isobutyl chloride

2-Methylpropene (Compound B)

Thus, compound A is isobutane (2-methylpropane), the two alkyl chlorides are *tert*-butyl chloride and isobutyl chloride, and alkene B is 2-methylpropene.

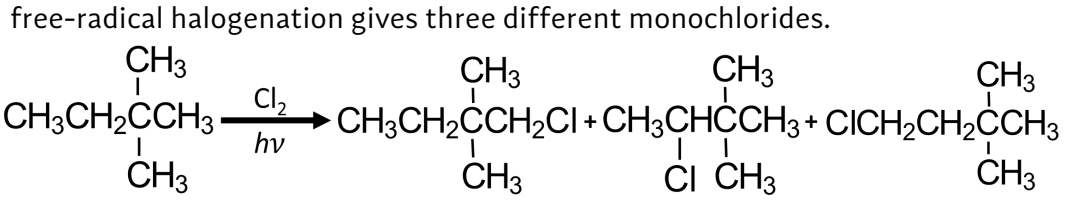
P.18 ➡ *Solution*

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 chlorine bears no hydrogens. This $C_6H_{13}Cl$ isomer is 1-chloro-2,2-dimethylbutane.



1-Chloro-2,2-dimethylbutane

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



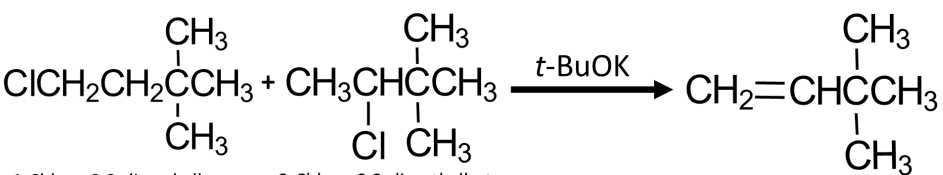
2,2-Dimethylbutane (Compound A)

1-Chloro-2,2-dimethylbutane

3-Chloro-2,2-dimethylbutane

1-Chloro-3,3-dimethylbutane

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



1-Chloro-3,3-dimethylbutane

3-Chloro-2,2-dimethylbutane

3,3-Dimethyl-1-butene (Compound B)

P.19 ➡ *Solution*

19.1: The entropy term is positive and may indicate that the reaction is spontaneous. The enthalpy term, in turn, is positive and may indicate that the reaction is not spontaneous.

19.2: The Gibbs free energy of the reaction is

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} = 26.6 - 298 \times 0.00481 = \boxed{+25.2 \text{ kJ mol}^{-1}}$$

Since $\Delta G^{o} > 0$, the reaction is not spontaneous and the hydrolysis reaction will not occur to any significant extent.

19.3: The equilibrium constant is determined as

$$-RT \ln K = \Delta G^{o} \rightarrow \ln K = -\frac{\Delta G^{o}}{RT}$$

$$\therefore \ln K = -\frac{25,200}{8.31 \times 298} = -10.2$$

$$\therefore \boxed{K = 3.72 \times 10^{-5}}$$

19.4: The equilibrium is very much more favorable in aqueous solution because solvation of the products (ethanol, hydronium ions and chloride ions) takes place and thereby stabilizes them.

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