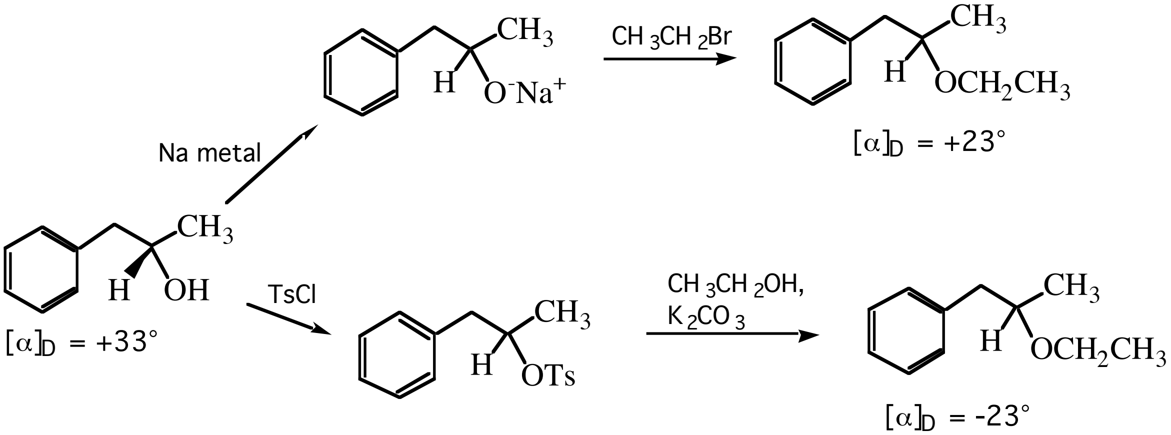
Section Eight – Substitution and Elimination Reactions

Nucleophilic Substitution and Elimination Reactions

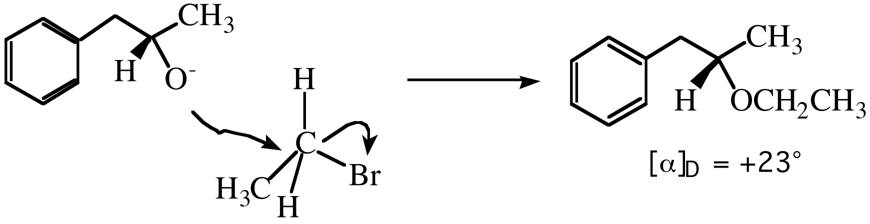
Question 8.1

Explain why the products of the following two reaction schemes result in products with opposite optical activity.

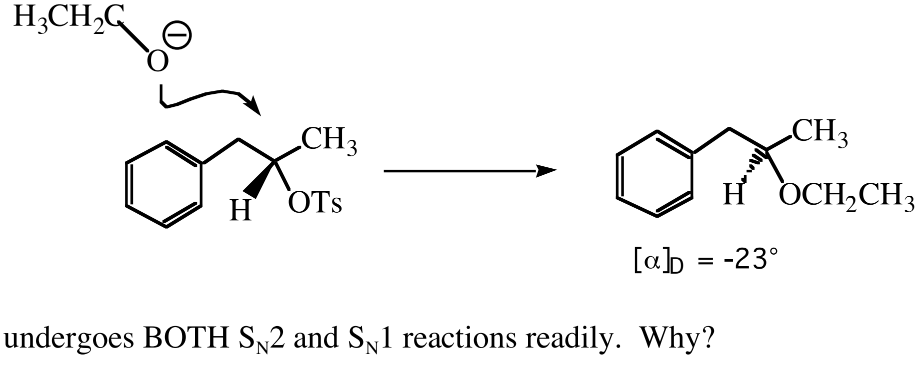


Answer 8.1

In the upper process, the first step converts the alcohol into a good nucleophile. This then displaces bromide in an S_N2 reaction to give the product. The chiral center is not involved in this reaction and is unchanged relative to the starting alcohol.



In the lower process, the alcohol is converted into a good leaving group that is itself displaced in an S_N2 process with ethoxide as the nucleophile. The chiral center is itself attacked and therefore undergoes inversion of absolute configuration. The net result is that the product is the enantiomer of the upper case.



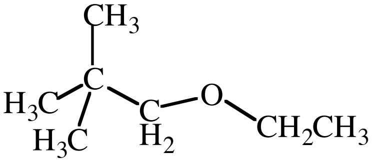
Question 8.2

Benzyl bromide undergoes BOTH S_N2 and S_N1 reactions readily. Why?

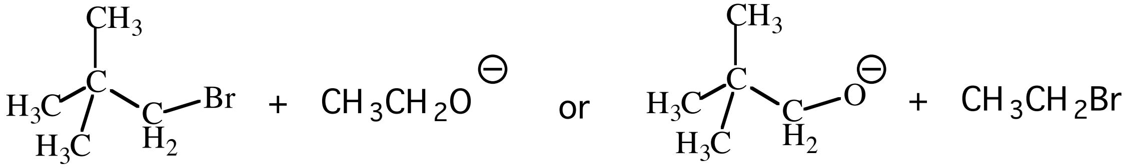
Answer 8.2

As a 1° alkyl halide, this substrate is a good substrate for S_N2. It also ionizes readily because the carbocation so formed (the benzyl cation) is stabilized by resonance.

Question 8.3
How would you prepare ethyl neopentyl ether via the Williamson ether synthesis? Explain your choice of reagents carefully.

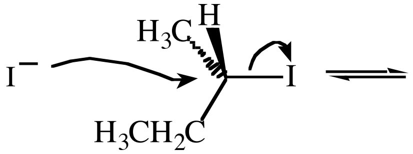


Answer 8.3
There are two ways of making this via a Williamson synthesis:



The first proposes the reaction of ethoxide with neopentyl bromide. Due to β-branching, neopentyl bromide does not undergo S_N2 reactions, hence this will fail. The second process is the way to go.

Question 8.4 (8 marks)
Optically pure *(S)*-2-Iodobutane is reacted with I^- (the iodide anion) in a nucleophilic substitution reaction.



a.) Draw a mechanism for this reaction using arrows to show electron movement and accurately draw the product of the forward reaction.

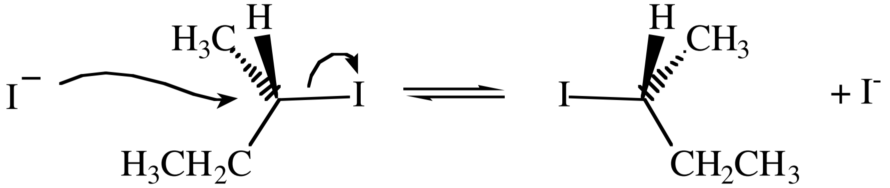
b.) Sketch the reaction profile (energy diagram) for this reaction and label it with the positions of the reactants, products, transition state and intermediates, if any.

c.) The measured rotation for this reaction is 12.15° initially. What is the measured rotation when the reaction reaches equilibrium?

d.) Draw the transition state for this reaction. Is it a chiral transition state?

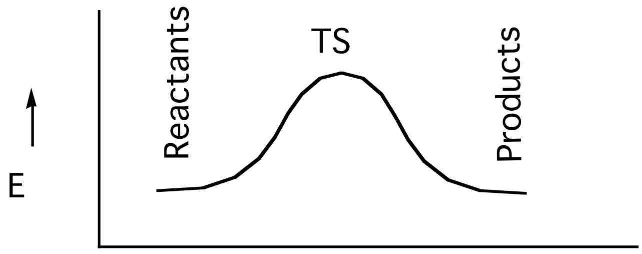
e.) Estimate the equilibrium constant for this reaction.

Answer 8.4
a.)



Note that the only difference between the organic starting material and its product is the absolute configuration.

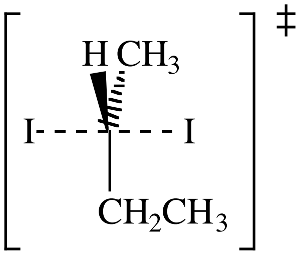
b.)



Enantiomers have identical free energies of formation, hence the energy level of products and reactants is the same.

c.) Given that this is an equilibrium reaction beween enantiomeric species of equal energy, the final result must be a racemic mixture, hence the final mixture will not be optically active (a = 0°).

d.)

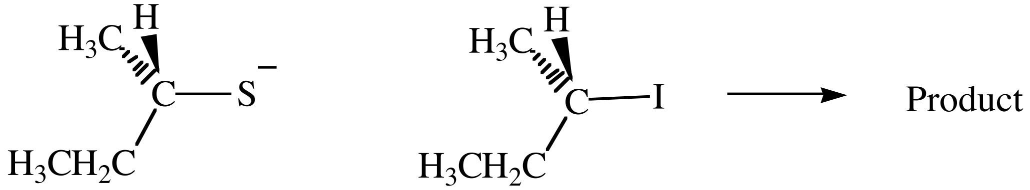


On your assignment, you were asked the same question. In that case, the nucleophile and the leaving group were different. In this case, they are the same. There is now an internal mirror plane of symmetry perpendicular to the I-C-I bond in the plane of three central substituents. This is, therefore, an achiral transition state.

e.) The biggest clue here is that since you need to supply a number, that it must be a simple number. Many came up with the number 0. Equilibrium constants, however, are never 0. Again, because the energies of both sides of this equation are the same, there concentrations will be equal at equilibrium and $K_c = 1$.

Question 8.5 (7 marks)

Optically pure *(S)*-2-Iodobutane is reacted with optically pure (S)-2-butanethioxide in a nucleophilic substitution reaction.



a.) Draw a mechanism for this reaction using arrows to show electron movement and accurately draw the product of the reaction.

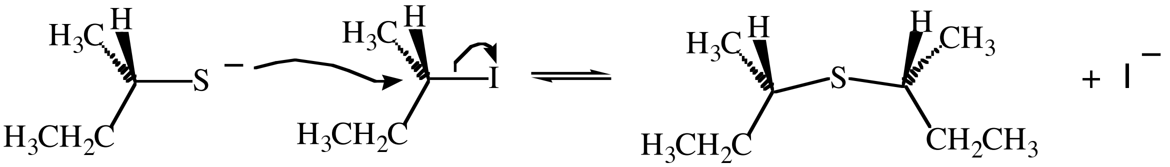
b.) Sketch the reaction profile (energy diagram) for this reaction and label it with the positions of the reactants, products, transition state and intermediates, if any.

c.) The measured rotation of the reactants before reaction is 12.15°. What is the measured rotation when the reaction is complete?

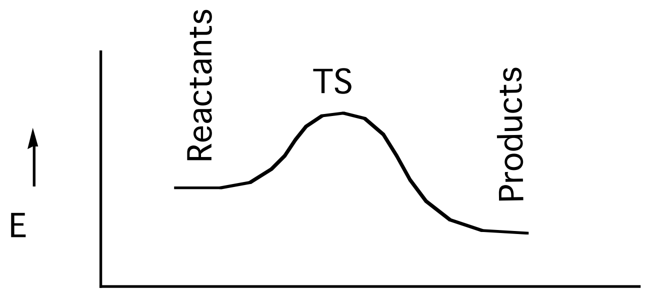
d.) If the reactants used were racemic (instead of being optically pure) then how many stereoisomeric organic products would have resulted?

Answer 8.5

a.)



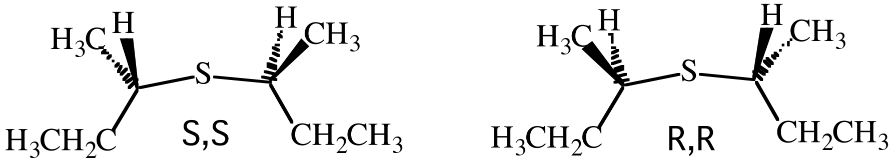
b.)



This assumes that the carbon-sulfur bond is stronger than the C-I bond, usually a good bet.

c.) The product is a meso-compound, hence the rotation will be zero.

d.) Three. The meso-compound and a racemic mixture of R,R- and S,S- sulfide.

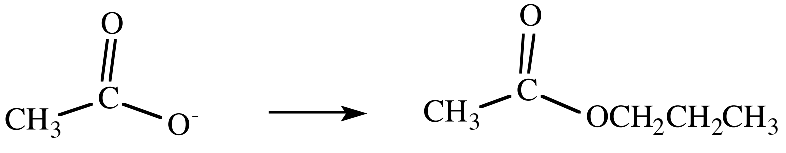


Question 8.6

In each of the following pairs of reactions, indicate which reaction is faster (if either) **AND** give an explanation for the relative rates of reaction.

a)

i.) $CH_3CH_2CH_2Br$ +



$CH_3C(=O)O^- \longrightarrow CH_3C(=O)OCH_2CH_2CH_3$

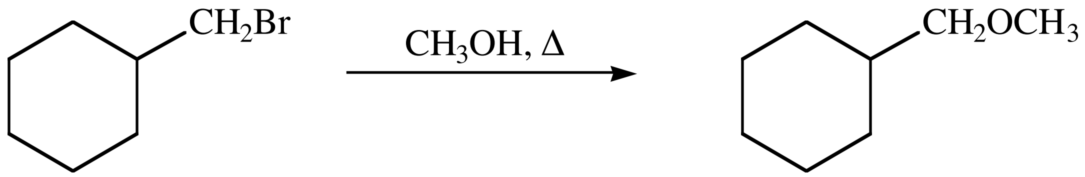
ii.) $CH_3CH_2CH_2Br + CH_3O^- \longrightarrow CH_3CH_2CH_2OCH_3$

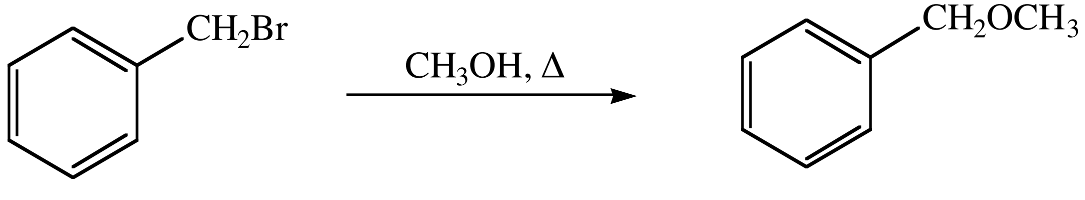
b)

i.) $(CH_3)_2CHCH_2Br + CH_3SH \rightarrow (CH_3)_2CHCH_2SCH_3$

ii.) $CH_3CH_2CH_2CH_2Br + CH_3SH \rightarrow CH_3CH_2CH_2CH_2SCH_3$

c)





Answer 8.6

a) The substrates are both 1° and identical - only the nucleophiles differ. This is an S_N2 process. The better nucleophile will give the faster reaction. Both are O- species. As such, whichever is more basic will be the better nucleophile. Acetate (in I) has a resonance stabilized anion, methoxide (in ii) does not. The latter is much more basic and therefore more nucleophilic. The second reaction will be faster.

b) Same nucleophile, both substrates are 1° indicating an S_N2 process. The upper substrate is b-branched, though, and will react more slowly.

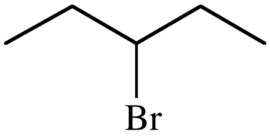
c) This is clearly a substitution reaction. Both substrates are 1° alkyl halides and therefore good substrates for S_N2. However, methanol (CH_3OH) is a poor nucleophile in S_N2 reactions, that's why its conjugate base methoxide (CH_3O-) is usually used. The second substrate (benzyl bromide) is readily ionizable because the resulting benzyl cation is resonance stabilized. As such, it is a good substrate for S_N1 reactions in which the strength of the nucleophile is not important. The second reaction occures faster, therefore, via an S_N1 pathway.

Question 8.7

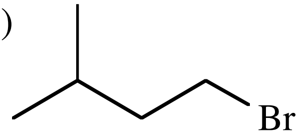
Which substrate reacts more quickly by S_N2?

a)

i)

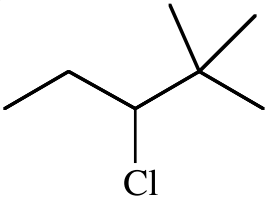


ii)

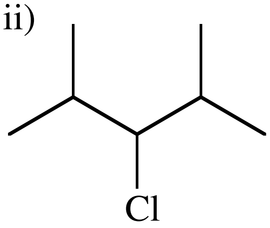


b)

i)

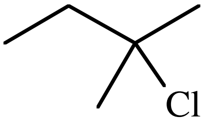


ii)

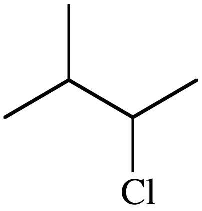


c)

i)



ii)



Answer 8.7

a) 1° substrates react more quickly, therefore the second will react faster.

b) Both substrates are 2°. The first has two β-branches on one arm and therefore will not react via S_N2. The second also has two β -branches - one on each arm - and while this will slow the S_N2 process, it will still be possible. Pretty slow, though.

c) 2° substrates react more quickly than 3° substrates so the second will react faster.

Question 8.8

Which is the better nucleophile?

i)

CH_3NH_2 or CH_3NH-

ii)

NH_3 or NH_4^+

iii)

CH_3OH or CH_3SH

Answer 8.8

i) A molecules conjugate base is always more nucleophilic, therefore the latter species in this case.

ii) In this case, the cationic ammonium ion cannot act as a nucleophile since it has no lone pair. In any event, the same explanation as in part i applies.

iii) As you go down the same row of the periodic table, atoms get more nucleophilic (due to more polarizable orbitals). The sulfur compound is the better nucleophile.

Question 8.9

Which reaction is faster?

a)

i.) $CH_3CH_2CH_2Br + CH_3OH \longrightarrow CH_3CH_2CH_2OCH_3$

ii.) $CH_3CH_2CH_2Br + CH_3O^- \longrightarrow CH_3CH_2CH_2OCH_3$

b)

i.) $CH_3CH_2Br + CH_3SH\ (1.0\ M) \longrightarrow CH_3CH_2SCH_3$

ii.) $CH_3CH_2Br + CH_3SH\ (2.0\ M) \longrightarrow CH_3CH_2SCH_3$

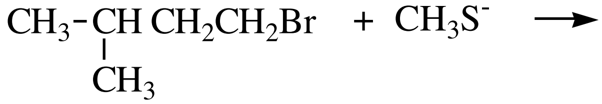
c)

i.) $CH_3CH_2CH_2Cl + Br^- \longrightarrow CH_3CH_2CH_2Br$

ii.) $CH_3CH_2CH_2Cl + I^- \longrightarrow CH_3CH_2CH_2I$

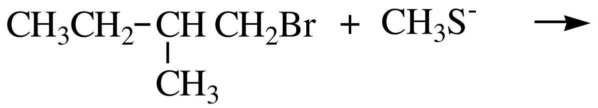
d)

i.)



$CH_3\text{-}\underset{\displaystyle CH_3}{CH}\,CH_2CH_2Br + CH_3S^- \longrightarrow$

ii.)



$CH_3CH_2\text{-}\underset{\displaystyle CH_3}{CH}\,CH_2Br + CH_3S^- \longrightarrow$

e)

i.) $CH_3CH_2CH_2Cl + {}^-CN \longrightarrow$

ii.) $CH_3CH_2CH_2Br + {}^-CN \longrightarrow$

Answer 8.9

a) Methoxide is the conjugate base of methanol and therefore more nucleophilic.

b) This is an S_N2 reaction and so its rate is proportional to the concentrations of both reactants. The second example will therefore be faster.

c) Atoms lower in the same periodic group are better nucleophiles, therefore the second reaction will be faster.

d) Both substrates are primary and CH_3S- is a good nucleophile therefore this is an S_N2 reaction. The upper substrate is β-branched while the lower is branced further from the reacting center. β-Branching inhibits S_N2, therefore the first reaction is faster.

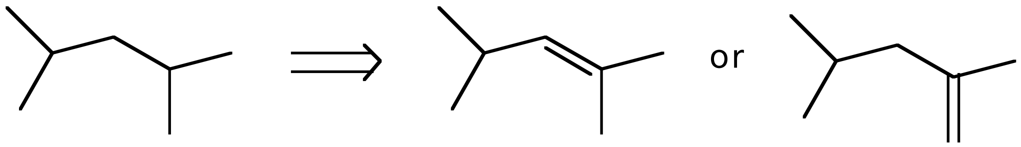
e) Bromide is a better leaving group than chloride therefore the second reaction will be faster. This is actually independent of which reaction is involved, but this is an S_N2 process.

Question 8.10

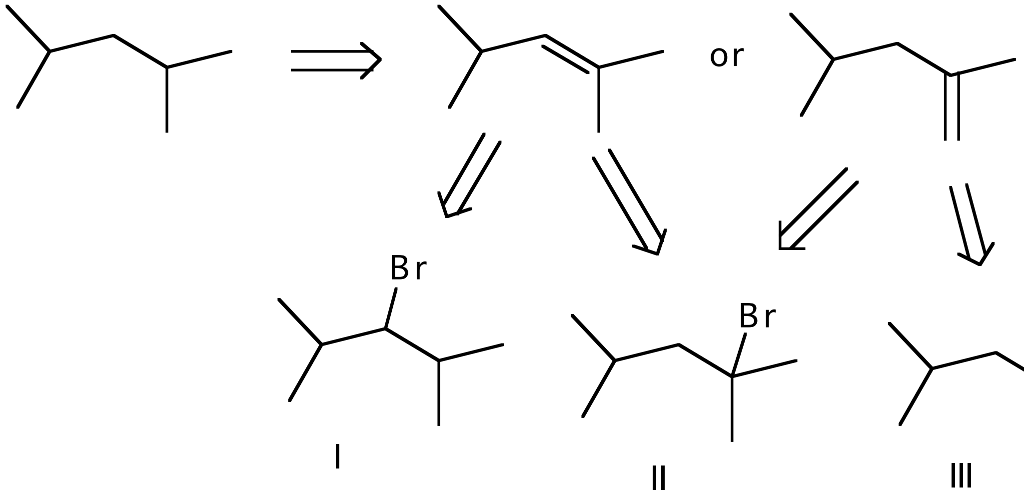
A compound with the formula $C_7H_{15}Br$ does not give a precipitate immediately upon treatment with NaI in acetone. It yields a single alkene with heated with sodium ethoxide in ethanol. Hydrogenation of the alkene gives 2,4-dimethylpentane. What is the structure of the alkyl halide and the alkene? Explain your reasoning.

Answer 8.10

The alkene must be one of two possibilities:



There are three possible bromides that can serve as precursors to these alkenes:

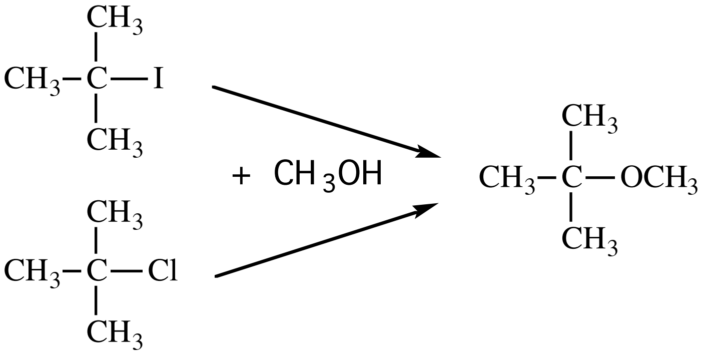


Bromide III would give a precipitate upon treatment with NaI, II would not, I would slowly. Bromide II would likely give a mixture of both alkenes therefore, bromide I is our alkyl halide.

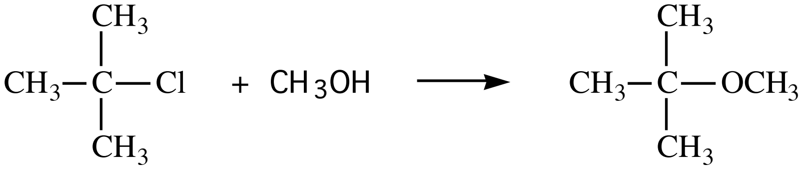
Question 8.11

Which of the following S_N1 reactions are faster?

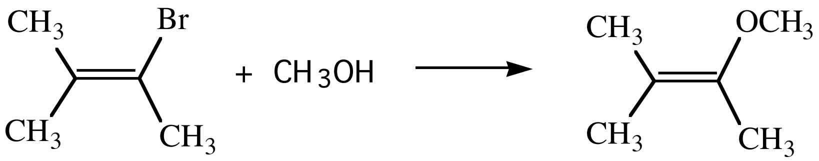
i)



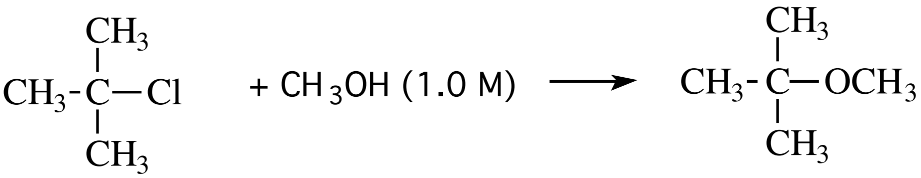
ii)



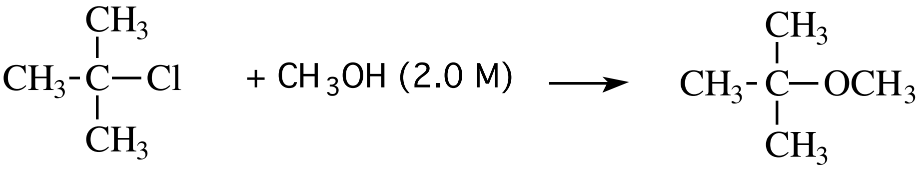
$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl} + \mathrm{CH_3OH} \longrightarrow \mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OCH_3}$$



iii)



$$\mathrm{CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl} + \mathrm{CH_3OH\ (1.0\ M)} \longrightarrow \mathrm{CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OCH_3}$$



$$\mathrm{CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl} + \mathrm{CH_3OH\ (2.0\ M)} \longrightarrow \mathrm{CH_3\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OCH_3}$$

Answer 8.11

i) The substrate with the better leaving group (I-) will react more quickly.

ii) Vinyl halides (as in the second example) do not ionize because the resulting vinyl carbocations are very unstable. The instability is the result of forcing an sp2 hybrid carbon to become electron deficient.

iii) The rate of S_N1 reactions depend only on the concentration of the substrate and not on the nucleophile. Therefore, these two reactions will occur at exactly the same rate.

Question 8.12

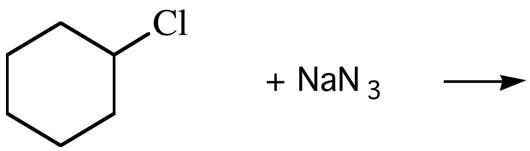
Which reaction is faster?

a.) $CH_3CH_2CH_2CH_2Br$ or $CH_3CH_2CH_2CH_2I$ with sodium cyanide in dimethyl sulfoxide

b.) 1-Chloro-2-methylbutane or 1-chloropentane with sodium iodide in acetone

c.)

i.)



ii.) $H_3C(H_2C)_4H_2C—Cl + NaN_3 \longrightarrow$

d.) Solvolysis of neopentyl bromide or tert-butyl bromide in ethanol

e.) Solvolysis of isobutyl bromide or sec-butyl bromide in aqueous formic acid (HCOOH)

f.) Reaction of 1-chlorobutane with sodium acetate in acetic acid or with sodium methoxide in methanol

g.) Reaction of 1-chlorobutane with sodium azide or sodium p-toluenesulfonate in aqueous ethanol.

h) Reaction of t-butyl iodide with ethanol **<u>or</u>** ethane thiol (CH_3CH_2SH).

Answer 8.12

a) The iodide will react faster because iodide is a better leaving group.

b) Both are 1° substrates, and cyanide is a weakly basic but good nucleophile indicating that an S_N2 process is operating. The first substrate is β-branched - the second is not and therefore reacts more quickly.

c) The azide is a good nucleophile and weak base. This must be an S_N2 reaction. The second (with the 1° substrate) will be faster than the first (a 2° substrate).

d) Solvolysis reactions are S_N1 processes in which the solvent is the nucleophile. The 3° substrate will undergo S_N1, the 1° substrate will not.

e) As for (d) - the 2° substrate will undergo S_N1, the 1° substrate will not.

f) With a 1° substrate, S_N2 is likely. Both nucleophiles are oxygen nucleophiles, the more basic being the more nucleophilic. Methoxide is more basic than acetate because the negative charge is not delocalized.

g) Sulfonates are good leaving groups and poor nucleophiles. Azide will react more quickly.

h) The thiol is the better nucleophile, but since the substrate is 3°, this must be an S_N1 process. As such, the nucleophile is not involved in the rate-determining step so both reactions will occur at the same rate.

Question 8.13

Give the mechanistic symbols (S_N1, S_N2, E1 or E2) that are most consistent with each of the following statements. **More than one** mechanism may apply. (7 marks)

a.) Methyl halides react with sodium ethoxide in ethanol only by this mechanism: ____________

b.) The principle substitution product obtained by reaction of t-butyl bromide in ethanol arises by this mechanism: ________

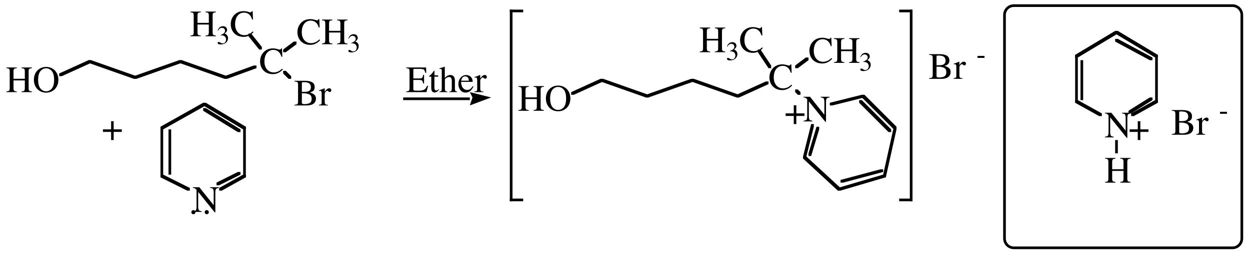
c.) Mechanism(s) that is (are) concerted (one step) process(es): _________

d.) Alkyl iodides react faster than alkyl bromides in reactions that proceed by: ____________

Answer 8.13

a) S_N2 b) S_N1 c) S_N2, E2 d) S_N1, S_N2, E1, E2

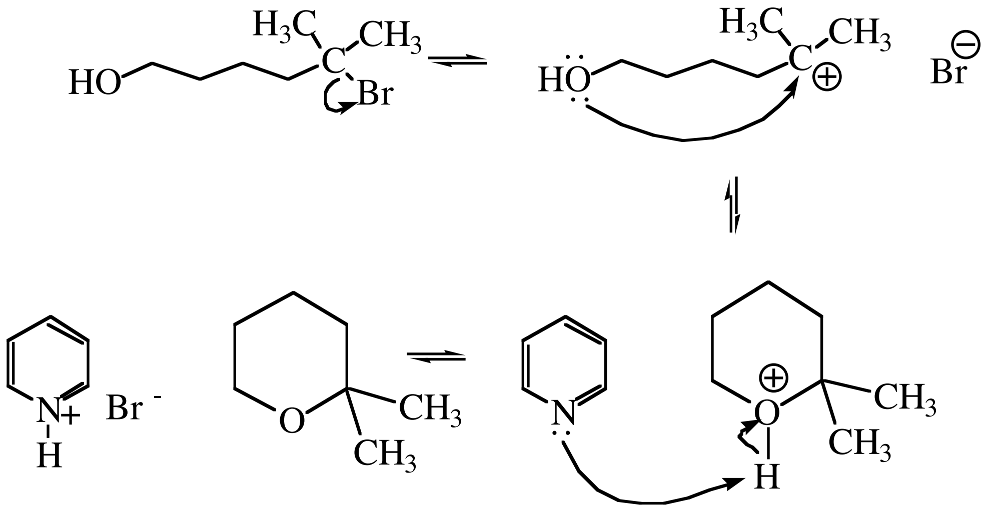
Question 8.14
You attempt the following preparation of a quaternary amine salt.



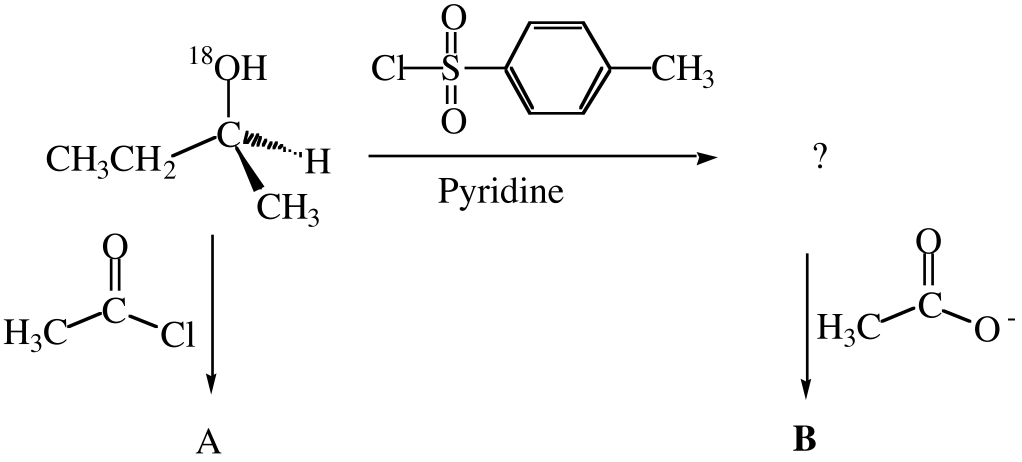
Anilinium
Bromide

To your horror, you do not get this product. Instead of getting this salt, you get anilinium bromide in addition to a liquid product that has no broad peaks above 3000 cm^{-1}.

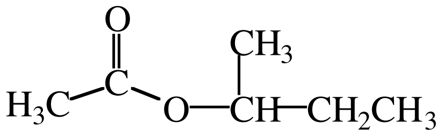
Answer 8.14
This molecule has in internal nucleophile in the OH group. An intramolecular S_N1 process is therefore possible.



Question 8.15
Consider the following reactions scheme in which the radiolabelled S-2-butanol is transformed into 2-butyl acetate via two different processes.



The two products A and B are not identical.



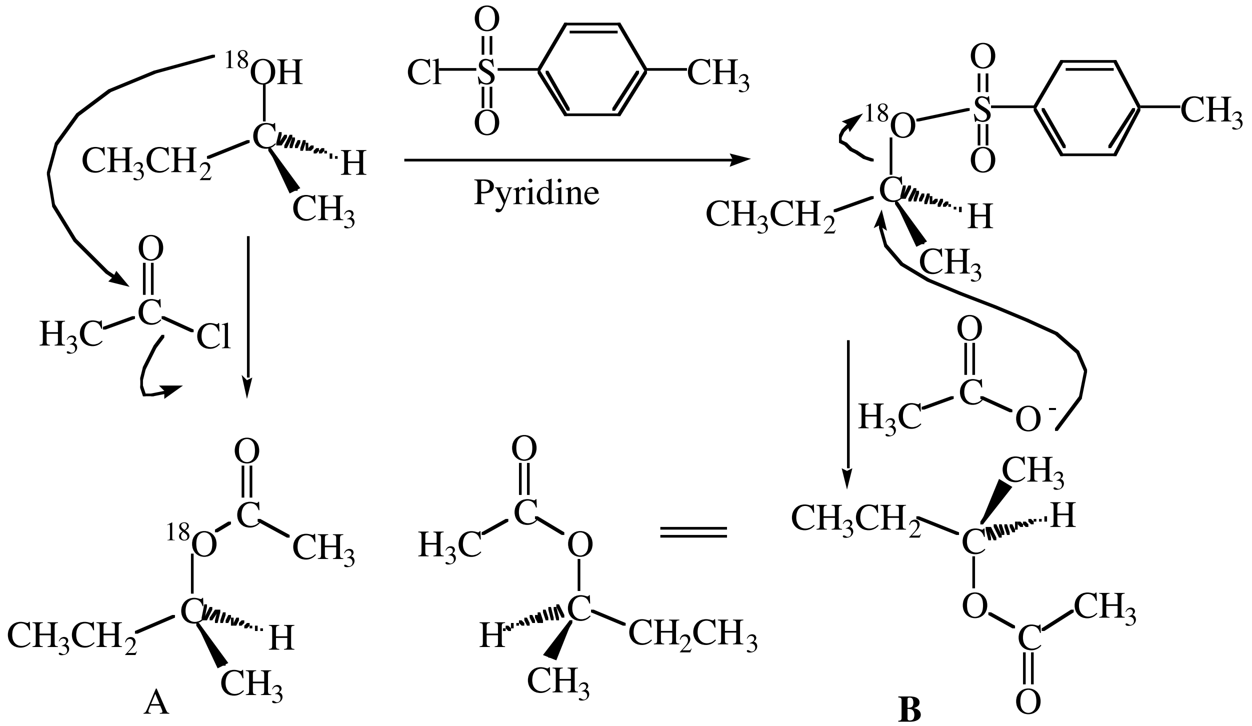
(2-Butyl acetate: no stereochemistry implied)

i.) What are the structures (including the absolute configurations about the chiral center) of A and B. Explain.

ii.) Which product, A or B, contains the ^{18}O label (if either)? Explain.

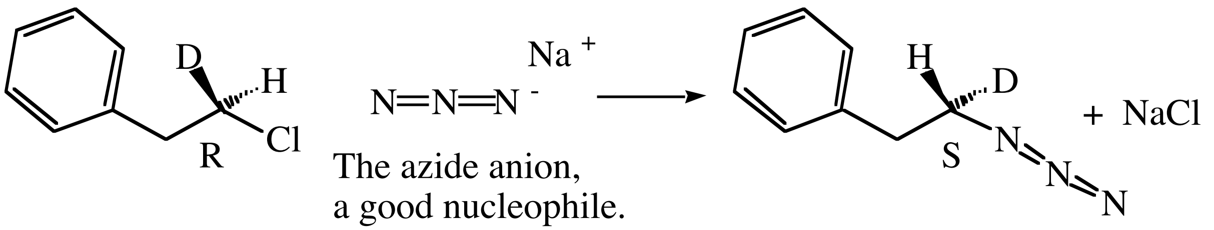
Answer 8.15

The path leading to product A involves the oxygen atom as the nucleophile. The chiral center is unaffected and the label is retained. In path B, the OH is converted into a sulphonate ester - a good leaving group. It is displaced by the nucleophile acetate. The label is lost in this process and the chiral center is inverted.



Question 8.16

An intrepid chemist wishes to carry out the following conversion of an optically pure alkyl halide into an alkyl azide by an S_N2 reaction. The azide anion, NaN_3 is a good nucleophile, but because chloride is a mediocre leaving group, this reaction is slow.



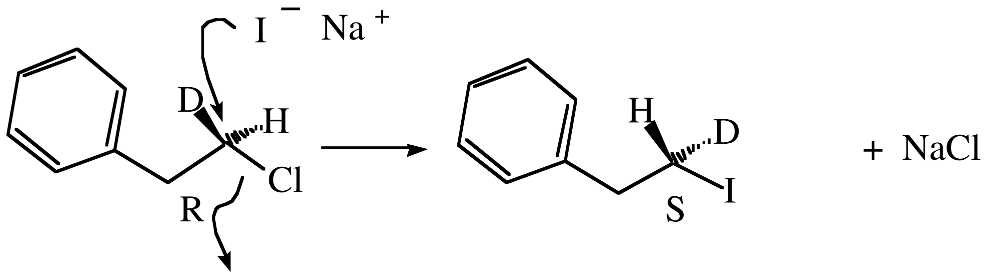
Our intrepid chemist has heard that NaI (sodium iodide) catalyzes the S_N2 reactions of alkyl chlorides (and bromides) so he/she tosses in a small amount of this substance. When he/she isolates his/her azide product, he/she is horrified to find that he/she has a substantial amount of ***both*** the S ***and*** R product.

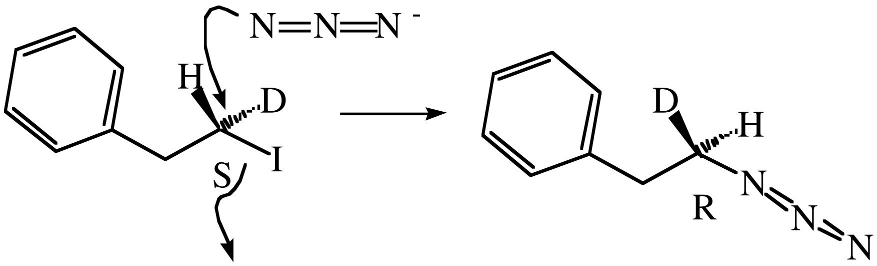
i.) How does I^- catalyze the S_N2 reactions of alkyl chlorides (and bromides)? Use this reaction as an example.
ii.) How does racemization occur?

Answer 8.16

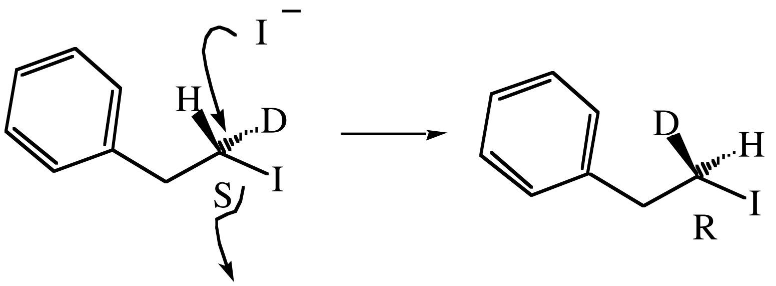
The important thing to remember in this question is that Iodide is a good nucleophile ***and*** a good leaving group. The S_N2 displacement of Chloride is slow because chloride is only a fair leaving group. How can iodide catalyze this process? If iodide is a good nucleophile (better than azide), then it can displace chloride at a faster rate than azide. Since iodide is a better leaving group than chloride, then azide can displace it faster than it can displace chloride. In essence you have changed the leaving group from chloride to iodide in a catalytic fashion.

The stereochemical consequences are important. Each S_N2 reaction results in inversion. A double inversion results in overall retention of the original center. This is the origin of R product when S is expected.





We are told that we have both S and R isomers. S can be formed two ways: from the reaction of azide with R chloride (the uncatalyzed reaction) and the reaction of azide with R iodide formed in the following reaction:

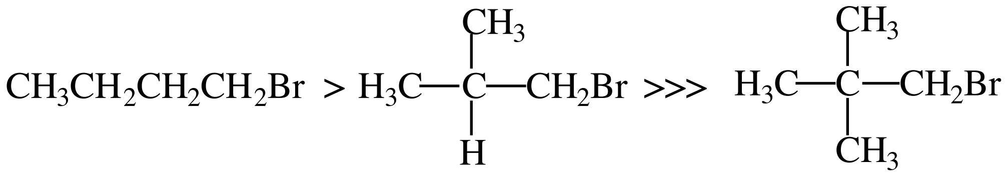


Question 8.17

Alkyl halides are converted to alkanes by treatment with lithium aluminum hydride in tetrahydrofuran (solvent). The following equiation illustrates the reaction.

$$\underset{\text{1-Bromooctane}}{CH_3(CH_2)_6CH_2Br} \xrightarrow[\text{25°C, 30 min}]{\overset{LiAlH_4}{\text{THF}}} \underset{\text{Octane}}{CH_3(CH_2)_6CH_3} \quad .$$

Rate studies on this reaction have established the following orders of reactivity.



$$CH_3CH_2CH_2CH_2Br > H_3C\text{—}\overset{CH_3}{\underset{H}{C}}\text{—}CH_2Br >>> H_3C\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}CH_2Br$$

$CH_3CH_2CH_2CH_2I$ > $CH_3CH_2CH_2CH_2Br$ > $CH_3CH_2CH_2CH_2Cl$.

i.) Propose a mechanism for the reaction, and discuss how the rate data support your mechanism.
ii.) What other experiments might you carry out to support your conclusion?

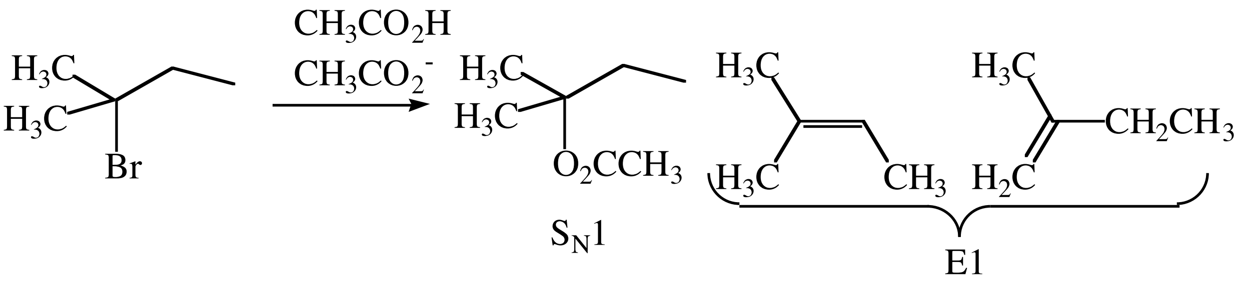
Answer 8.17

The trend shown in the first series of compounds all involve 1° alkyl halides with differing degrees of β-branching. The trend clearly follows that of any S_N2 process. The second series of reactions tells you nothing - only that the leaving group departs during the rate-determining step.

Question 8.18

Solvolysis of 2-bromo-2-methylbutane in acetic acid/potassium acetate gave three products. Give their structures and identify by what mechanism they were formed.

Answer 8.18



Question 8.19

For which of the four mechanisms, S_N1, S_N2, E1 and E2, are the following statements valid. More than one mechanism may be correct.

a.) Tertiary alkyl halides react faster than primary alkyl halides.
b.) The absolute configuration of the product is opposite to that of the reactant when an optically active substrate is used.
c.) The rate of reaction depends markedly on the nucleophilicity of the attacking nucleophile.
d.) Carbonium ions are intermediates.
e.) The rate of reaction depends on the nature of the leaving group.

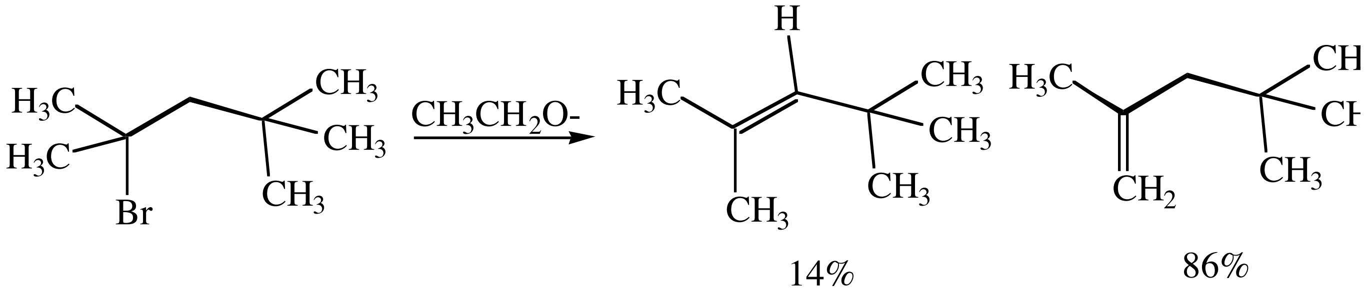
Answer 8.19

a) S_N1, E1 b) S_N2 c) S_N2 d) S_N1, E1 e) All 4

Question 8.20

An apparent exception to the original formulation of the Zaitsev rule (which states that in an elimination reaction, the most substituted alkene is formed) can be found in the elimination of 2-bromo-2,4,4-trimethylpentane, which reacts with potassium ethoxide in ethanol (70°C) to yield an alkene mixture containing 86% 2,4,4-trimethyl-1-pentene and 14% 2,4,4-trimethyl-2-pentene. Given that the heats of hydrogenation of the two alkenes are 27.2 and 28.4 kcal/mol, respectively, suggest an explanation for the observation that the major alkene product is the one with the less highly substituted double bond.

Answer 8.20

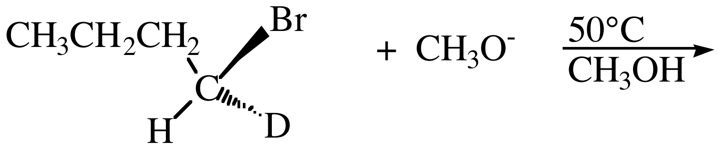


In the minor product, a methyl group is cis to a t-butyl group. Steric interactions destabilize this product and the transition state leading to it.

Question 8.21

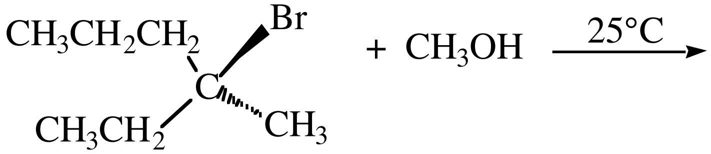
For each of the following, give the structure of the product or products you would expect from this reaction and the mechanism ($S_N1$or S_N2) by which the product(s) are formed. If a mixture of products results, what are the proportions? (5 marks)

1.)



R-1-Bromo-deuteriobutane

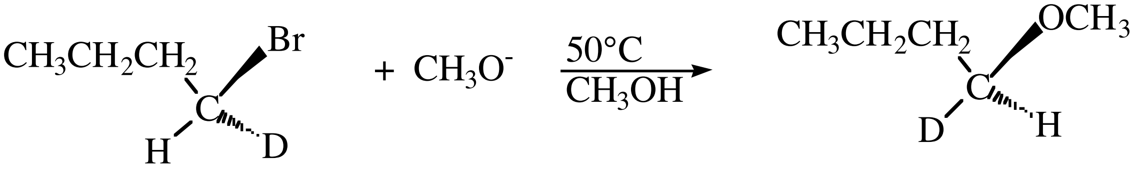
2.)



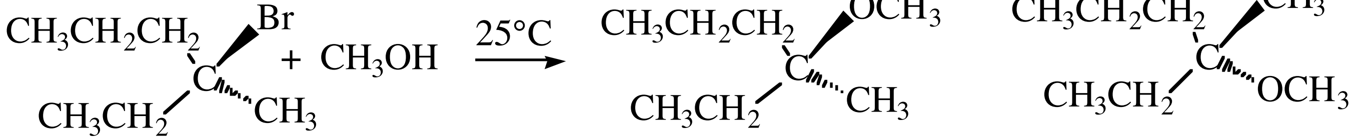
S-3-Bromo-3-methylhexane

Answer 8.21

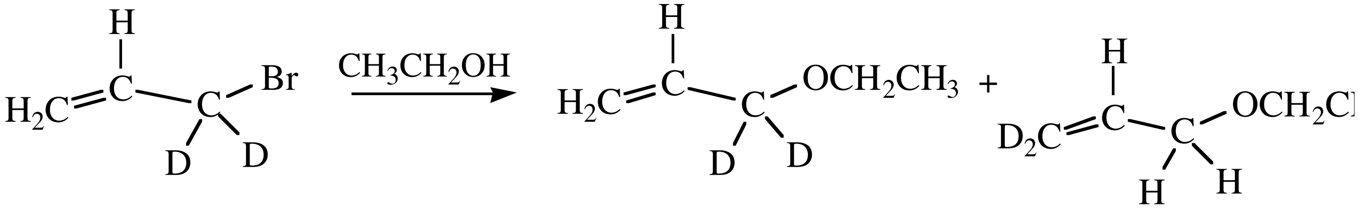
1) This reaction involves a 1° alkyl halide and a reactive nucleophile. It must be S_N2. This reaction occurs with inversion of stereochemistry to give a product with the opposite absolute stereochemistry.



2) This reaction involves a 3° alkyl halide making S_N1 the only possible substitution mechanism. A carbocation intermediate is formed during this process which can give either R or S configured product. A small amount of E1 product is also likely.

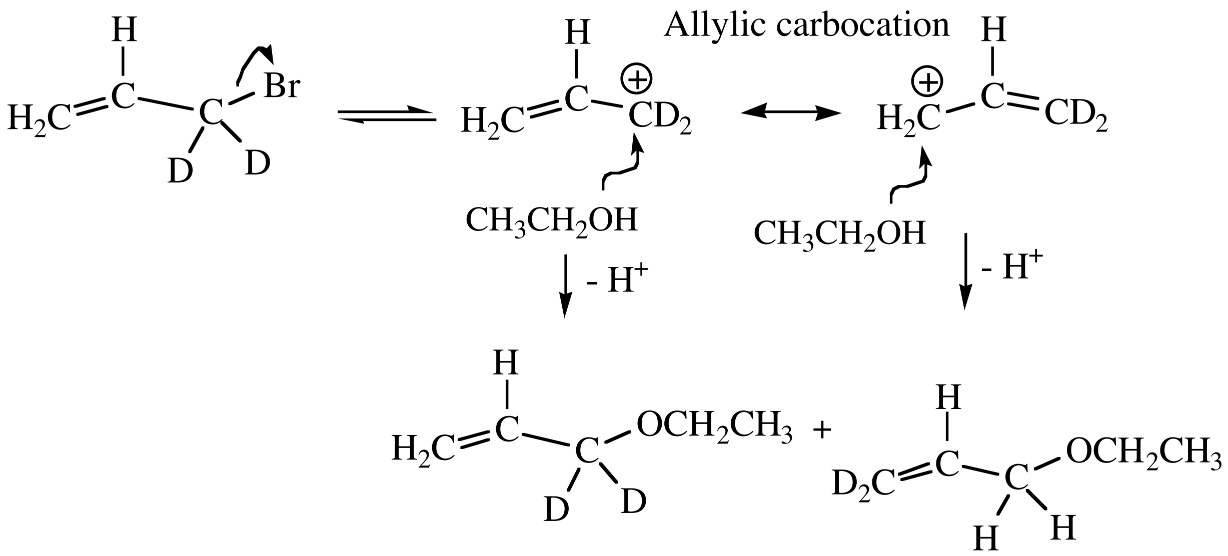


Question 8.22 (5 marks)
In the S_N1 solvolysis reaction of 3-bromo-3,3-dideuteropropene, a mixture of the following substitution products was obtained.

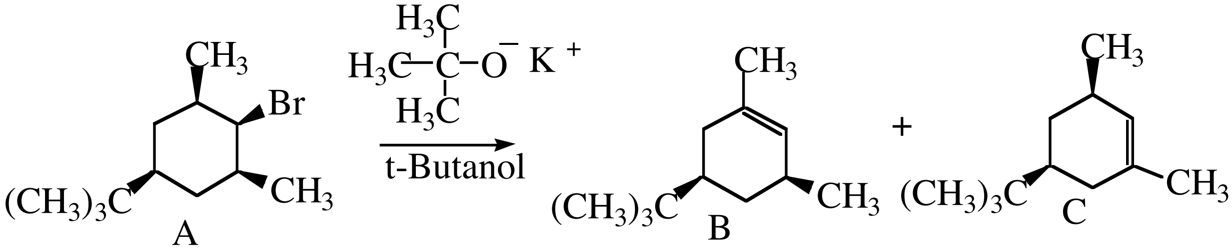


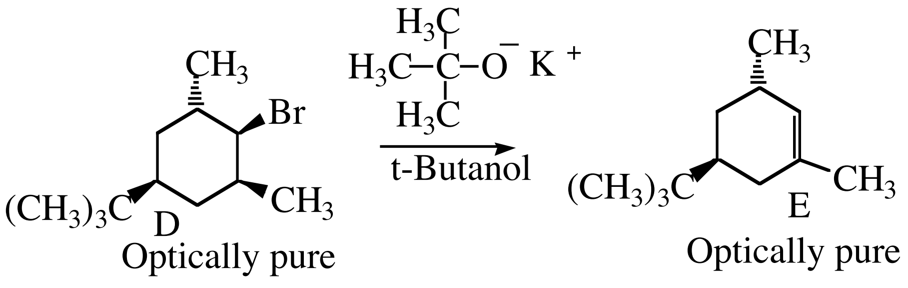
What is the mechanism for this reaction? Show how both products are formed. (Solvolysis reactions are simply reactions where the solvent is also the nucleophile).

Answer 8.22



Question 8.23 (5 marks)
Examine the following two dehydrohalogenations of diastereomers A and D with potassium t-butoxide. Compound A gives a mixture of products B and C. Compound D, which is optically pure, gives a single optically pure product under the same reaction conditions.



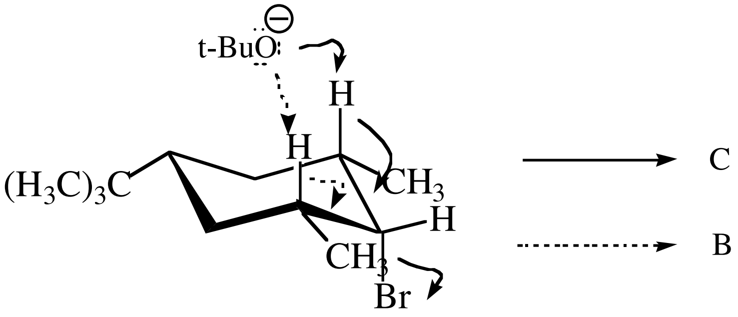


Keep in mind that a t-butyl substituent anchors the cyclohexane ring in a particular chair conformation.

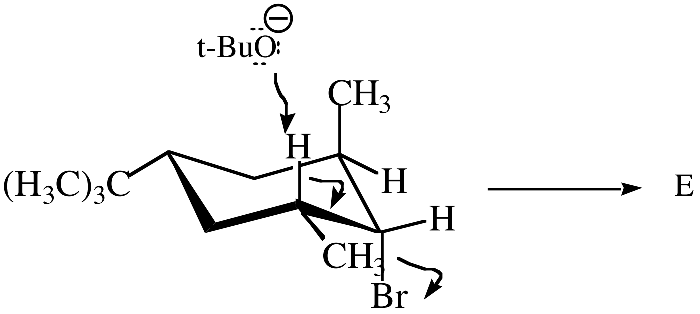
i.) What is the stereoisomeric relationship between B and C?
ii.) Making reference to the important aspects of the mechanism, explain the different outcomes of these two reactions.
iii.) Compound A, while a single pure compound, is not designated as being optically pure. Why not?

Answer 8.23

i) They are enantiomers. Trust me.
ii) In the top reaction, there are two β-hydrogens, both anti-periplanar to the leaving group, that can be removed with equal liklihood. Depending on which proton is abstracted, one obtains one enantiomer or the other.



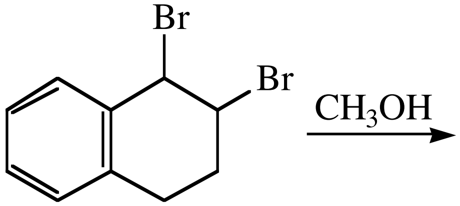
In the bottom reaction, only one of the two β-hydrogens is anti-periplanar to the leaving group, so only a single enantiomeric product can result.



iii) It is a meso-compound and not optically active.

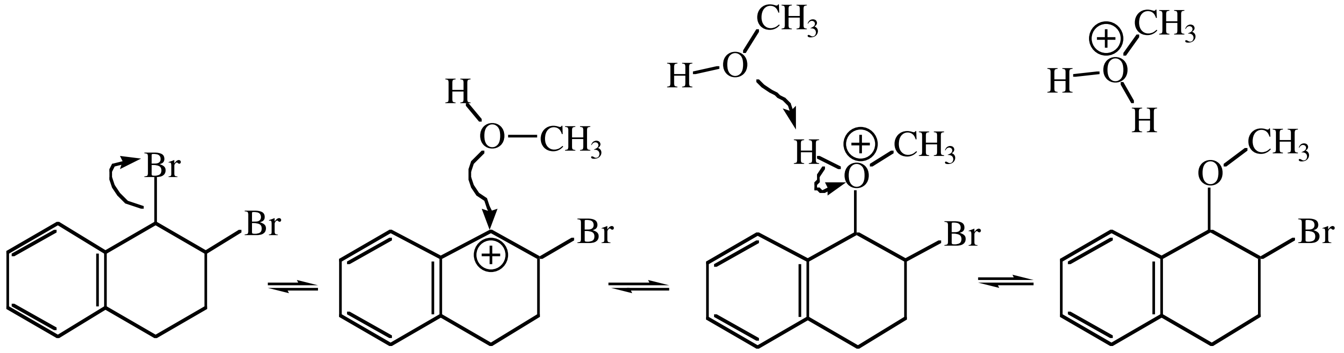
Question 8.24

What is the product formed when the following compound is reacted with methanol (as solvent). Give a mechanism for its formation that explains why this product, and not another, is formed.



Answer 8.24

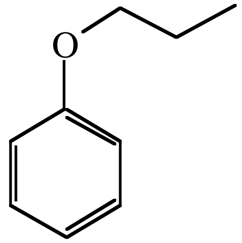
Both bromines are attached to 2° carbons so S_N2 and S_N1 reactions at either site might be expected to be sluggish. But one of the carbons is also benzylic and can therefore form a relatively stable 2° benzylic carbocation. The benzylic bromide undergoes S_N1 reaction readily as shown.



The other bromide does not react because a 2° carbocation is needed for the S_N1 process and a more reactive nucleophile is needed for S_N2.

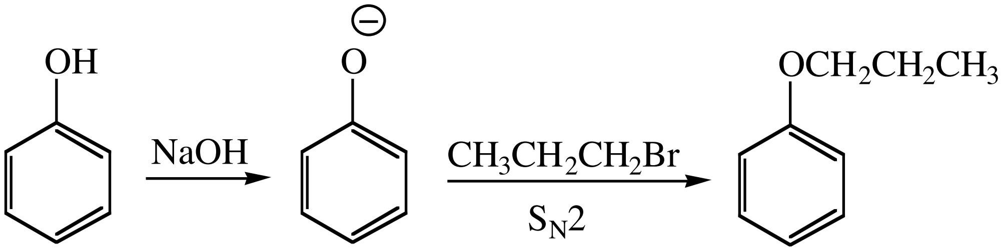
Question 8.25

Using the alkyl bromide and alcohol of your choice (and Na metal or NaOH) how would you prepare the following ether? Justify your strategy.

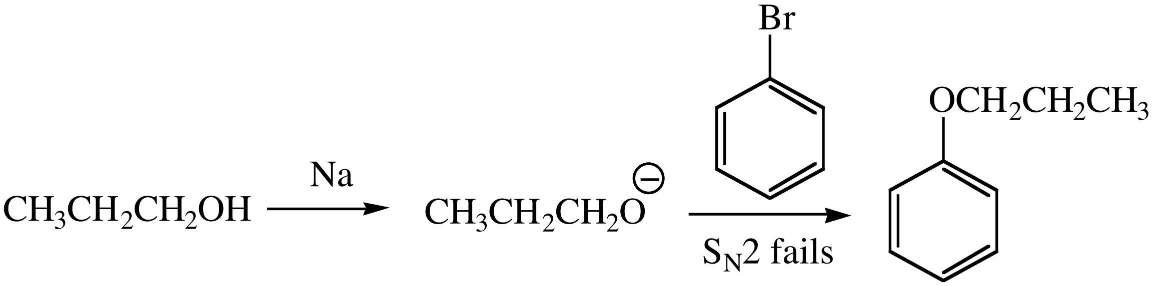


Answer 8.25

The following process would be a suitable method for preparing this ether.



An alternative method (below) would fail because aryl halides cannot undergo S_N 2 reactions.



Question 8.26

Give the product(s) expected when 3-methyl-1-bromobutane reacts with:

a.) KI in aqueous acetone

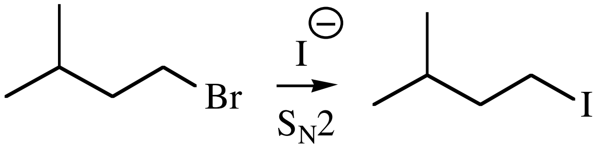
b.) KOH in aqueous ethanol

c.) potassium t-butoxide in t-butanol

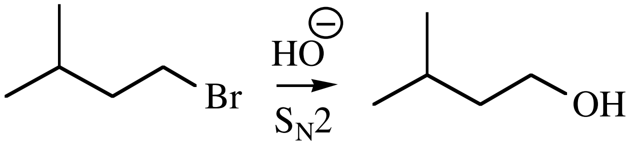
d.) Sodium methoxide in methanol

Answer 8.26

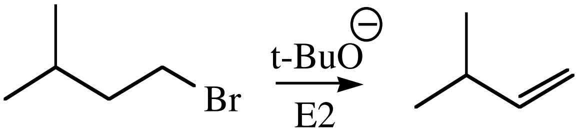
a.)



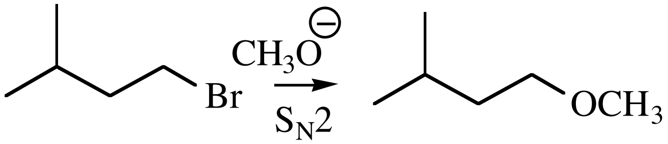
b.)



c.



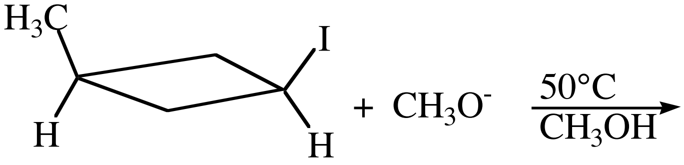
d.)



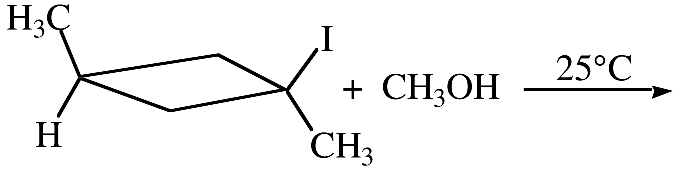
Question 8.27

For each of the following, give the structure of the product or products you would expect from this reaction and the mechanism (S_N 1or S_N 2) by which the product(s) are formed. If a mixture of products results, take a stab at estimating which is the major or minor product.

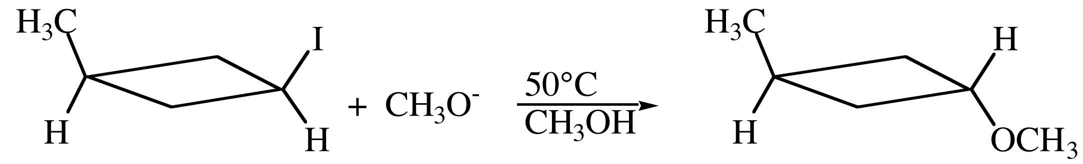
1.)



2.)



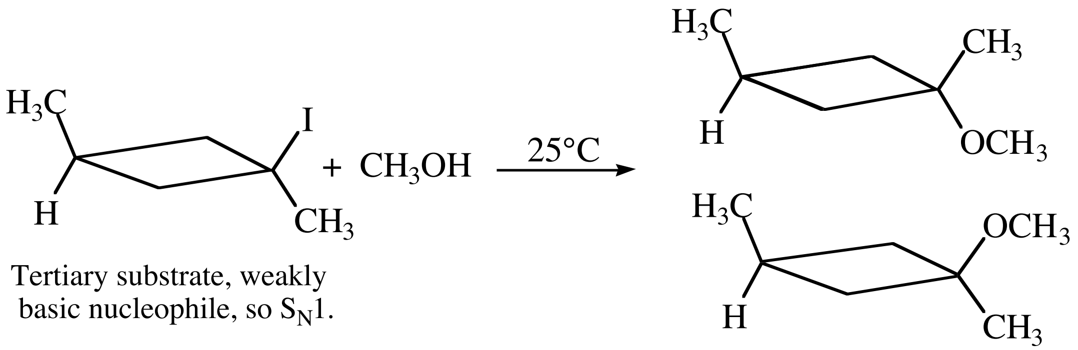
1.)



Good nucleophile, secondary substrate.

S_N2 occurs with inversion.
E2 may compete.

2.)



Tertiary substrate, weakly basic nucleophile, so S_N1.

Reaction occurs with loss of stereochemistry at the reaction center. A mixture of diastereomers results in this case.

Answer 8.27

Question 8.28

Rank the following compounds in order of increasing rate of the S_N2 reaction with KI in aqueous acetone:

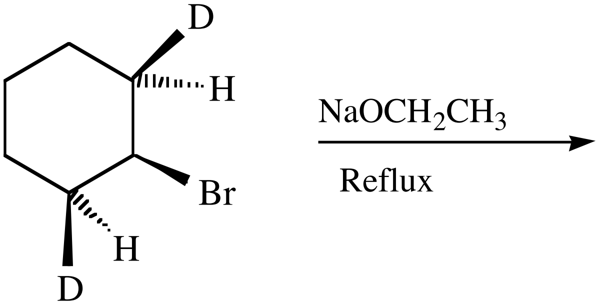
a.) t-butyl chloride b.) 2-methyl-1-chloropropane (isobutyl chloride) c.) 2-bromopropane (isopropyl bromide) d.) 2-chloropropane (isopropyl chloride) e.) 1-bromobutane (n-butyl bromide)

Answer 8.28

e (1°, bromide best leaving group) > b (1°, chloride poorer leaving group than bromide) > c (2°, bromide) > d (2°, chloride) >> a (3° substrate, very slow S_N2).

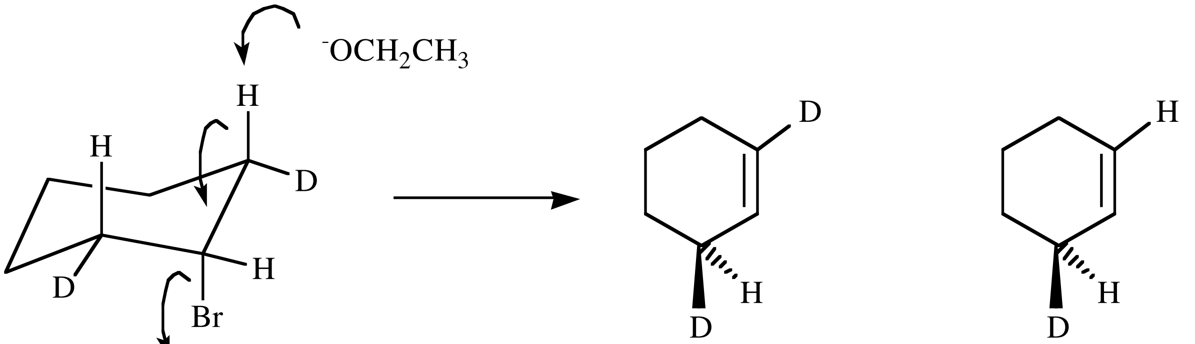
Question 8.29 (three marks)

What is the E2 product of the following reaction? Explain your reasoning. (D = deuterium, the ^2H isotope of hydrogen)



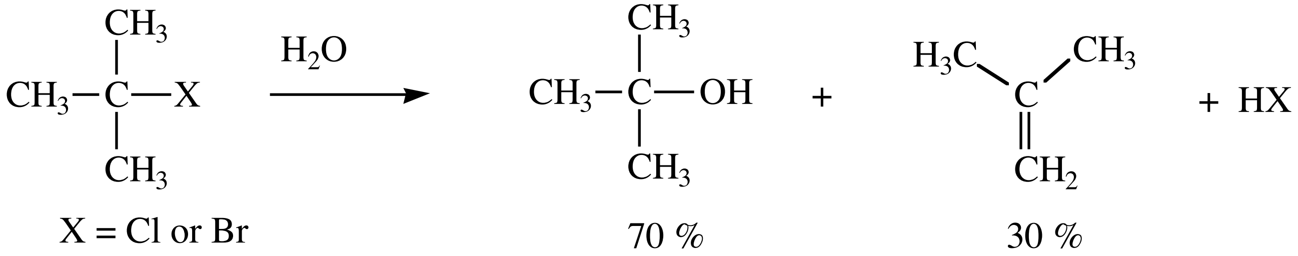
Answer 8.29

An anti-periplanar orientation of the leaving group with respect to the hydrogen being abstracted by the base is critical. There are only H's anti to the Br leaving group in the starting material so only H's can be abtracted by the base. The **sole product** in this reaction is the one which contains two D atoms.



Sole E2 product.

Question 8.30 (5 marks)
Although 2-bromo-2-methylpropane (t-butyl bromide) solvolyzes in water to give t-butyl alcohol and 2-methylpropene ten times more rapidly than does 2-chloro-2-methylpropane (t-butyl chloride), the ratio of elimination to substitution products is the same for these two alkyl halides.
Explain why making reference to the mechanisms involved.



i.) Identify the mechanism by which the major and minor products are formed.
ii.) Compare the activation energies for the first step in each mechanism. Explain your reasoning.
iii.) Compare the activation energies for the second step in each mechanism. Explain your reasoning.

Answer 8.30
i.) The mechanisms involved are S_N1 and E1 respectively. Since bromine is a better leaving group than chloride, the alkyl bromide reacts more quickly (since the leaving group is lost in the rate-determining step). BUT, irrespective of the nature of the leaving group, both the alkyl chloride and the alkyl bromide form an identical carbocation intermediate. For this reason, the subsequent results of the reaction must be identical in all respects.

ii.) The first step in both E1 and S_N1 processes (ionization to form a 3° carbocation) is identical for both mechanisms. So is the activation energy, needless to say.

iii.) This is intuitively obvious but an interesting question. Because more S_N1 product is formed, then clearly its second step must be faster and its activation energy lower than the second step in the E1 process. But keep in mind that **both products are formed at the same rate**. It is the first step which is rate-determining, not the second. Think of it this way perhaps. The carbocation is formed relatively slowly. Once formed it can (quickly) go two ways. One path (S_N1) is a little easier than the other so more of the cations react this way. Some cations however will still have sufficient energy to react by the higher energy E1 pathway but the not as often as the S_N1 route.

Question 8.31

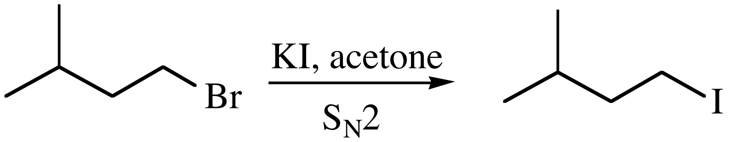
Give the product(s) expected when 3-methyl-1-bromobutane reacts with:

a.) KI in aqueous acetone

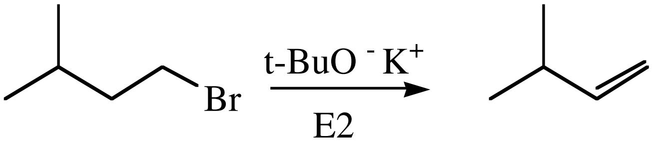
b.) potassium t-butoxide in t-butanol

Answer 8.31

a.)

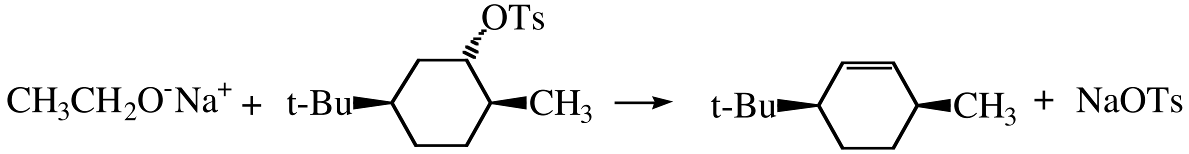


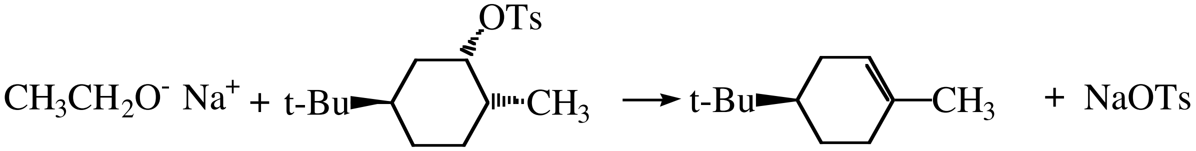
b.)



Question 8.32

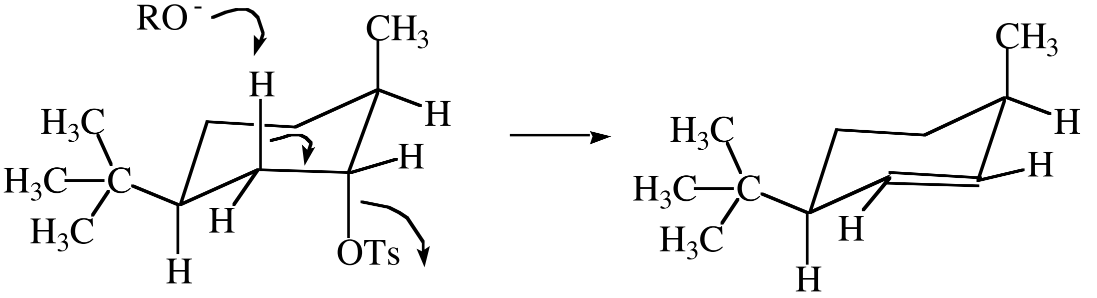
Account for the different outcome of the following E_2 reactions. You will need to remember that a t-butyl group greatly prefers to adopt an equatorial position in a cyclohexane chair conformation. OTs = tosylate = toluenesulfonate = a good leaving group.



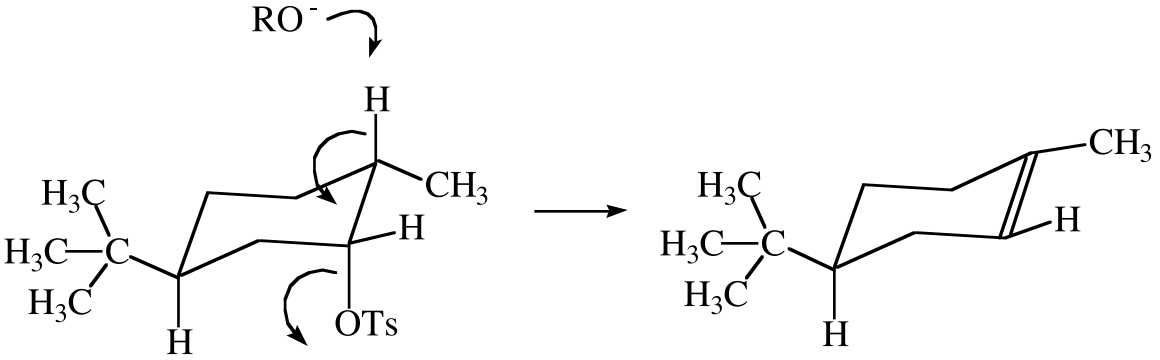


Answer 8.32

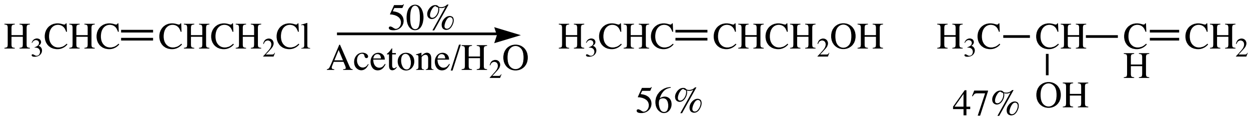
The t-butyl group anchors the ring in a conformation in which it occupies an equatorial group. The other substituents must then adopt a certain position. You must also recognize that this reaction, an E2 elimination, occurs in a single step such that the proton being abstracted and the leaving group must be anti-periplanar to one another. In the first example, a methyl group occupies one of the anti-periplanar positions in the ring leaving only one proton on the molecule properly aligned for the E2 reaction. Thus, the disubstituted alkene is the only possible product.



In the second case the methyl group is equatorial. There are protons anti-periplanar to the tosylate on both carbons adjacent to the leaving group. The preferred product is the more highly substituted alkene.



Question 8.33 (four marks)
When 1-chloro-2-butene reacts in 50% aqueous acetone at 47 °C, the product is a mixture of two alcohols.



$$H_3CHC{=}CHCH_2Cl \xrightarrow[\text{Acetone/H}_2\text{O}]{50\%} H_3CHC{=}CHCH_2OH \qquad H_3C-\underset{OH}{CH}-\underset{H}{C}{=}CH_2$$

56% 47%

This S_N 1 reaction features an ***allylic*** carbocation intermediate. Write a detailed mechanism that shows how these two products are formed

Answer 33