

A Sampler to
A Guide to
Organic Chemistry Mechanisms

*A Guided Inquiry Workbook
Easy to Follow Curved Arrows*

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*Curved Arrow Press
Princeton, New Jersey*

1 — Getting Ready for Reactions

Guide to Drawing Resonance Structures

Resonance Structures

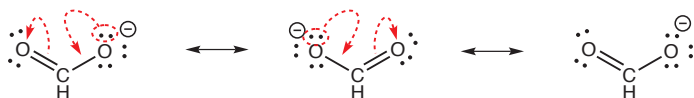
If you are unfamiliar with the use of the curved arrow, refer to the discussion in the *Notes* section. A good place to start pushing electrons is in drawing resonance structures. They have the elements of electron movement, but the problems will be more limited in scope.

Resonance Structures of Anions

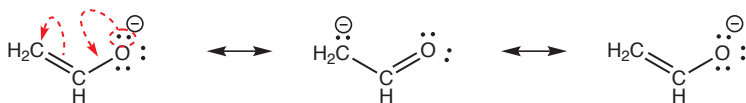
The principle for understanding resonance structures is to understand that electrons will operate by a push-pull mode or model. If there's a net negative charge, it will be the electrons of the atom with the negative charge that will push toward the pi bond. We will start our curved arrow with those electrons. Continue to move them toward any neighboring pi bonds (push) to create and break new bonds. You should note that two curved arrows are required to avoid structures with more than eight valence electrons.

For the following examples, add curved arrows, where needed, to show how the electrons move to form the next structure. For 1-6, the first and last structures are the same. In that case, you are converting it back to the starting structure.

1.

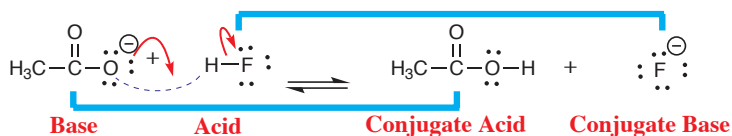


2.



2 -Acid-Base Chemistry

1. For this example, the acids and bases are labeled. HF is the strongest acid as it has the lower pK_a . Therefore, F^- , its conjugate base, is the weakest base.



L/R

 pK_a 3.2 pK_a 4.75

weakest base

Notice the curved arrows. They describe the reaction that is taking place. We could write the following sentences to describe the curved arrows.

A bond is being made between the oxygen and hydrogen atom with the electrons from the oxygen atom.

A bond is being broken between the hydrogen and the fluorine atom with the electrons remaining attached to the fluorine atom.

3.

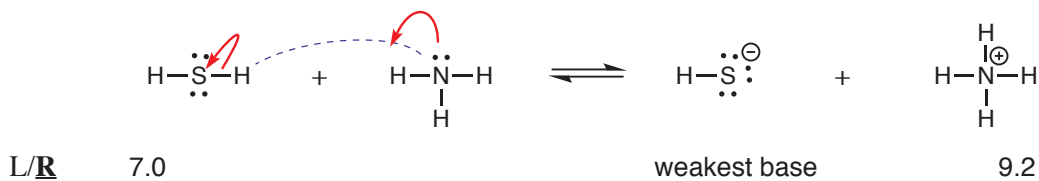


L/R

weakest base

 pK_a 3.2 pK_a -1.7

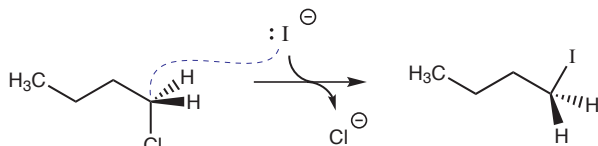
4.



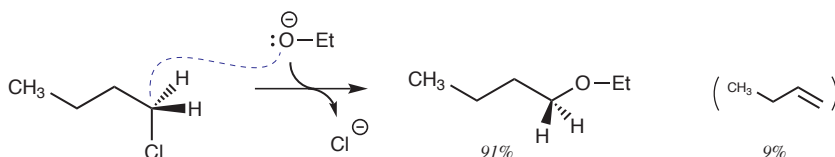
3 - Substitution Reactions

S_N2 Substitution Reactions

1. An S_N2 reaction of 1-chlorobutane with sodium iodide to give 1-iodobutane. (See *Notes*.)

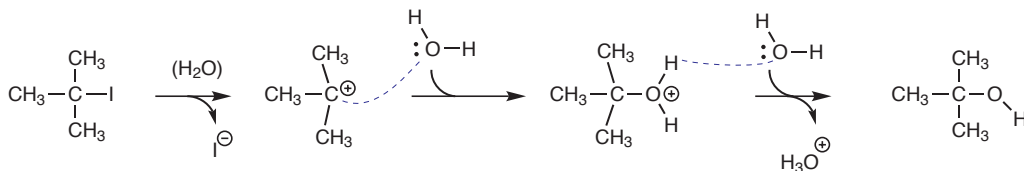


2. An S_N2 reaction of 1-chlorobutane with ethoxide to give 1-ethoxybutane (butyl ethyl ether). (See *Notes*.)

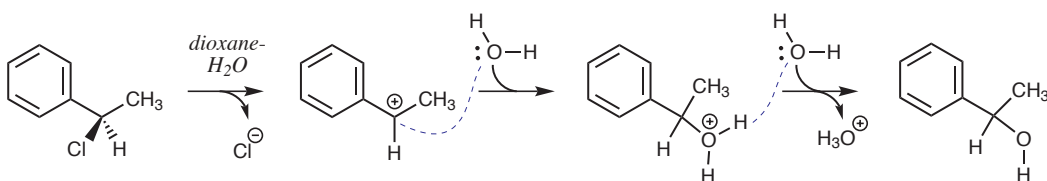


S_N1 Substitution Reactions

20. An S_N1 solvolysis reaction of *t*-butyl iodide to give *t*-butyl alcohol. (See *Notes*.)



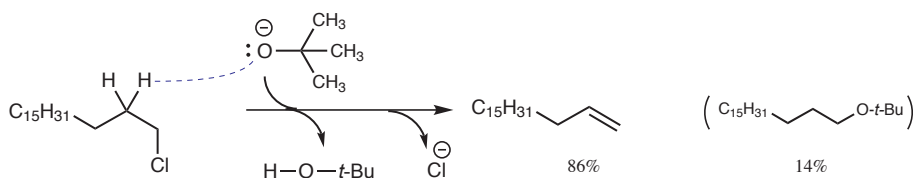
21. An S_N1 solvolysis reaction of (*R*)-(1-chloroethyl)benzene to give *rac*-1-phenylethanol.



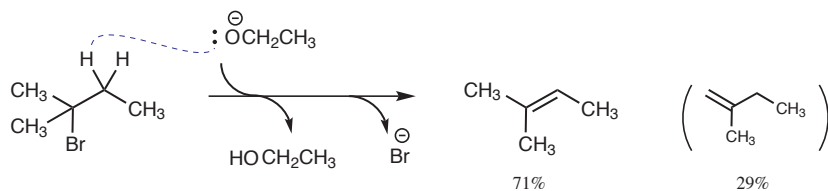
4 – Elimination Reactions

Alkene Formation

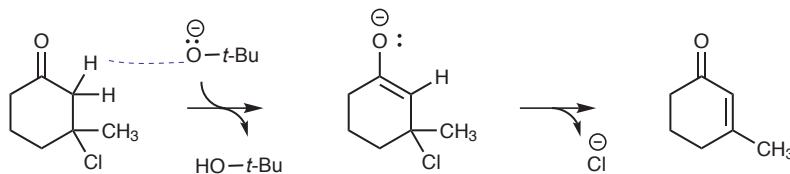
1. An E2 elimination reaction of hydrogen chloride from 1-chlorooctadecane with potassium *t*-butoxide to give 1-octadecene. (See *Notes*.)



3. An E2 elimination reaction of 2-bromo-2-methylbutane to give 2-methyl-2-butene, a Zaitsev product.

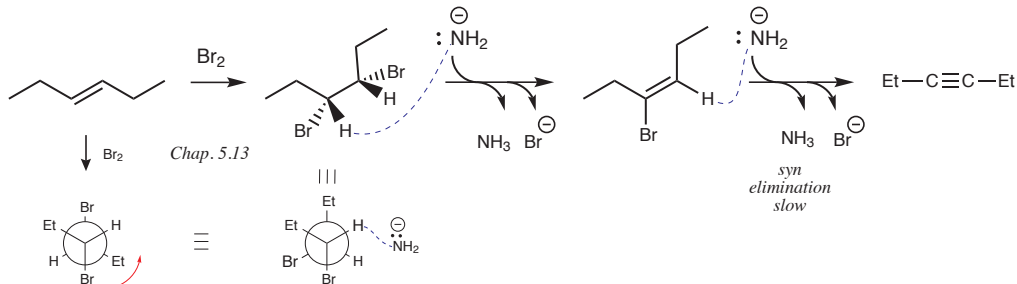


10. An E1cb elimination reaction of 3-chloro-3-methylcyclohexanone with *t*-butoxide to give 3-methyl-2-cyclohexenone. (See Notes.)



Acetylene Formation

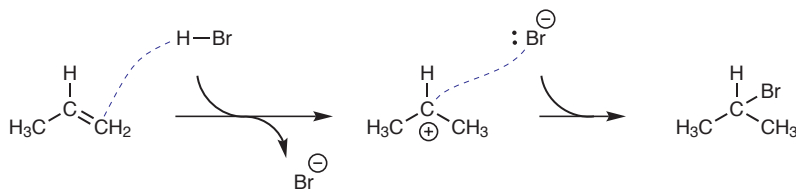
20. A synthesis of 3-hexyne from *trans*-3-hexene by bromination and two elimination reactions. (See Notes.)



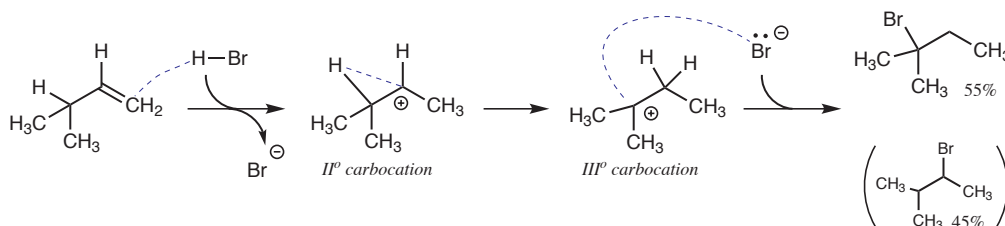
5 — Electrophilic Addition to Alkenes and Alkynes

Addition of HX and H₂O to Alkenes

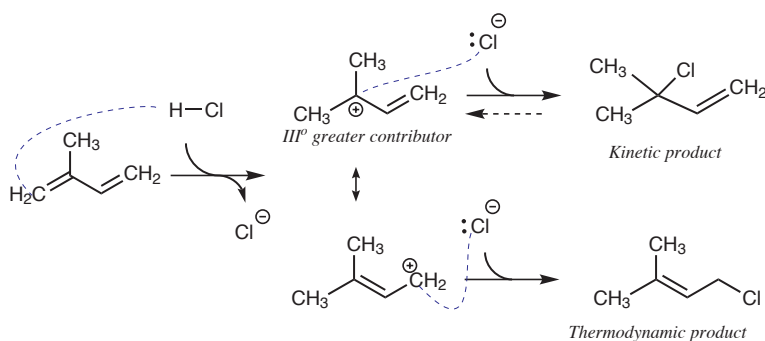
1. Addition of hydrogen bromide to propene to give 2-bromopropane. (See Notes.)



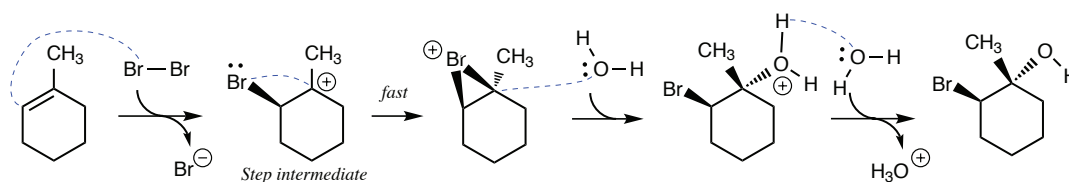
7. Addition of hydrogen bromide to 3-methyl-1-butene to give after rearrangement, 2-bromo-2-methylbutane. (See Notes.)



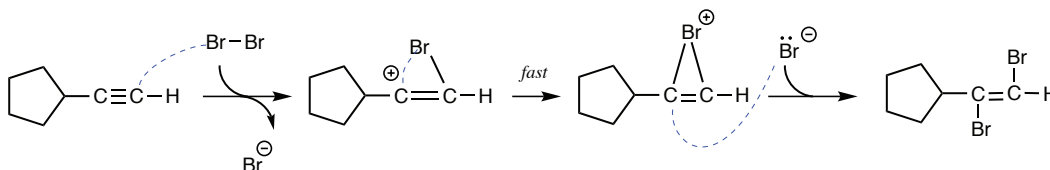
10. Addition of hydrogen chloride to 2-methyl-1,3-butadiene (isoprene) to give, 3-chloro-3-methyl-1-butene, the kinetic product, or 1-chloro-3-methyl-2-butene, the thermodynamic product. (See *Notes*.)



15. Bromination of methylcyclohexene to give (1*R*,2*R*)- and (1*S*,2*S*)-2-bromo-1-methylcyclohexanol. (See *Notes*.)



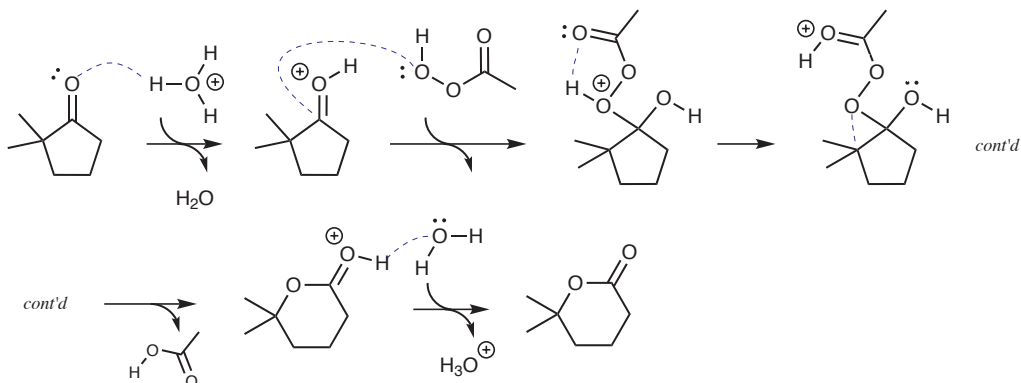
21. Addition of bromine to ethynylcyclopentane to give (*E*)-(1,2-dibromovinyl)cyclopentane and (1,1,2,2-tetrabromoethyl)cyclopentane. (See *Notes*.)



6 — Rearrangement Reactions

Baeyer-Villiger Oxidation

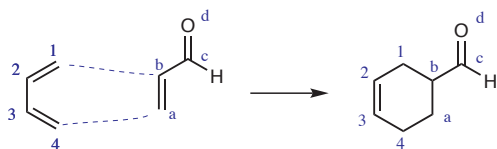
1. Acid catalyzed Baeyer-Villiger oxidation of 2,2-dimethylcyclopentanone with peracetic acid. (See *Notes*.)



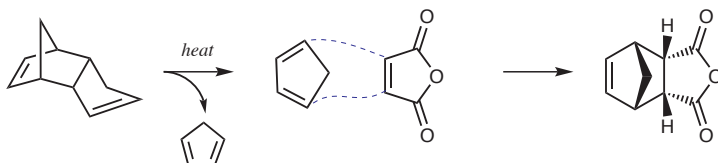
7 – Electrocyclic Reactions

Diels Alder Reactions

1. A Diels-Alder reaction between 1,3-butadiene and 2-propenal (acrolein).



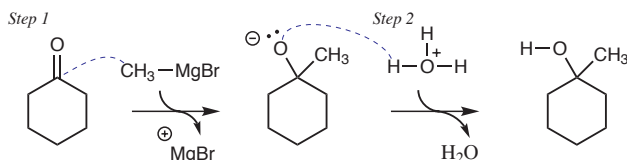
8. A reverse-forward Diels-Alder reaction between cyclopentadiene and maleic anhydride.



8 – Carbonyl Addition and Addition-Elimination Reactions

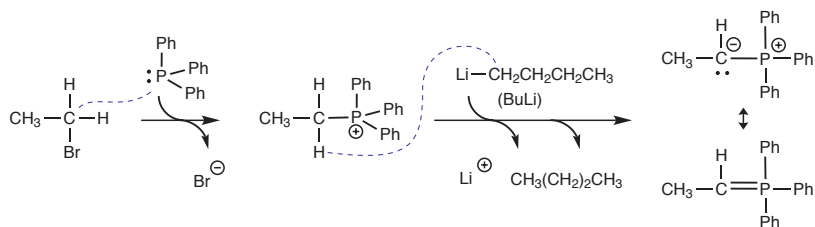
Grignard Addition to a Carbonyl Group

1. Addition of methyl magnesium bromide to cyclohexanone to give 1-methylcyclohexanol (for formation of Grignard reagents, see *Notes*).

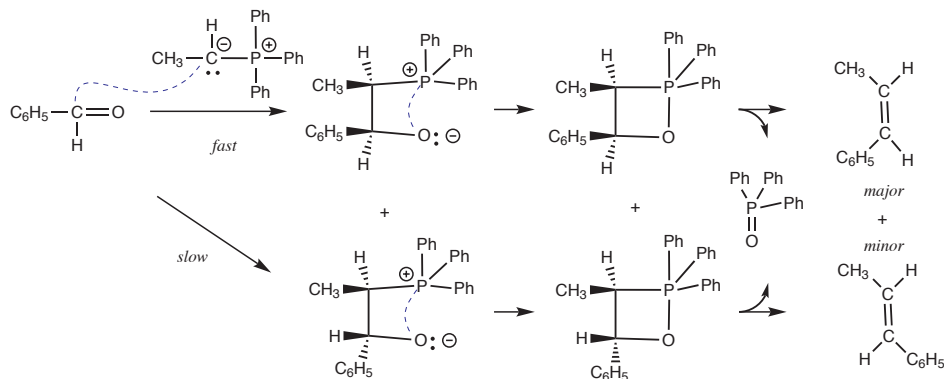


Wittig Reaction

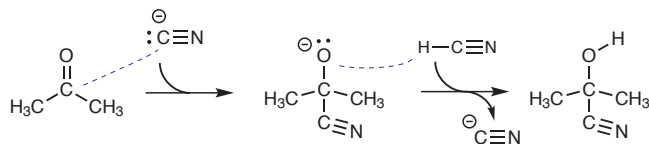
5. Wittig reaction, Step 1, formation of Wittig reagent. (See *Notes*.)



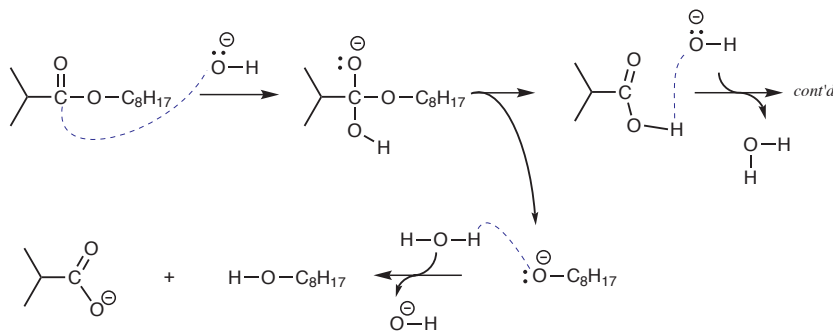
Step 2, reaction with benzaldehyde



10. Formation of the cyanohydrin (2-hydroxy-2-methylpropanenitrile) from acetone. (See *Notes*.)

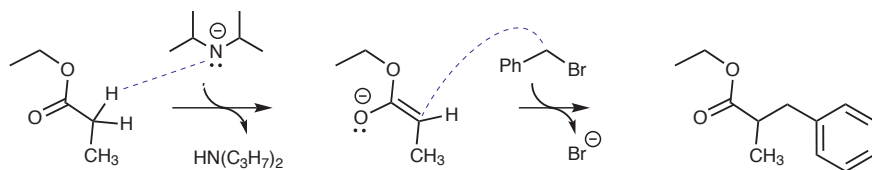


23. Base hydrolysis of octyl isobutyrate to give octanol and isobutyric acid. Step 1, treatment with base. (See *Notes*.)

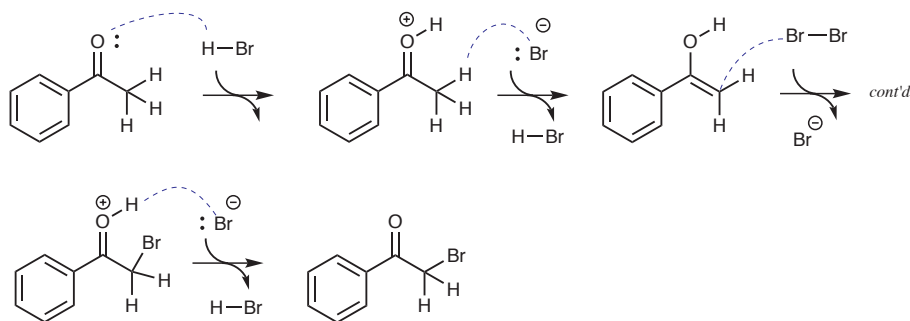


9 — Reactions of Enols and Enolates

9. Enolization and alkylation of ethyl propionate with benzyl bromide. (See *Notes*.)

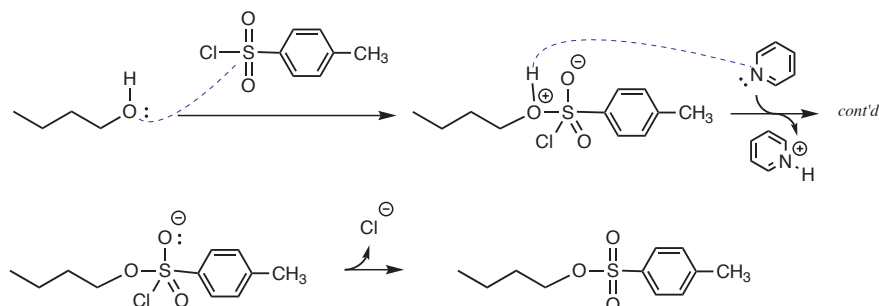


14. Acid catalyzed bromination of acetophenone to give α -bromoacetophenone. (See *Notes*.)

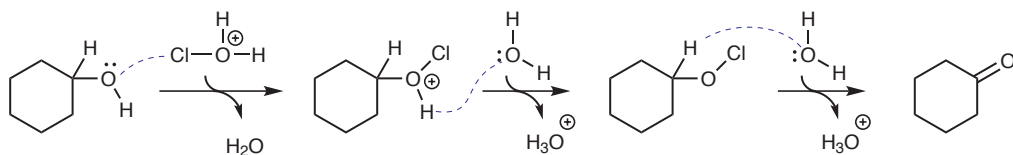


10 — Dehydration/Halogenation Agents

3. Reaction of 1-butanol with tosyl chloride and pyridine to give butyl tosylate. (See *Notes*.)



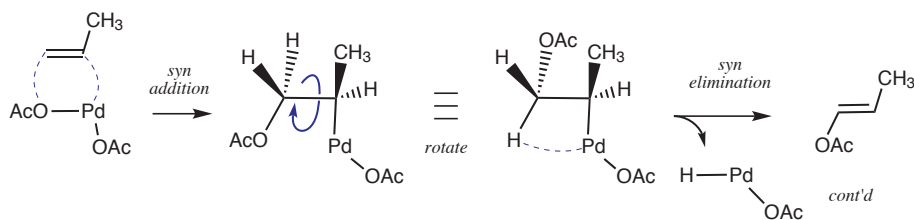
5. Oxidation of cyclohexanol to cyclohexanone with sodium hypochlorite (NaOCl, bleach).



13 — Organometallic Reactions

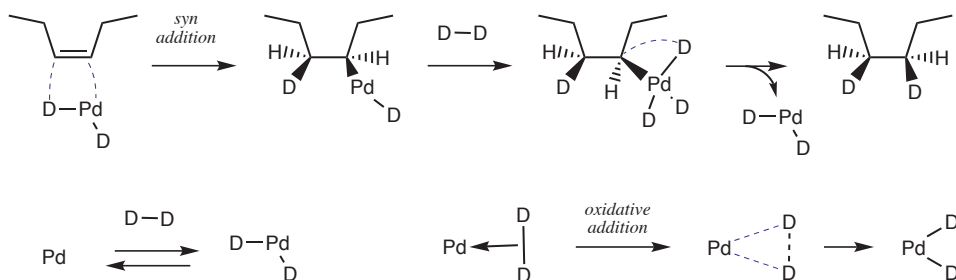
Acyclic Heck Reaction

1. Step 1, reduction of palladium (II) to zero valent palladium with propene. (See *Notes*.)



Catalytic Reduction of an Alkene (See *Notes*.)

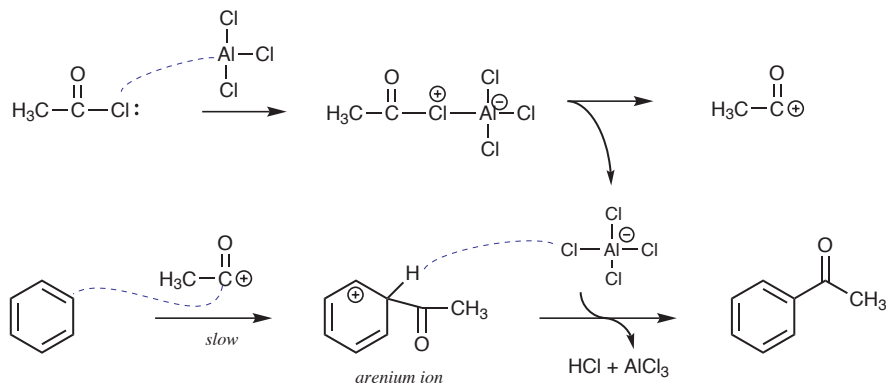
3. Catalytic hydrogenation of *cis*-3-hexene to hexane.



14 — Aromatic Substitution Reactions

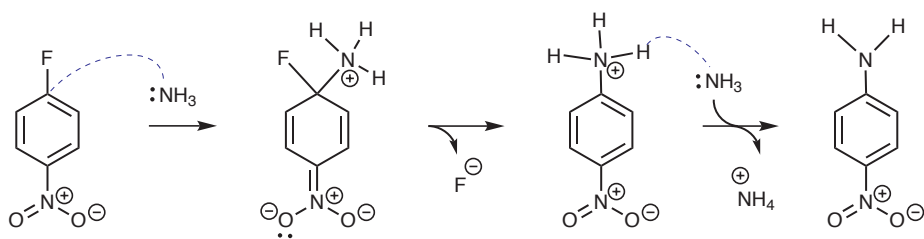
Electrophilic Aromatic Substitution of Benzene

1. Friedel Crafts acylation of benzene.

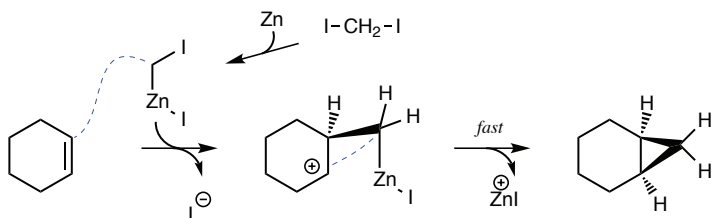


Nucleophilic Aromatic Substitution

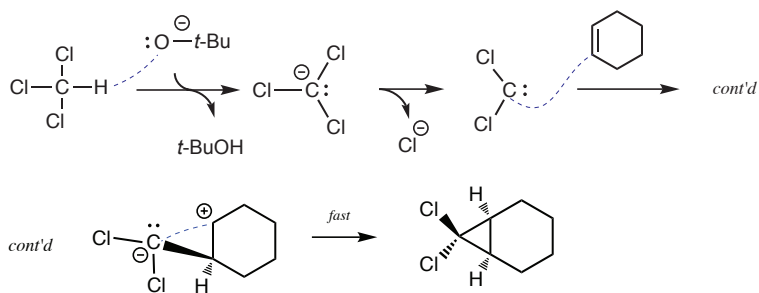
11. Nucleophilic aromatic substitution of 1-fluoro-4-nitrobenzene with ammonia to give 4-nitroaniline. (See *Notes*.)

**15 – Carbene and Nitrene Reactions****Carbene Reactions**

1. Simmons-Smith carbene addition to cyclohexene to give a bicyclo[4.1.0]heptane. (See *Notes*.)

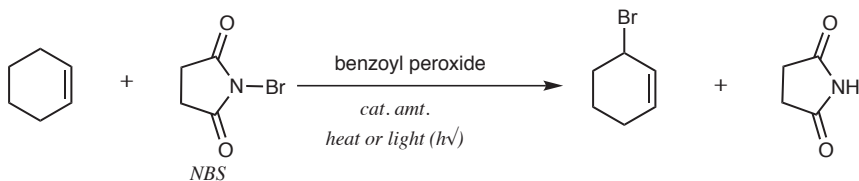


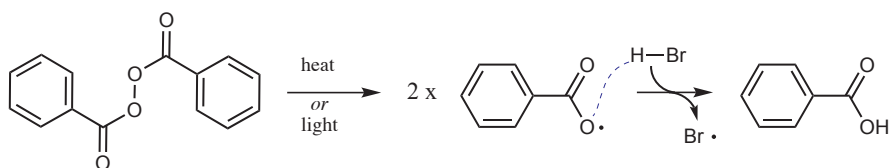
3. Dihalocarbene addition to cyclohexene to give 7,7-dichlorobicyclo[4.1.0]heptane.

**16 – Radical Reactions****Allylic Bromination with NBS**

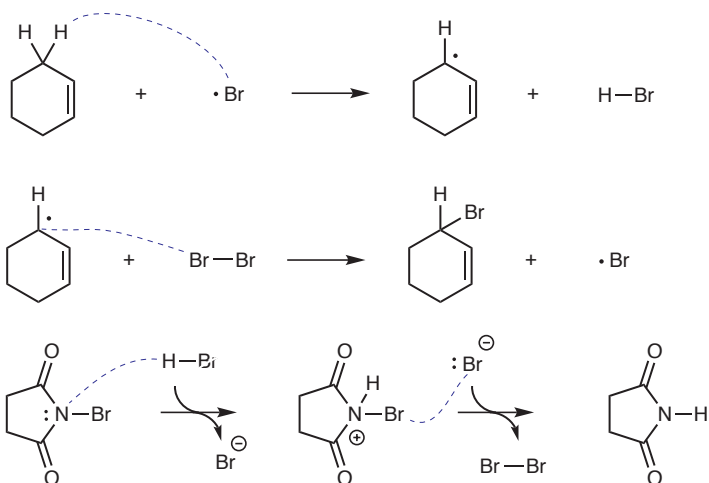
2. Free radical bromination of cyclohexene with *N*-bromosuccinimide, an allylic bromination.

Overall reaction

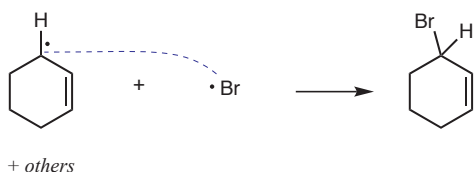


2. Free radical bromination of cyclohexene with *N*-bromosuccinimide, an allylic bromination -- continued.Initiation (See *Notes*.)

Propagation



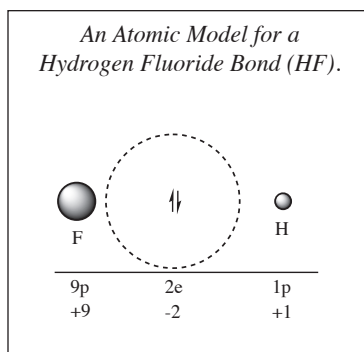
Termination



Notes

A challenge to maintaining the utility of this book as a guide is to maintain the organization of the different parts. While it would be useful to have notes in different parts, doing so makes it very difficult to maintain the overall organization of the book. It is simpler to keep notes to a minimum within each part and to place notes elsewhere. As a result, additional comments have been added in the following *Notes* section.

Chapter 1 Getting Ready for Reactions

*About the Atom*

A commonly held view is that, 'There is a strong correlation between the length of a covalent bond (i.e., the distance between the bonding atoms) and the strength of the bond.' This notion is consistent with Coulomb's Law.

An alternate model may be drawn in which bonds are made up of electron pairs that are mutually attracted to pairs of positively charged nuclei. This model is represented in *An Atomic Model for a Hydrogen-Fluorine Bond* on the left. This model is in agreement with the acidities for the atoms C, N, O, and F. It can be used explain why a proton, connected to a triple bond which is shorter, can be more acidic than a proton attached to a double or single bond. Because the C-H bond lengths are the shortest in a terminal triple bond, the electrons are closest to the carbon nucleus and the electron-proton distance is larger. With that model, the key variable for acidity (bond strength) is the proton-electron pair distance. Since the force varies inversely with the square of the

distance, a greater distance will result in a weaker bond. For acidity, that longer proton-electron pair distance results in greater acidity.

Resonance Structures

With resonance structures, a neighboring atom can donate electrons or pull electrons away. Examples 14 and 15 (page 4), illustrate electron donation and Examples 16, 17, and 26 (pages 4 & 6) illustrate electrons being pulled to the more electron withdrawing atom. When the neighboring atom donates electrons, it will release the electrons on the atom to which they are being donated. As a result, the electrons of the receiver atom will be held less tightly and can react more easily, see Example 17, Step 2, page 60. Conversely, if the electrons are pulled away, the electrons of the donor atom will now be held more tightly.

Chapter 3 Substitution Reactions

You should consult with your textbook for a more thorough discussion of S_N1 and S_N2 reactions. Substitution reactions can be described in two extremes. In an S_N1 reaction, the leaving group must pull its electrons from the carbon in the rate-limiting step. No bond formation occurs until a carbocation exists long enough for the leaving group to diffuse away and the group having left does not influence any incoming nucleophile. If the RX carbon had been optically active, then the product of the reaction would be completely racemic.

On the other extreme is an S_N2 reaction in which bond formation precedes bond cleavage. The nucleophile must *push* into the carbon nucleus. If the RX carbon were optically active, the product would retain that optical activity but it will be of the opposite configuration due to an inversion that takes place.

In between these extremes will be the reactions for which you have to predict the products and sometimes there are ambiguities or exceptions. Therefore, I find that predicting the products can be challenging. However, there are some simple principles,

- An S_N1 reaction requires conditions that favor carbocation formation, namely a good leaving group preferably on a tertiary carbon, a polar solvent, usually water, and a weak nucleophiles (often uncharged). Tertiary halides can undergo S_N1 reactions while primary halides (unless allylic or benzylic) do not.
- S_N2 reactions require conditions in which a pair of electrons are able to attack the carbon attached to the leaving group. That attack must precede bond cleavage. In order to extend the reach of the electrons, anions and especially anions of weak acids are common. However, nucleophiles whose conjugate acid is greater than 11 increases the amount of elimination products. High nucleophile concentrations and polar aprotic solvents (DMF, DMSO) are common.
- The ease of nucleophilic substitution is: methyl halide > primary halide > secondary halide. Tertiary halides fail to react via S_N2 mechanisms. Secondary halides are more difficult to displace by an S_N2 reaction and the conditions of the reaction are more important in predicting the products.
- Any factors that interfere with S_N2 reactions will increase the amount of elimination. In Chapter 4, Examples 2, 3, and 5 result in elimination reactions. Elimination increases as steric hindrance to an S_N2 reaction increases.
- The solvent effect for S_N2 reactions is rationalized by the formation of reactivity reducing hydrogen bonds (or their absence). Polar aprotic solvents cannot hydrogen bond and therefore facilitate S_N2 reactions. This can explain why fluoride, the most basic halide, can react faster in a polar aprotic solvent, and iodide can react faster in protic solvents. It is presumed that the electrons of fluoride would contain hydrogen bonds and thus limit their availability. Iodide would be more immune to that effect.

For a given set of problems, students will not experience many difficulties in substitution reactions. Just focus on bond making and breaking, and the orientation of the nucleophiles and substrates. However, some nucleophiles may have two different sites to react (ambident anions). When resonance structures exist, only the greatest resonance contributor is usually shown. However, bonds may form to a charged atom of an unshown resonance isomer. It may be useful to write the resonance structure and consider why a reaction might occur on one atom versus another.

Chap. 3.1 This reaction is usually run in acetone because it is aided by the insolubility of NaCl. Sodium chloride precipitates and suppresses a reverse reaction.

Chapter 5 Electrophilic Addition to Alkenes and Alkynes

Hydroboration-Oxidation of Alkene

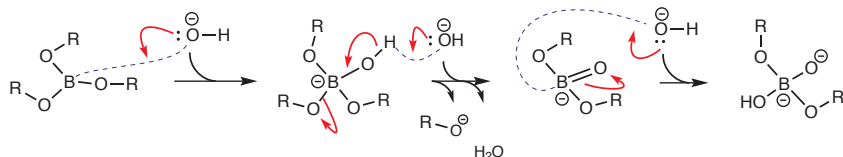
Chap. 5.17 In Example 17, note how similar step one of this reaction is to the prior reactions in this chapter. Boron is the electrophile and reacts with the electrons from the alkene. The second part of this reaction takes place before any atom movement can take place. The electrons from the negatively charged boron are donated to the carbocation. In this case, a proton is attached to the donated electrons.

I formerly wrote to repeat the first reaction 2X. While this is expedient, I found many students didn't understand what was happening with the repeat statement. If in learning the mechanism, when it becomes clear to you that it is the same reaction being

repeated three times, you can just write the first hydroboration and then indicate that the hydroboration step is repeated 2X.

In step 2, boron is still an electrophile except the nucleophile is now a hydroperoxy anion. Note, it is the same reaction repeated three times. You can just write the first oxidation step and then indicate that the oxidation step is repeated 2X.

You may also use this alternate mechanism for the hydrolysis. I like the deprotonation to promote the loss of the alkoxide. However, the product of that elimination is an sp^2 -hybridized boron with a negative charge. The next step requires that boron attract an additional pair of electrons. The product of that addition is an sp^3 -hybridized boron with an alkoxide oxygen neighbor. While I did not use this mechanism, if your textbook or your instructor uses it, then you may use it also.



Stepwise versus Concerted Reactions

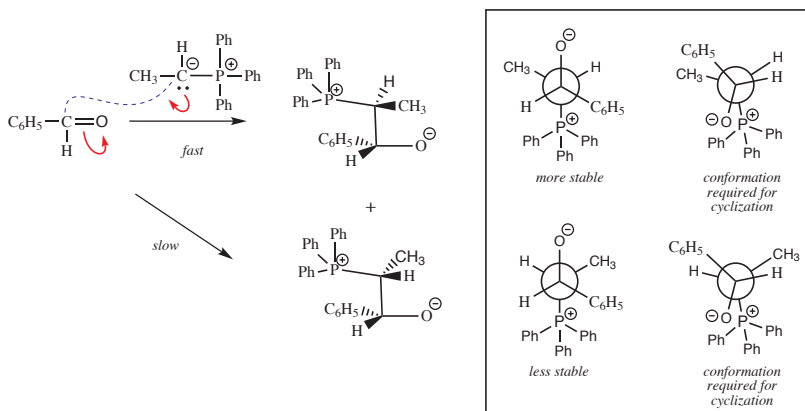
Many textbooks write the hydroboration step as a concerted reaction. I have not done so for two reasons. One is that this appears to be a symmetry forbidden $2 + 2$ reaction. The symmetry rules can be used to explain why alkenes and HBr do not thermally add to an alkene in a concerted reaction. Because the addition of borane to an alkene is a syn addition, many books write it as a concerted reaction. If the reaction were concerted, then charges should be minimized and the product will form in a single step. I suggest a definition of a concerted reaction as, *any electron movements that occur faster than bond rotation are concerted*. Therefore a reaction may be concerted and have additional steps provided they occur faster than atom movements. In this case, the stepwise mechanism preserves the reactivity of an alkene as a nucleophile and borane as an electrophile. This is consistent with the majority of boron and alkene reactions. The movement of electrons to form a bond can be expected to occur faster than atom movements and thus be consistent with a concerted reaction.

Chapter 8 Carbonyl Addition and Addition-Elimination Reactions

Wittig Reaction and Horner-Wadsworth-Emmons Reaction

Chap. 8.5

The Wittig and Horner-Wadsworth-Emmons variation of the Wittig reaction are complementary reactions having different advantages. The details of the Wittig reaction are useful in understanding the stereochemistry of the product. After formation of the reagent (Step 1), the addition (of the ylide) to an aldehyde gives an intermediate in which the more stable conformation predominates. Note the conformation shown below. This has been drawn conventionally and as the corresponding Newman projection (see box). This conformation was not included in the reaction scheme. This conformation must undergo a bond rotation in order to bring the phosphorus and oxygen atoms together. That rotation gives the conformation that results in a *cis*-alkene. The Wittig reaction stereochemistry is determined by the fast addition to the carbonyl group.



Chapter 13 Organometallic Reactions

Organometallic chemistry often involves reactions in which the mechanism is not understood, incompletely understood, or complex. In some reactions, I show how it *might* take place.

Catalytic Reduction of an Alkene

Chap. 13.3

This mechanism is hypothetical. I extrapolated from the Heck reaction to similar mechanisms and other metals. This mechanism can broadly explain formation of the products and by-products of catalytic reduction reactions. It also explains how *trans*-fatty acids can be produced.

1 — Getting Ready for Reactions

Guide to Drawing Resonance Structures

Resonance Structures

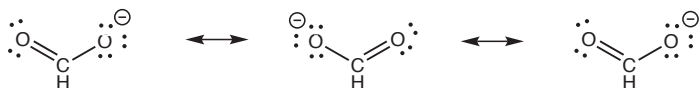
If you are unfamiliar with the use of the curved arrow, refer to the discussion in the *Notes* section. A good place to start pushing electrons is in drawing resonance structures. They have the elements of electron movement, but the problems will be more limited in scope.

Resonance Structures of Anions

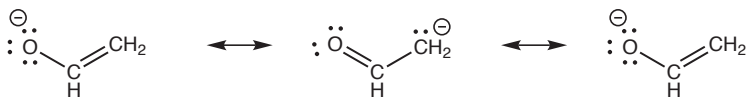
The principle for understanding resonance structures is to understand that electrons will operate by a push-pull mode or model. If there's a net negative charge, it will be the electrons of the atom with the negative charge that will push toward the pi bond. We will start our curved arrow with those electrons. Continue to move them toward any neighboring pi bonds (push) to create and break new bonds. You should note that two curved arrows are required to avoid structures with more than eight valence electrons.

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1.

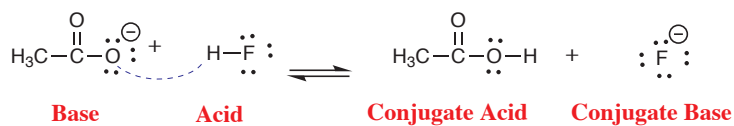


2.



2 -Acid-Base Chemistry

1. For this example, the acids and bases are labeled. HF is the strongest acid as it has the lower pK_a . Therefore, F^- , its conjugate base, is the weakest base.

**L/R** pK_a 3.2 pK_a 4.75

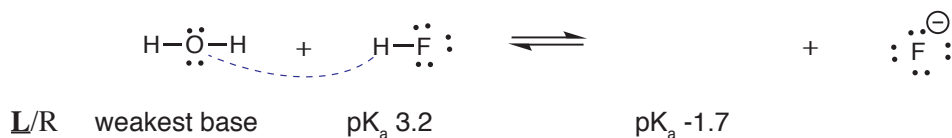
weakest base

Notice the curved arrows. They describe the reaction that is taking place. We could write the following sentences to describe the curved arrows.

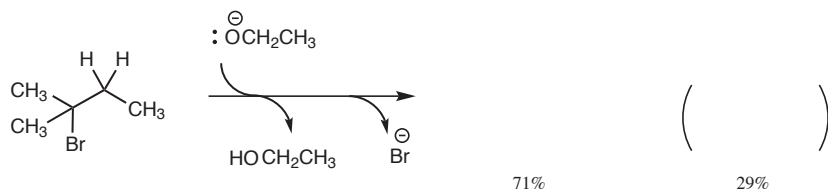
A bond is being made between the oxygen and hydrogen atom with the electrons from the oxygen atom.

A bond is being broken between the hydrogen and the fluorine atom with the electrons remaining attached to the fluorine atom.

3.



3. An E2 elimination reaction of 2-bromo-2-methylbutane to give 2-methyl-2-butene, a Zaitsev product.

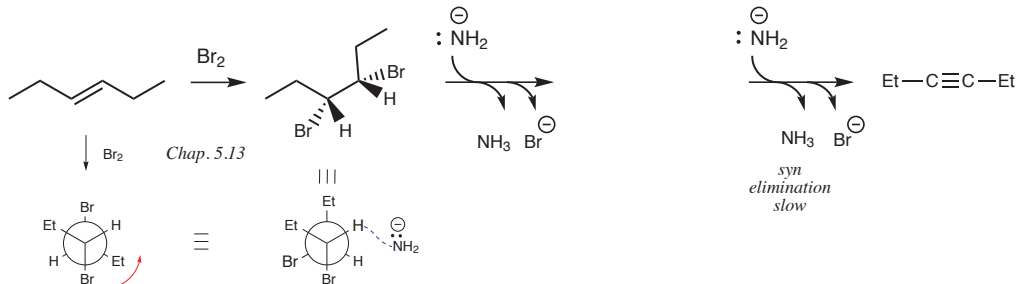


10. An E1cb elimination reaction of 3-chloro-3-methylcyclohexanone with *t*-butoxide to give 3-methyl-2-cyclohexenone. (See *Notes*.)



Acetylene Formation

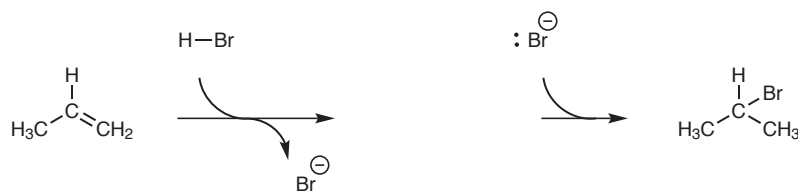
20. A synthesis of 3-hexyne from *trans*-3-hexene by bromination and two elimination reactions. (See *Notes*.)



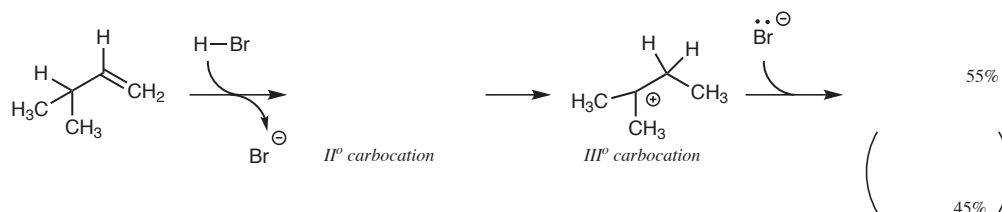
5 — Electrophilic Addition to Alkenes and Alkynes

Addition of HX and H₂O to Alkenes

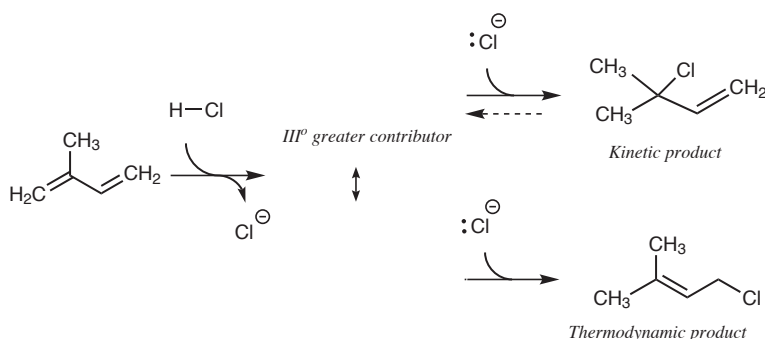
1. Addition of hydrogen bromide to propene to give 2-bromopropane. (See *Notes*.)



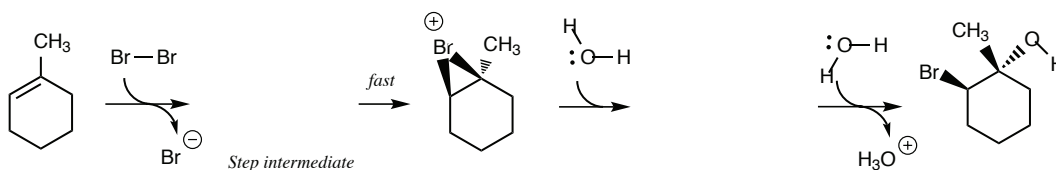
7. Addition of hydrogen bromide to 3-methyl-1-butene to give after rearrangement, 2-bromo-2-methylbutane. (See *Notes*.)



10. Addition of hydrogen chloride to 2-methyl-1,3-butadiene (isoprene) to give, 3-chloro-3-methyl-1-butene, the kinetic product, or 1-chloro-3-methyl-2-butene, the thermodynamic product. (See *Notes*.)



15. Bromination of methylcyclohexene to give (1*R*,2*R*)- and (1*S*,2*S*)-2-bromo-1-methylcyclohexanol. (See *Notes*.)



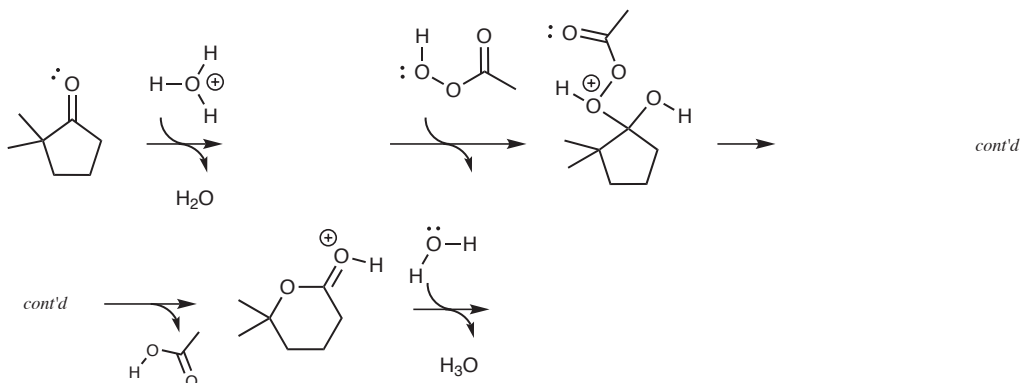
21. Addition of bromine to ethynylcyclopentane to give (*E*)-(1,2-dibromovinyl)cyclopentane and (1,1,2,2-tetrabromoethyl)cyclopentane. (See *Notes*.)



6 — Rearrangement Reactions

Baeyer-Villiger Oxidation

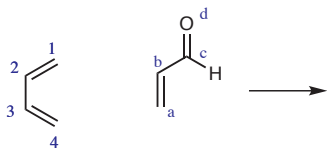
1. Acid catalyzed Baeyer-Villiger oxidation of 2,2-dimethylcyclopentanone with peracetic acid. (See *Notes*.)



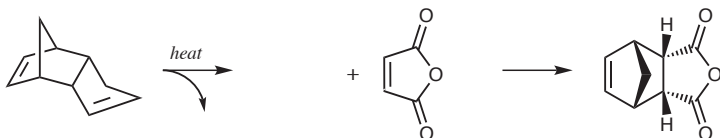
7 — Electrocyclic Reactions

Diels Alder Reactions

1. A Diels-Alder reaction between 1,3-butadiene and 2-propenal (acrolein).



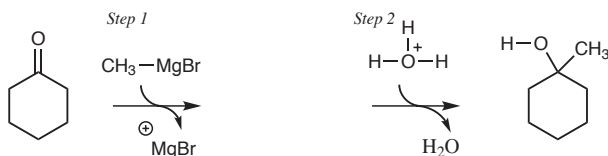
8. A reverse-forward Diels-Alder reaction between cyclopentadiene and maleic anhydride.



8 — Carbonyl Addition and Addition-Elimination Reactions

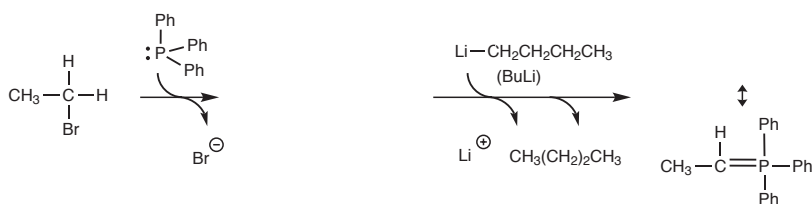
Grignard Addition to a Carbonyl Group

1. Addition of methyl magnesium bromide to cyclohexanone to give 1-methylcyclohexanol (for formation of Grignard reagents, see *Notes*).

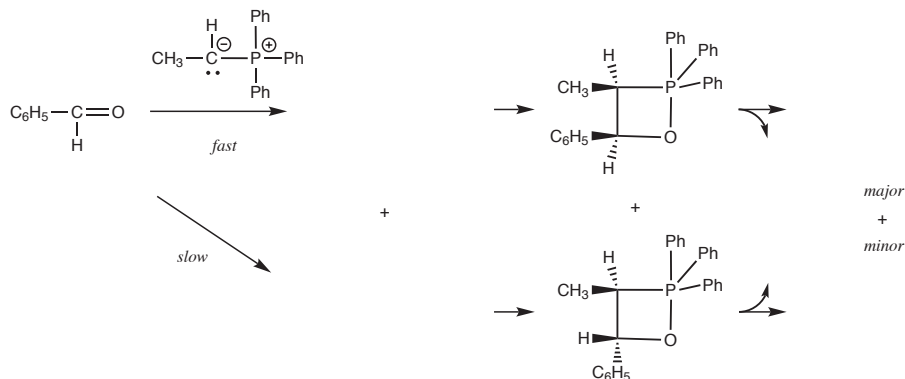


Wittig Reaction

5. Wittig reaction, Step 1, formation of Wittig reagent. (See *Notes*.)



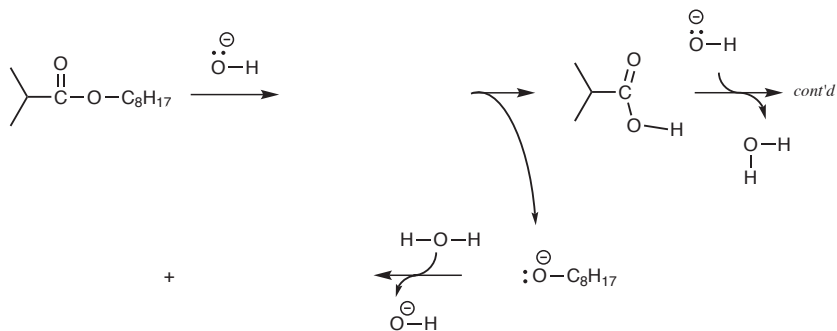
Step 2, reaction with benzaldehyde



10. Formation of the cyanohydrin (2-hydroxy-2-methylpropanenitrile) from acetone. (See *Notes*.)

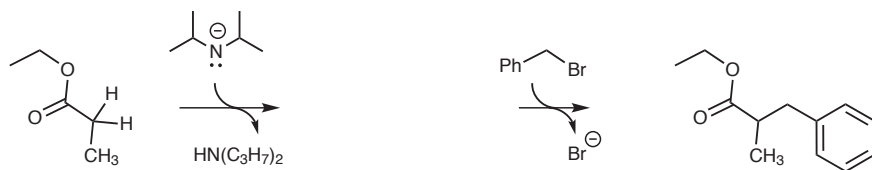


23. Base hydrolysis of octyl isobutyrate to give octanol and isobutyric acid. Step 1, treatment with base. (See *Notes*.)

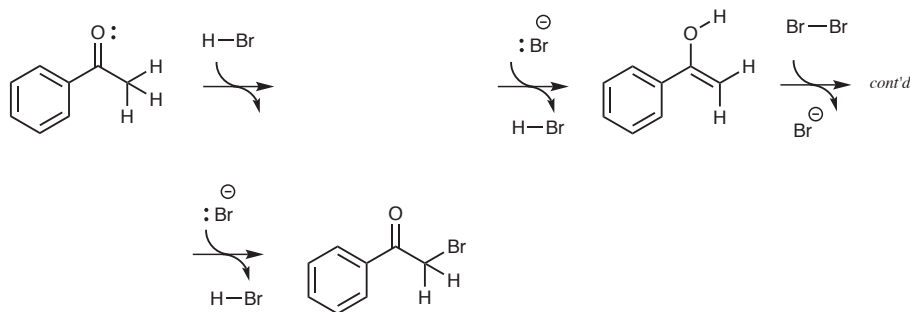


9 — Reactions of Enols and Enolates

9. Enolization and alkylation of ethyl propionate with benzyl bromide. (See *Notes*.)

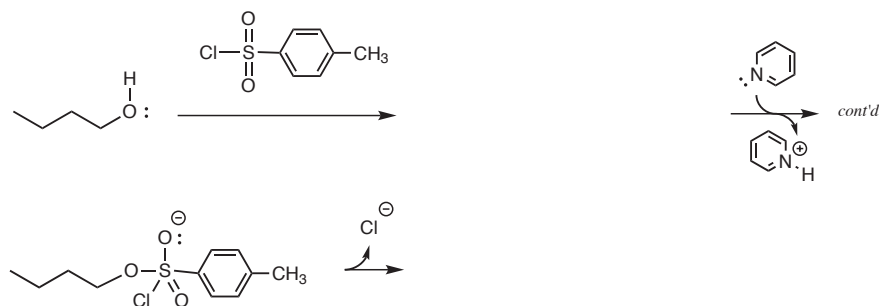


14. Acid catalyzed bromination of acetophenone to give α -bromoacetophenone. (See *Notes*.)

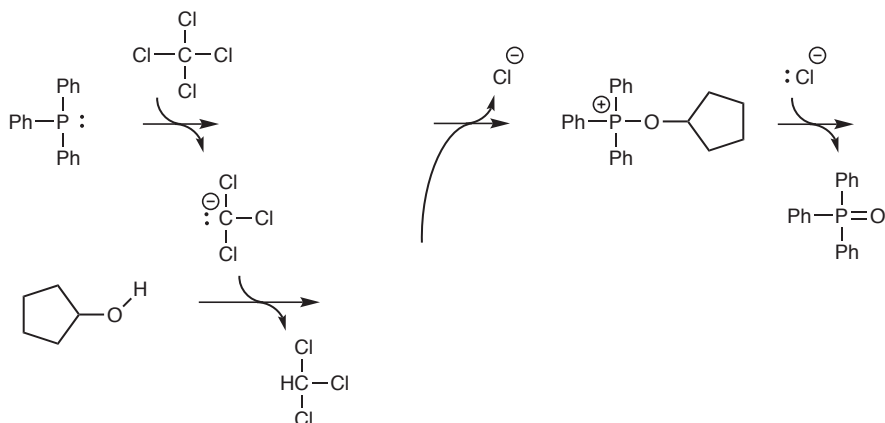


10 — Dehydration/Halogenation Agents

3. Reaction of 1-butanol with tosyl chloride and pyridine to give butyl tosylate. (See *Notes*.)

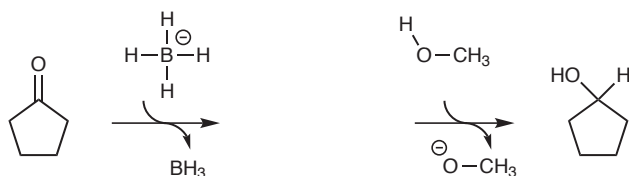


7. Reaction of triphenylphosphine, carbon tetrachloride and cyclopentanol to give chlorocyclopentane. (See *Notes*.)



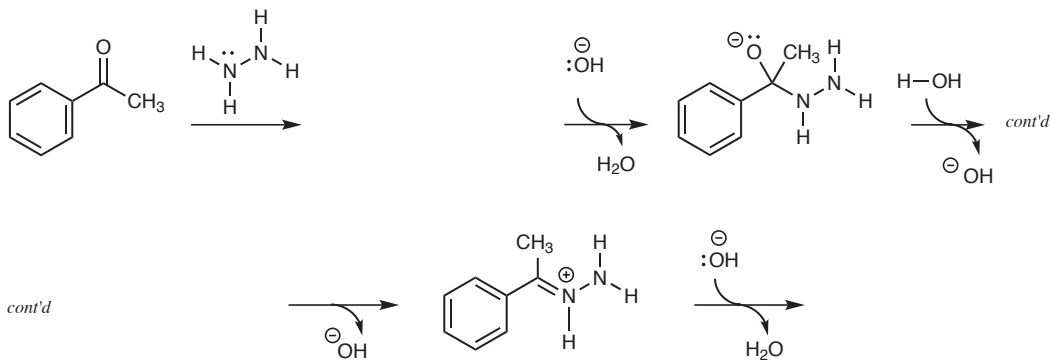
11 — Reduction Reactions

2. Sodium borohydride reduction of cyclopentanone to cyclopentanol.



Wolff Kischner Reduction

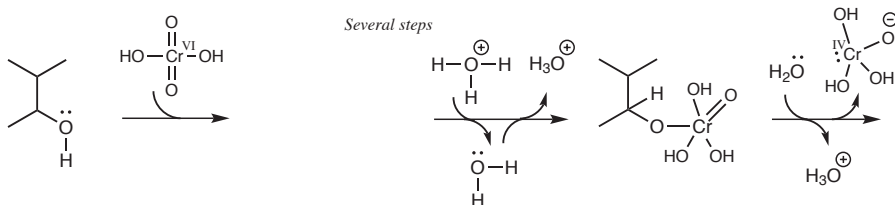
12. Reaction of the ketone with hydrazine under basic conditions to form the hydrazone.



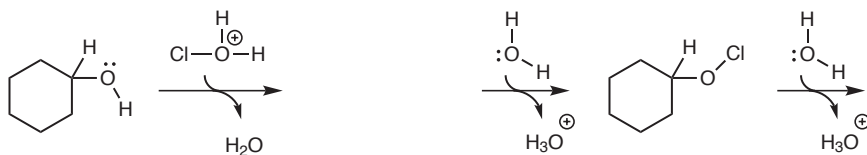
12 — Oxidation Reactions

Chromic Acid Oxidation

1. Chromic acid oxidation (Jones oxidation) of 3-methyl-2-butanol to 3-methyl-2-butanone. (See *Notes*.)



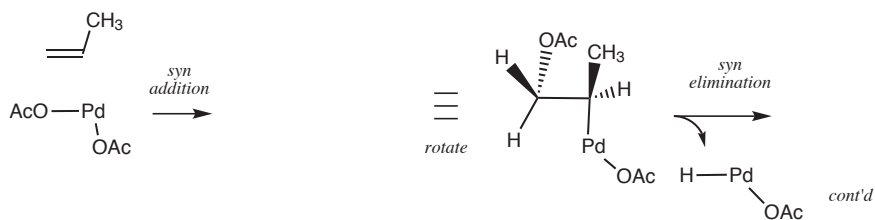
5. Oxidation of cyclohexanol to cyclohexanone with sodium hypochlorite (NaOCl, bleach).



13 — Organometallic Reactions

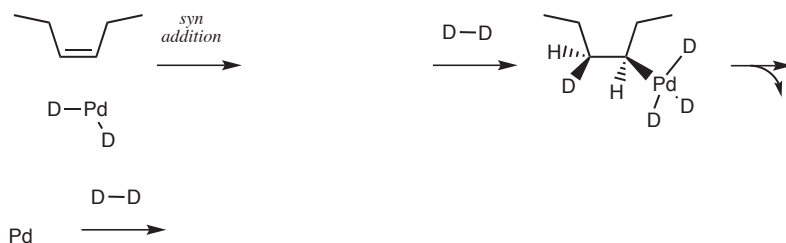
Acyclic Heck Reaction

1. Step 1, reduction of palladium (II) to zero valent palladium with propene. (See *Notes*.)



Catalytic Reduction of an Alkene (See *Notes*.)

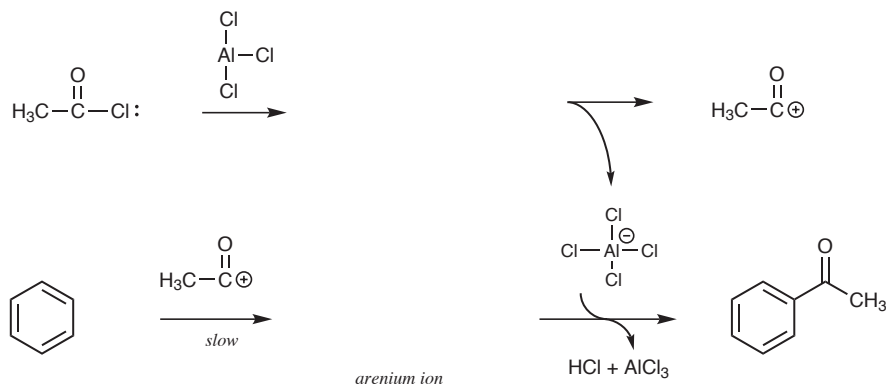
3. Catalytic hydrogenation of *cis*-3-hexene to hexane.



14 — Aromatic Substitution Reactions

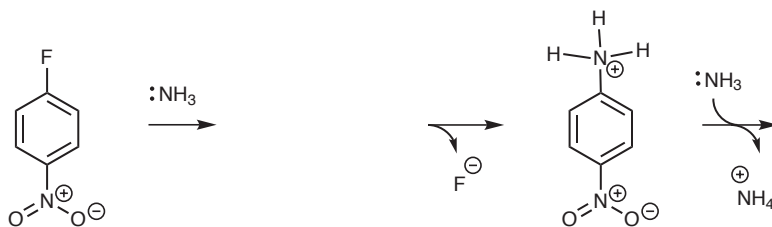
Electrophilic Aromatic Substitution of Benzene

1. Friedel Crafts acylation of benzene.

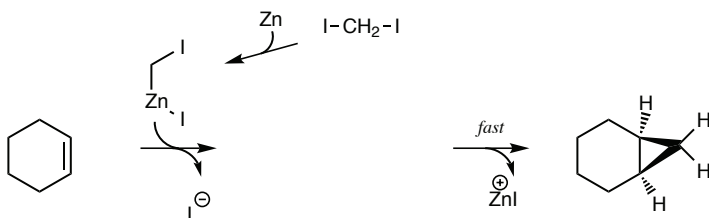


Nucleophilic Aromatic Substitution

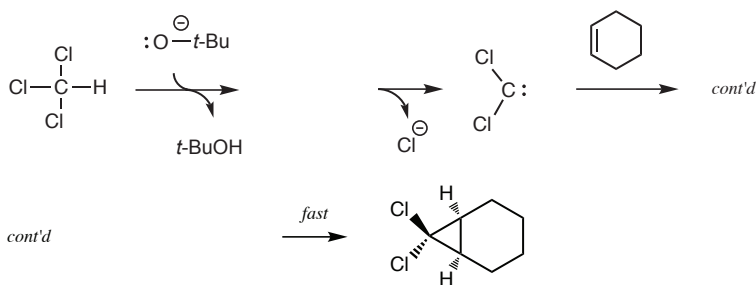
11. Nucleophilic aromatic substitution of 1-fluoro-4-nitrobenzene with ammonia to give 4-nitroaniline. (See *Notes*.)

**15 – Carbene and Nitrene Reactions****Carbene Reactions**

1. Simmons-Smith carbene addition to cyclohexene to give a bicyclo[4.1.0]heptane. (See *Notes*.)

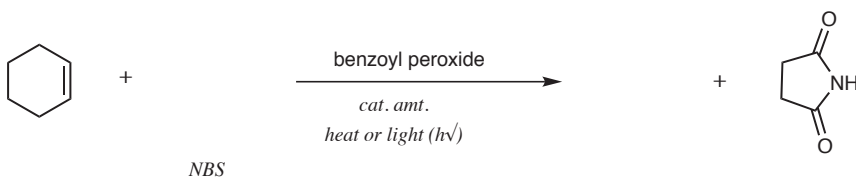


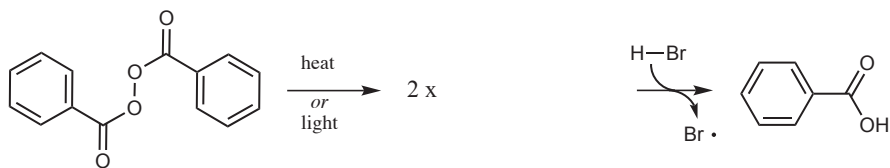
3. Dihalocarbene addition to cyclohexene to give 7,7-dichlorobicyclo[4.1.0]heptane.

**16 – Radical Reactions****Allylic Bromination with NBS**

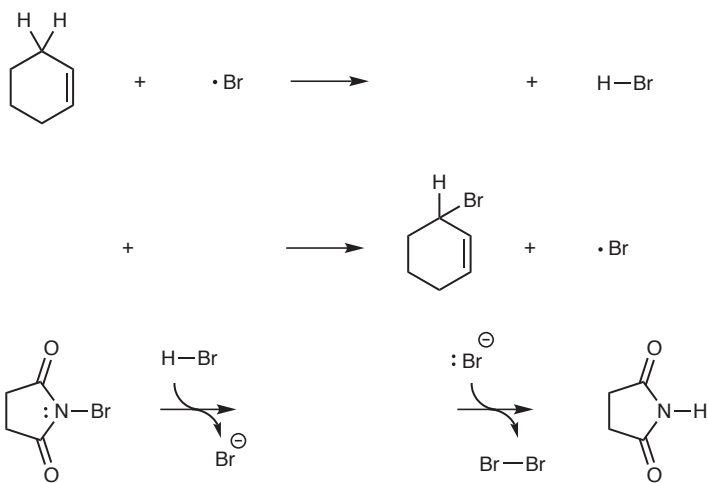
2. Free radical bromination of cyclohexene with *N*-bromosuccinimide, an allylic bromination.

Overall reaction



2. Free radical bromination of cyclohexene with *N*-bromosuccinimide, an allylic bromination -- continued.Initiation (See *Notes*.)

Propagation



Termination



1 — Getting Ready for Reactions

Guide to Drawing Resonance Structures

Resonance Structures

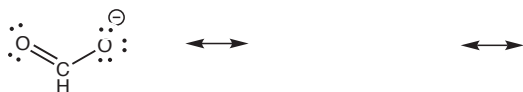
If you are unfamiliar with the use of the curved arrow, refer to the discussion in the *Notes* section. A good place to start pushing electrons is in drawing resonance structures. They have the elements of electron movement, but the problems will be more limited in scope.

Resonance Structures of Anions

The principle for understanding resonance structures is to understand that electrons will operate by a push-pull mode or model. If there's a net negative charge, it will be the electrons of the atom with the negative charge that will push toward the pi bond. We will start our curved arrow with those electrons. Continue to move them toward any neighboring pi bonds (push) to create and break new bonds. You should note that two curved arrows are required to avoid structures with more than eight valence electrons.

For the following examples, add curved arrows, where needed, to show how the electrons move to form the next structure. For 1-6, the first and last structures are the same. In that case, you are converting it back to the starting structure.

1.

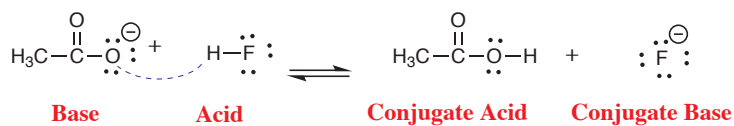


2.



2 -Acid-Base Chemistry

1. For this example, the acids and bases are labeled. HF is the strongest acid as it has the lower pK_a . Therefore, F^- , its conjugate base, is the weakest base.

**L/R** pK_a 3.2 pK_a 4.75

weakest base

Notice the curved arrows. They describe the reaction that is taking place. We could write the following sentences to describe the curved arrows.

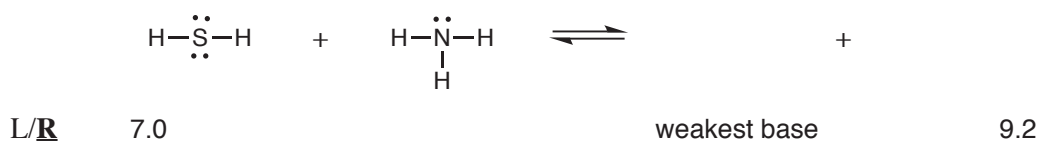
A bond is being made between the oxygen and hydrogen atom with the electrons from the oxygen atom.

A bond is being broken between the hydrogen and the fluorine atom with the electrons remaining attached to the fluorine atom.

3.

**L/R** weakest base pK_a 3.2 pK_a -1.7

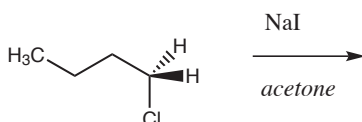
4.



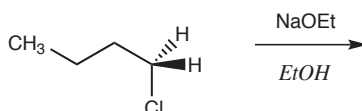
3 - Substitution Reactions

S_N2 Substitution Reactions

1. An S_N2 reaction of 1-chlorobutane with sodium iodide to give 1-iodobutane. (See *Notes*.)



2. An S_N2 reaction of 1-chlorobutane with ethoxide to give 1-ethoxybutane (butyl ethyl ether). (See *Notes*.)



S_N1 Substitution Reactions

20. An S_N1 solvolysis reaction of *t*-butyl iodide to give *t*-butyl alcohol. (See *Notes*.)



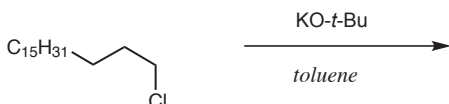
21. An S_N1 solvolysis reaction of (*R*)-(1-chloroethyl)benzene to give *rac*-1-phenylethanol.



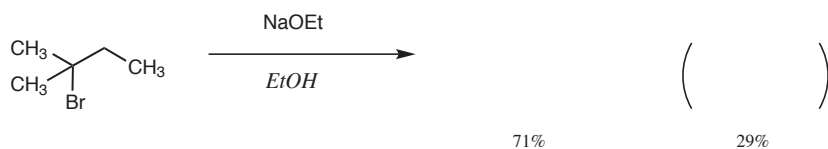
4 – Elimination Reactions

Alkene Formation

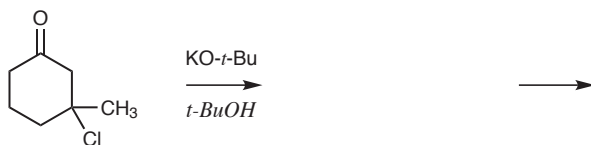
1. An E2 elimination reaction of hydrogen chloride from 1-chlorooctadecane with potassium *t*-butoxide to give 1-octadecene. (See *Notes*.)



3. An E2 elimination reaction of 2-bromo-2-methylbutane to give 2-methyl-2-butene, a Zaitsev product.

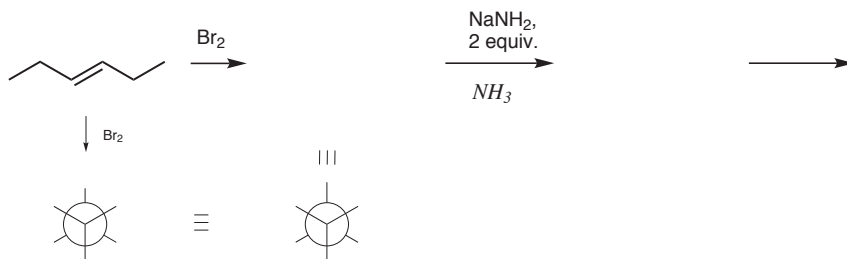


10. An E1cb elimination reaction of 3-chloro-3-methylcyclohexanone with *t*-butoxide to give 3-methyl-2-cyclohexenone. (See *Notes*.)



Acetylene Formation

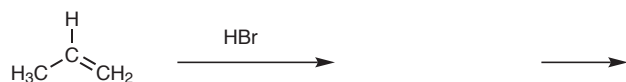
20. A synthesis of 3-hexyne from *trans*-3-hexene by bromination and two elimination reactions. (See *Notes*.)



5 — Electrophilic Addition to Alkenes and Alkynes

Addition of HX and H₂O to Alkenes

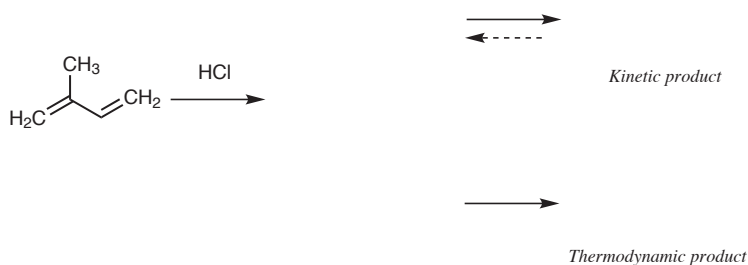
1. Addition of hydrogen bromide to propene to give 2-bromopropane. (See *Notes*.)



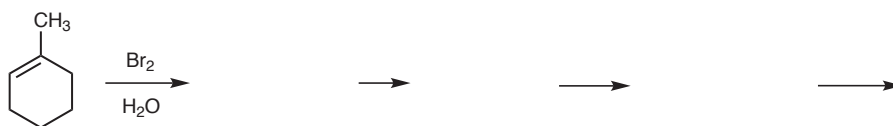
7. Addition of hydrogen bromide to 3-methyl-1-butene to give after rearrangement, 2-bromo-2-methylbutane. (See *Notes*.)



10. Addition of hydrogen chloride to 2-methyl-1,3-butadiene (isoprene) to give, 3-chloro-3-methyl-1-butene, the kinetic product, or 1-chloro-3-methyl-2-butene, the thermodynamic product. (See *Notes*.)



15. Bromination of methylcyclohexene to give (1*R*,2*R*)- and (1*S*,2*S*)-2-bromo-1-methylcyclohexanol. (See *Notes*.)



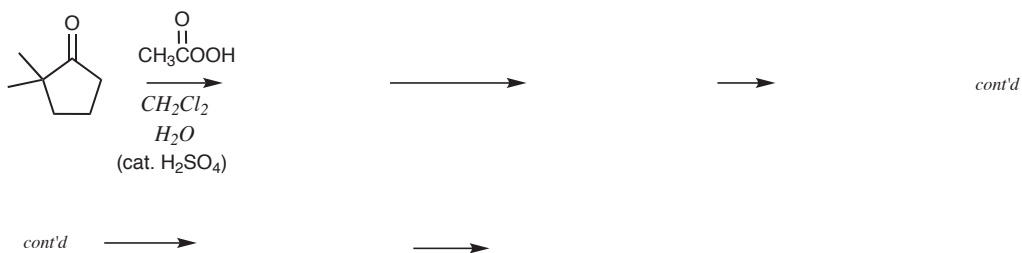
21. Addition of bromine to ethynylcyclopentane to give (*E*)-(1,2-dibromovinyl)cyclopentane and (1,1,2,2-tetrabromoethyl)cyclopentane. (See *Notes*.)



6 — Rearrangement Reactions

Baeyer-Villiger Oxidation

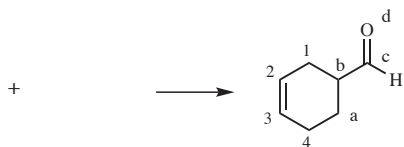
1. Acid catalyzed Baeyer-Villiger oxidation of 2,2-dimethylcyclopentanone with peracetic acid. (See *Notes*.)



7 — Electrocyclic Reactions

Diels Alder Reactions

1. A Diels-Alder reaction between 1,3-butadiene and 2-propenal (acrolein).



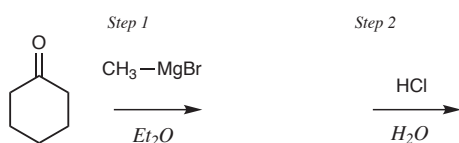
8. A reverse-forward Diels-Alder reaction between cyclopentadiene and maleic anhydride.



8 — Carbonyl Addition and Addition-Elimination Reactions

Grignard Addition to a Carbonyl Group

1. Addition of methyl magnesium bromide to cyclohexanone to give 1-methylcyclohexanol (for formation of Grignard reagents, see *Notes*).

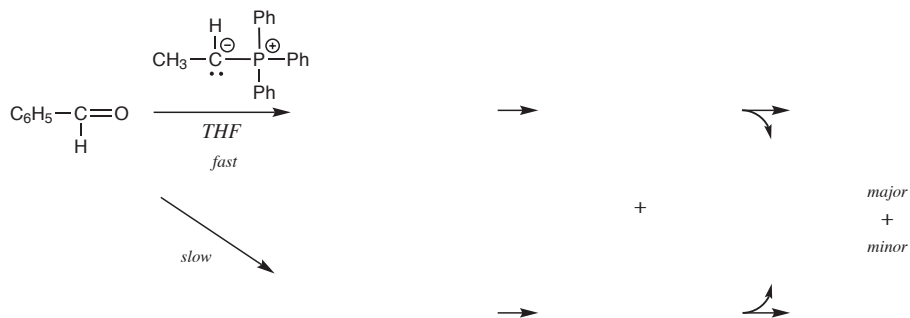


Wittig Reaction

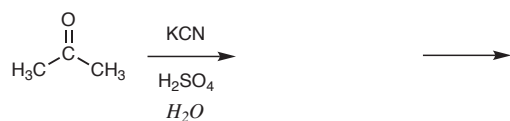
5. Wittig reaction, Step 1, formation of Wittig reagent. (See *Notes*.)



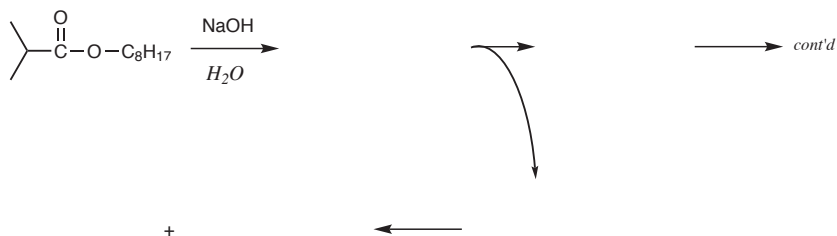
Step 2, reaction with benzaldehyde



10. Formation of the cyanohydrin (2-hydroxy-2-methylpropanenitrile) from acetone. (See *Notes*.)

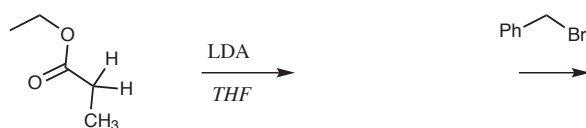


23. Base hydrolysis of octyl isobutyrate to give octanol and isobutyric acid. Step 1, treatment with base. (See *Notes*.)

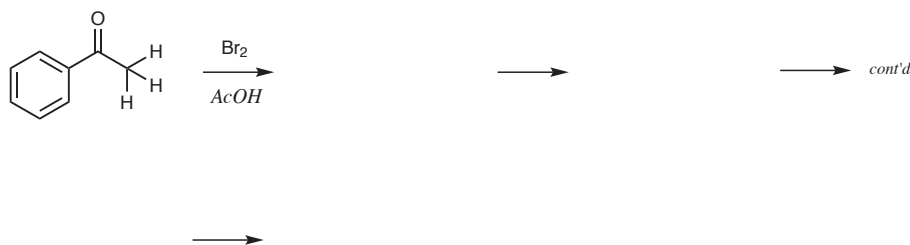


9 — Reactions of Enols and Enolates

9. Enolization and alkylation of ethyl propionate with benzyl bromide. (See *Notes*.)

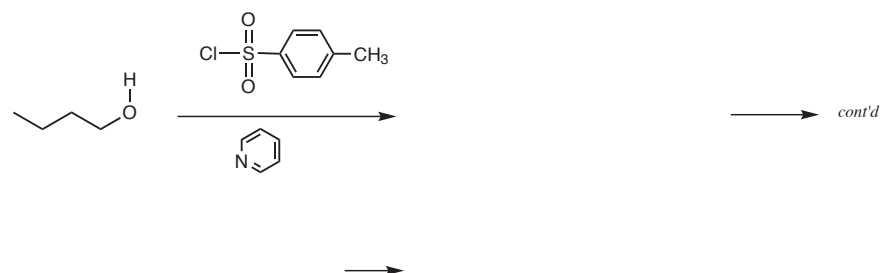


14. Acid catalyzed bromination of acetophenone to give α -bromoacetophenone. (See *Notes*.)

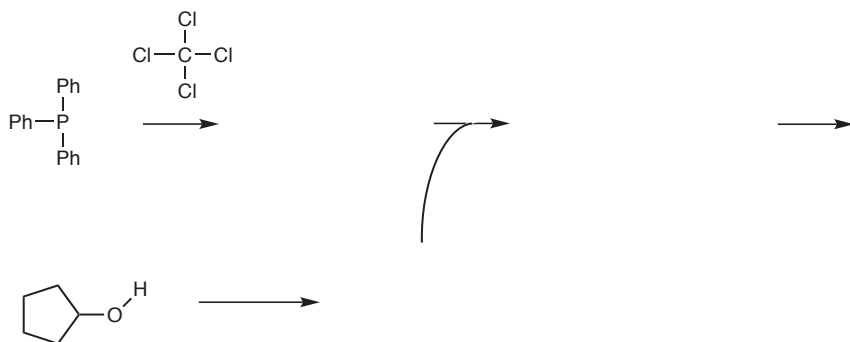


10 — Dehydration/Halogenation Agents

3. Reaction of 1-butanol with tosyl chloride and pyridine to give butyl tosylate. (See *Notes*.)

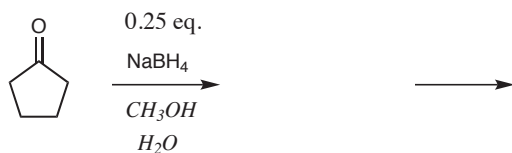


7. Reaction of triphenylphosphine, carbon tetrachloride and cyclopentanol to give chlorocyclopentane. (See *Notes*.)



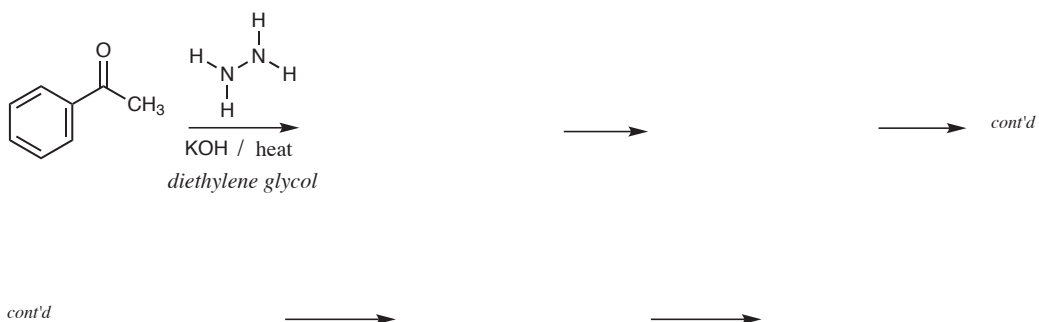
11 — Reduction Reactions

2. Sodium borohydride reduction of cyclopentanone to cyclopentanol.



Wolff Kischner Reduction

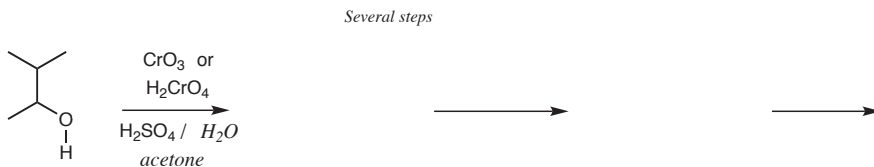
12. Reaction of the ketone with hydrazine under basic conditions to form the hydrazone.



12 — Oxidation Reactions

Chromic Acid Oxidation

1. Chromic acid oxidation (Jones oxidation) of 3-methyl-2-butanol to 3-methyl-2-butanone. (See *Notes*.)



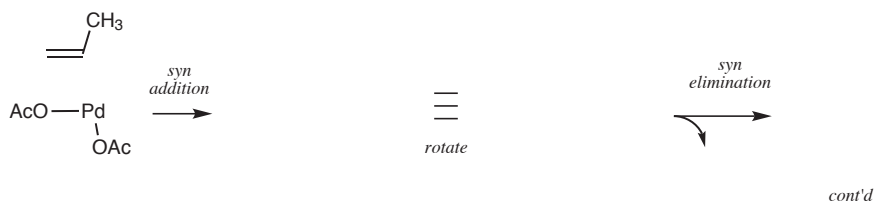
5. Oxidation of cyclohexanol to cyclohexanone with sodium hypochlorite (NaOCl, bleach).



13 — Organometallic Reactions

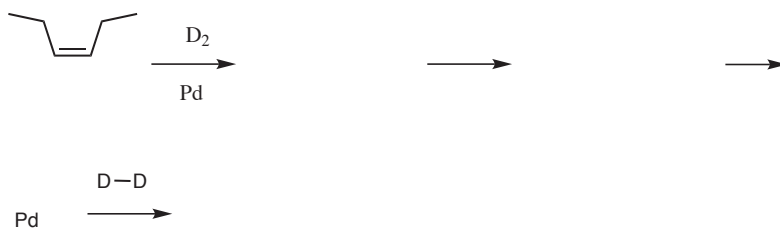
Acyclic Heck Reaction

1. Step 1, reduction of palladium (II) to zero valent palladium with propene. (See *Notes*.)



Catalytic Reduction of an Alkene (See *Notes*.)

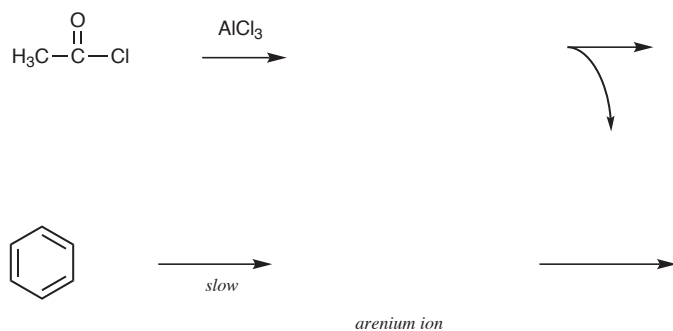
3. Catalytic hydrogenation of *cis*-3-hexene to hexane.



14 — Aromatic Substitution Reactions

Electrophilic Aromatic Substitution of Benzene

1. Friedel Crafts acylation of benzene.

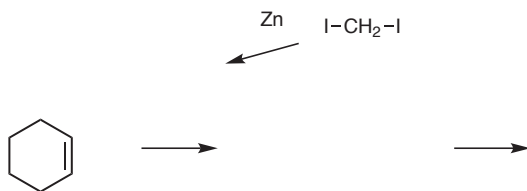


Nucleophilic Aromatic Substitution

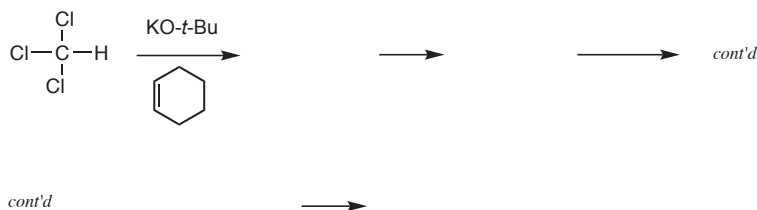
11. Nucleophilic aromatic substitution of 1-fluoro-4-nitrobenzene with ammonia to give 4-nitroaniline. (See *Notes*.)

**15 – Carbene and Nitrene Reactions****Carbene Reactions**

1. Simmons-Smith carbene addition to cyclohexene to give a bicyclo[4.1.0]heptane. (See *Notes*.)

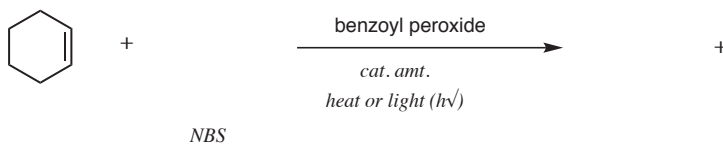


3. Dihalocarbene addition to cyclohexene to give 7,7-dichlorobicyclo[4.1.0]heptane.

**16 – Radical Reactions****Allylic Bromination with NBS**

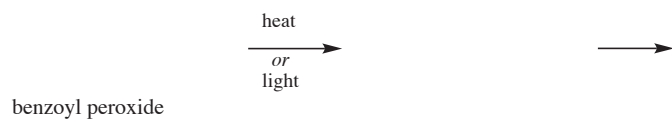
2. Free radical bromination of cyclohexene with *N*-bromosuccinimide, an allylic bromination.

Overall reaction



2. Free radical bromination of cyclohexene with *N*-bromosuccinimide, an allylic bromination -- continued.

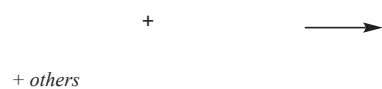
Initiation (See *Notes*.)



Propagation



Termination



1 — Getting Ready for Reactions

Guide to Drawing Resonance Structures

Resonance Structures

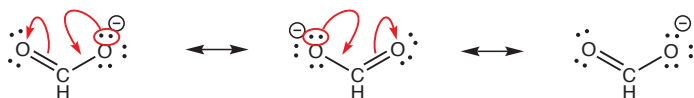
If you are unfamiliar with the use of the curved arrow, refer to the discussion in the *Notes* section. A good place to start pushing electrons is in drawing resonance structures. They have the elements of electron movement, but the problems will be more limited in scope.

Resonance Structures of Anions

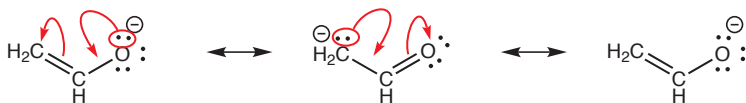
The principle for understanding resonance structures is to understand that electrons will operate by a push-pull mode or model. If there's a net negative charge, it will be the electrons of the atom with the negative charge that will push toward the pi bond. We will start our curved arrow with those electrons. Continue to move them toward any neighboring pi bonds (push) to create and break new bonds. You should note that two curved arrows are required to avoid structures with more than eight valence electrons.

For the following examples, add curved arrows, where needed, to show how the electrons move to form the next structure. For 1-6, the first and last structures are the same. In that case, you are converting it back to the starting structure.

1.

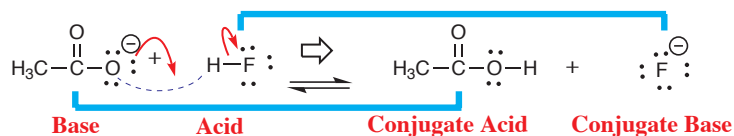


2.



2 -Acid-Base Chemistry

1. For this example, the acids and bases are labeled. HF is the strongest acid as it has the lower pK_a . Therefore, F^- , its conjugate base, is the weakest base.



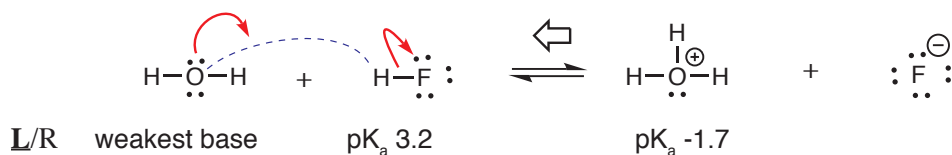
L/R pK_a 3.2 pK_a 4.75 weakest base

Notice the curved arrows. They describe the reaction that is taking place. We could write the following sentences to describe the curved arrows.

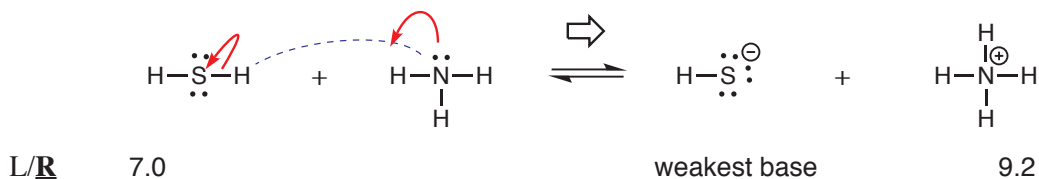
A bond is being made between the oxygen and hydrogen atom with the electrons from the oxygen atom.

A bond is being broken between the hydrogen and the fluorine atom with the electrons remaining attached to the fluorine atom.

3.



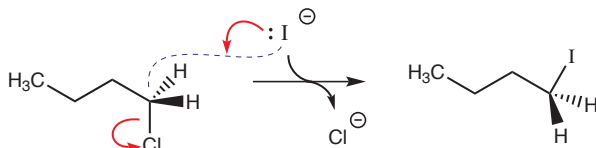
4.



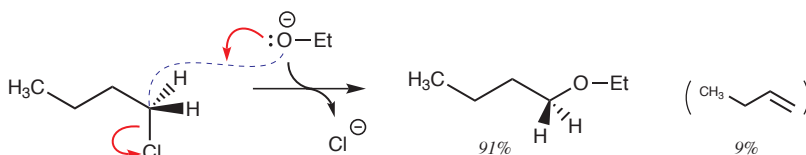
3 - Substitution Reactions

$\text{S}_{\text{N}}2$ Substitution Reactions

1. An $\text{S}_{\text{N}}2$ reaction of 1-chlorobutane with sodium iodide to give 1-iodobutane. (See *Notes*.)

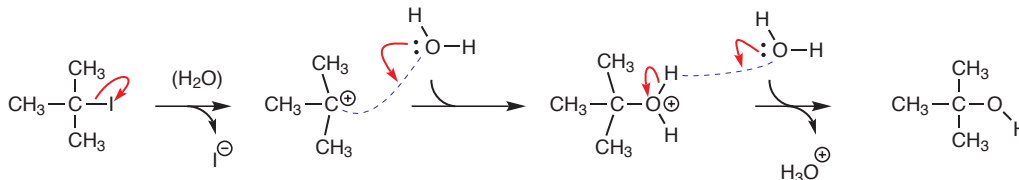


2. An $\text{S}_{\text{N}}2$ reaction of 1-chlorobutane with ethoxide to give 1-ethoxybutane (butyl ethyl ether). (See *Notes*.)

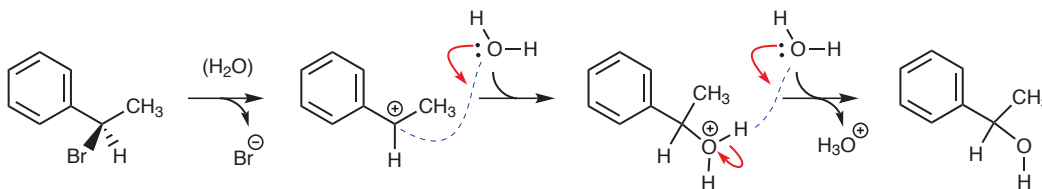


$\text{S}_{\text{N}}1$ Substitution Reactions

20. An $\text{S}_{\text{N}}1$ solvolysis reaction of *t*-butyl iodide to give *t*-butyl alcohol. (See *Notes*.)



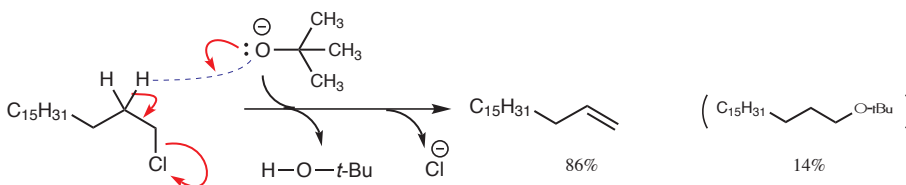
21. An $\text{S}_{\text{N}}1$ solvolysis reaction of (*R*)-(1-chloroethyl)benzene to give *rac*-1-phenylethanol.



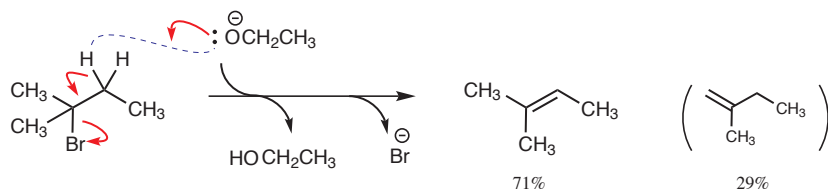
4 — Elimination Reactions

Alkene Formation

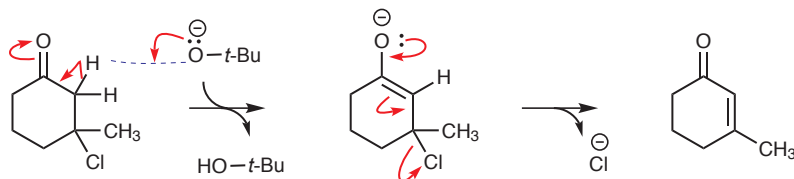
1. An $\text{E}2$ elimination reaction of hydrogen chloride from 1-chlorooctadecane with potassium *t*-butoxide to give 1-octadecene. (See *Notes*.)



3. An E2 elimination reaction of 2-bromo-2-methylbutane to give 2-methyl-2-butene, a Zaitsev product.

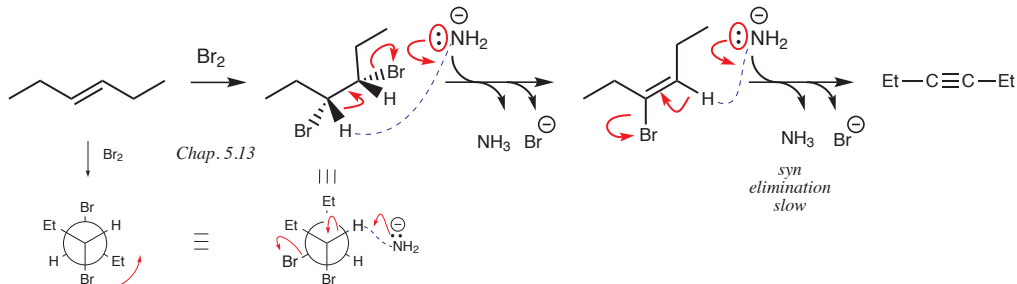


10. An E1cb elimination reaction of 3-chloro-3-methylcyclohexanone with *t*-butoxide to give 3-methyl-2-cyclohexenone. (See Notes.)



Acetylene Formation

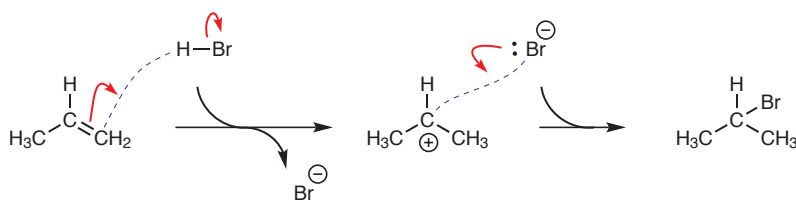
20. A synthesis of 3-hexyne from *trans*-3-hexene by bromination and two elimination reactions. (See Notes.)



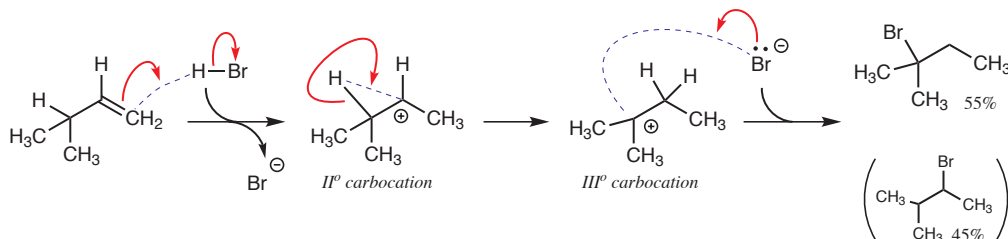
5 — Electrophilic Addition to Alkenes and Alkynes

Addition of HX and H_2O to Alkenes

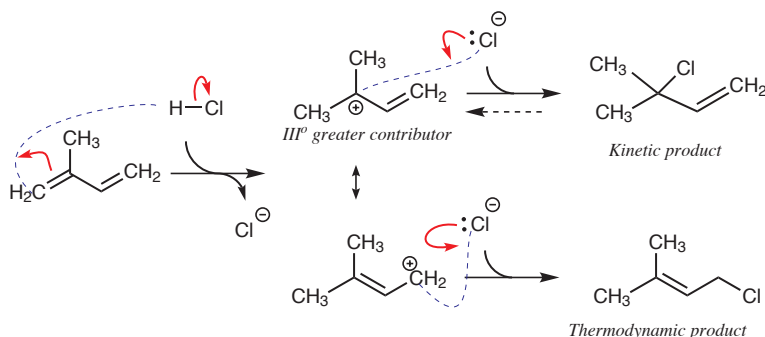
1. Addition of hydrogen bromide to propene to give 2-bromopropane. (See Notes.)



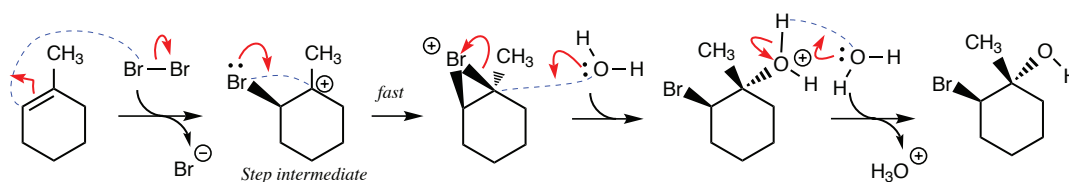
7. Addition of hydrogen bromide to 3-methyl-1-butene to give after rearrangement, 2-bromo-2-methylbutane. (See Notes.)



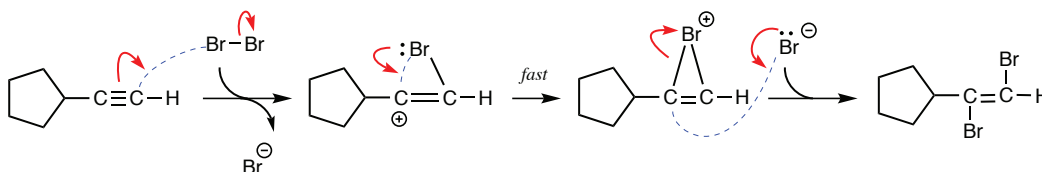
10. Addition of hydrogen chloride to 2-methyl-1,3-butadiene (isoprene) to give, 3-chloro-3-methyl-1-butene, the kinetic product, or 1-chloro-3-methyl-2-butene, the thermodynamic product. (See *Notes*.)



15. Bromination of methylcyclohexene to give (1*R*,2*R*)- and (1*S*,2*S*)-2-bromo-1-methylcyclohexanol. (See *Notes*.)



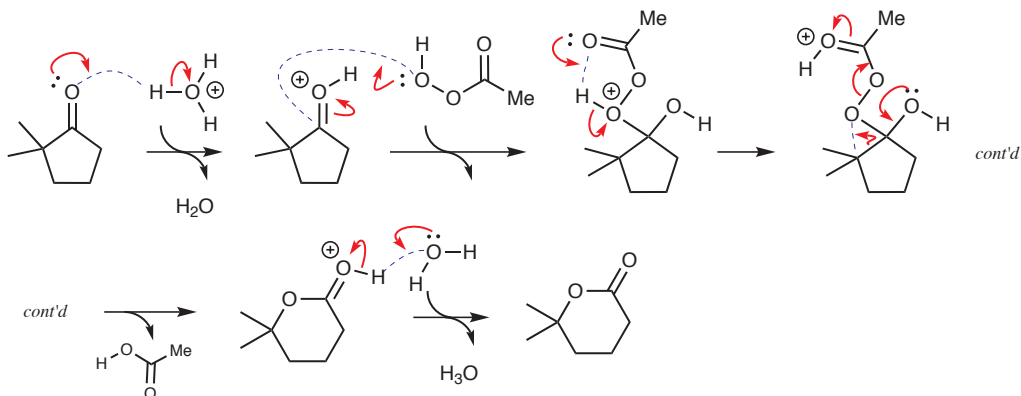
21. Addition of bromine to ethynylcyclopentane to give (*E*)-(1,2-dibromovinyl)cyclopentane and (1,1,2,2-tetrabromoethyl)cyclopentane. (See *Notes*.)



6 — Rearrangement Reactions

Baeyer-Villiger Oxidation

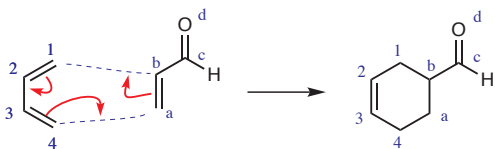
1. Acid catalyzed Baeyer-Villiger oxidation of 2,2-dimethylcyclopentanone with peracetic acid. (See *Notes*.)



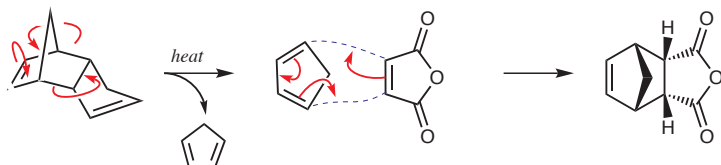
7 – Electrocyclic Reactions

Diels Alder Reactions

1. A Diels-Alder reaction between 1,3-butadiene and 2-propenal (acrolein).



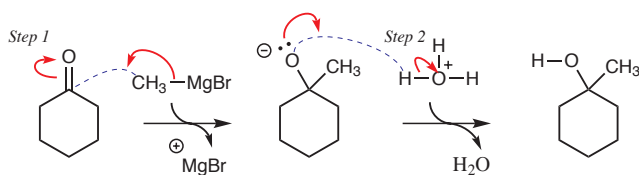
8. A reverse-forward Diels-Alder reaction between cyclopentadiene and maleic anhydride.



8 – Carbonyl Addition and Addition-Elimination Reactions

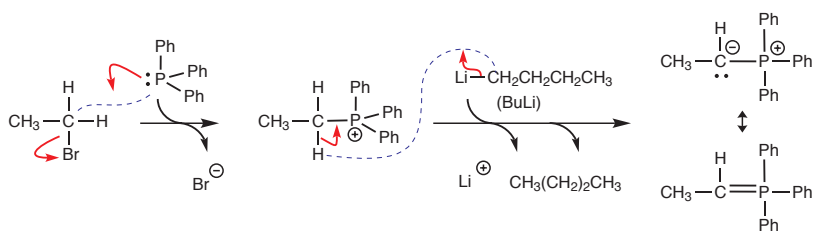
Grignard Addition to a Carbonyl Group

1. Addition of methyl magnesium bromide to cyclohexanone to give 1-methylcyclohexanol (for formation of Grignard reagents, see *Notes*).

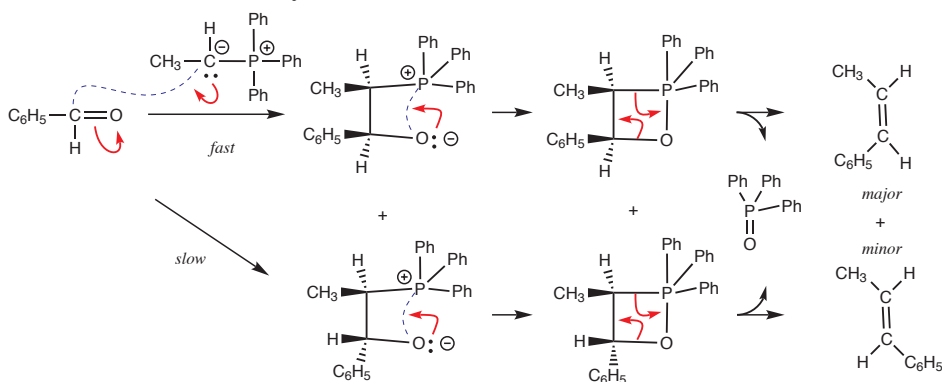


Wittig Reaction

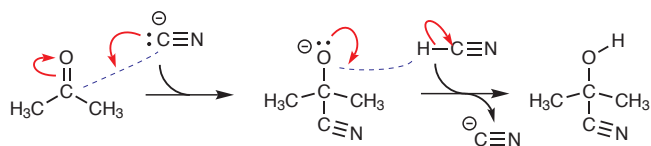
5. Wittig reaction, Step 1, formation of Wittig reagent. (See *Notes*.)



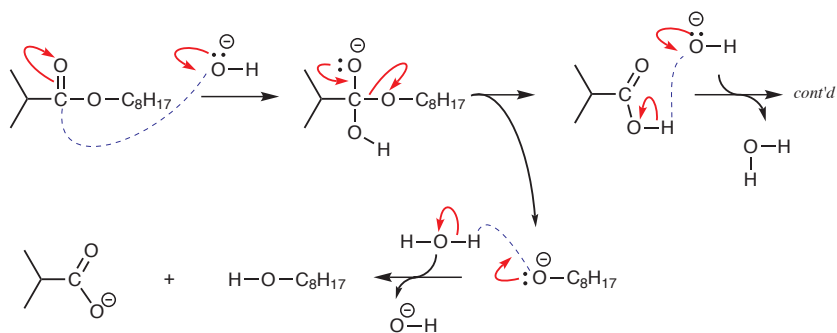
Step 2, reaction with benzaldehyde



10. Formation of the cyanohydrin (2-hydroxy-2-methylpropanenitrile) from acetone. (See *Notes*.)

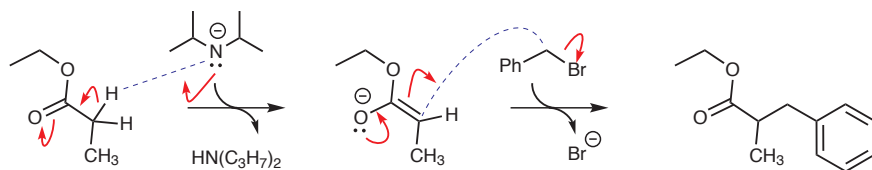


23. Base hydrolysis of octyl isobutyrate to give octanol and isobutyric acid. Step 1, treatment with base. (See *Notes*.)

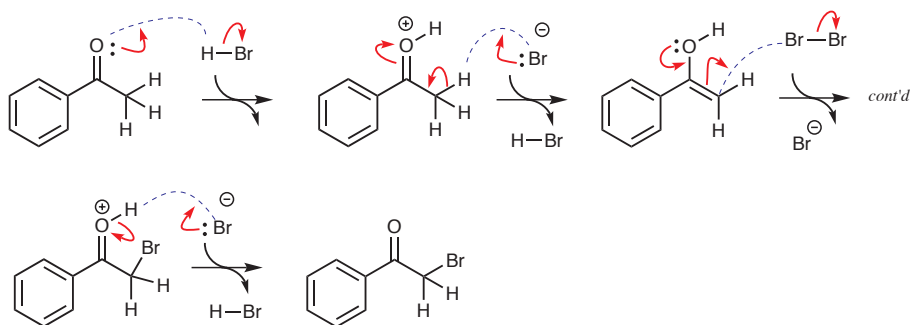


9 — Reactions of Enols and Enolates

9. Enolization and alkylation of ethyl propionate with benzyl bromide. (See *Notes*.)

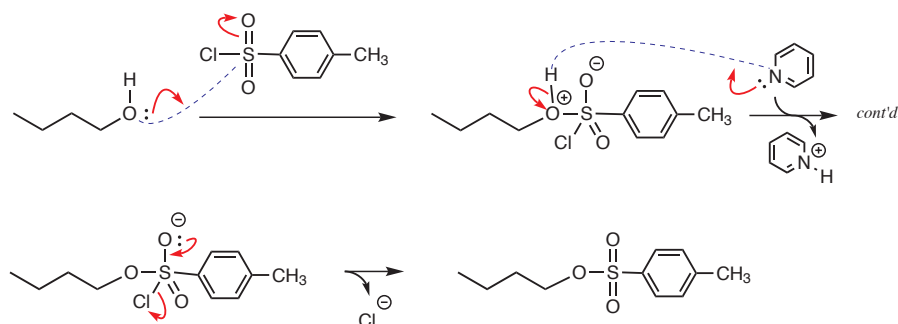


14. Acid catalyzed bromination of acetophenone to give α -bromoacetophenone. (See *Notes*.)

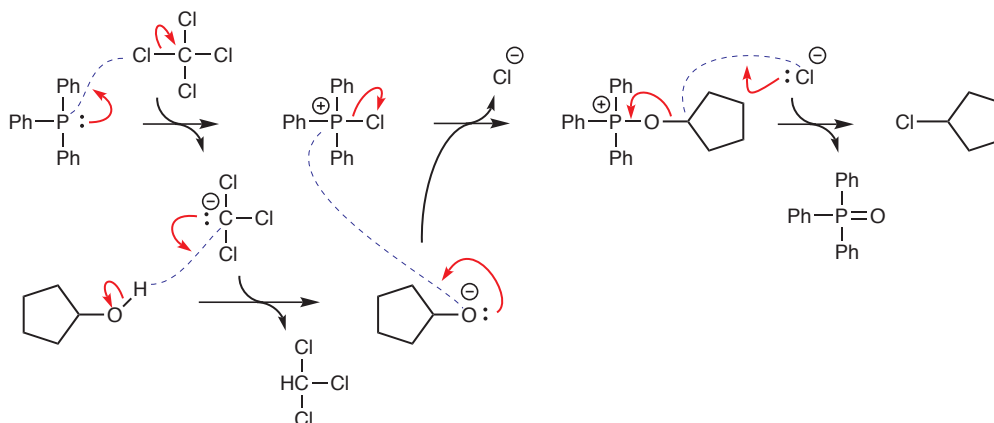


10 — Dehydration/Halogenation Agents

3. Reaction of 1-butanol with tosyl chloride and pyridine to give butyl tosylate. (See *Notes*.)

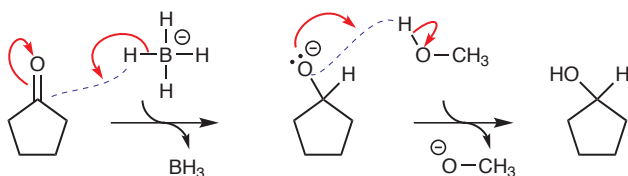


7. Reaction of triphenylphosphine, carbon tetrachloride and cyclopentanol to give chlorocyclopentane. (See *Notes*.)



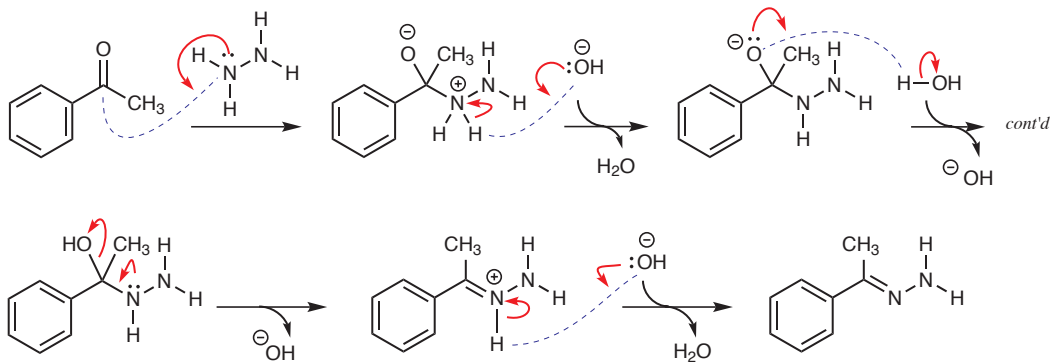
11 – Reduction Reactions

2. Sodium borohydride reduction of cyclopentanone to cyclopentanol.



Wolff Kischner Reduction

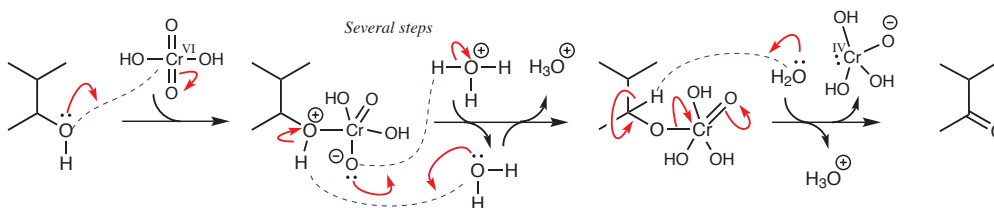
12. Reaction of the ketone with hydrazine under basic conditions to form the hydrazone.



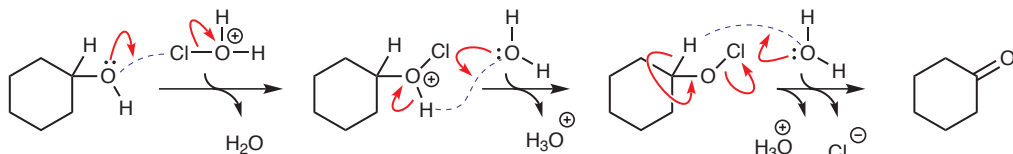
12 – Oxidation Reactions

Chromic Acid Oxidation

1. Chromic acid oxidation (Jones oxidation) of 3-methyl-2-butanol to 3-methyl-2-butanone. (See *Notes*.)



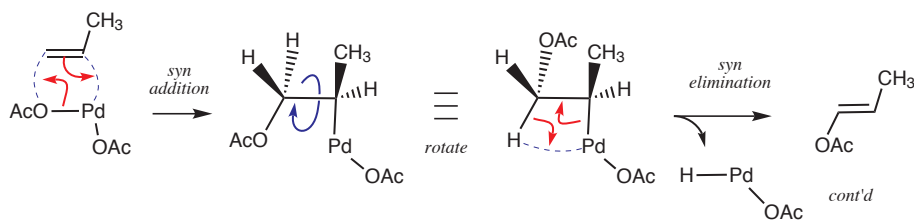
5. Oxidation of cyclohexanol to cyclohexanone with sodium hypochlorite (NaOCl, bleach).



13 — Organometallic Reactions

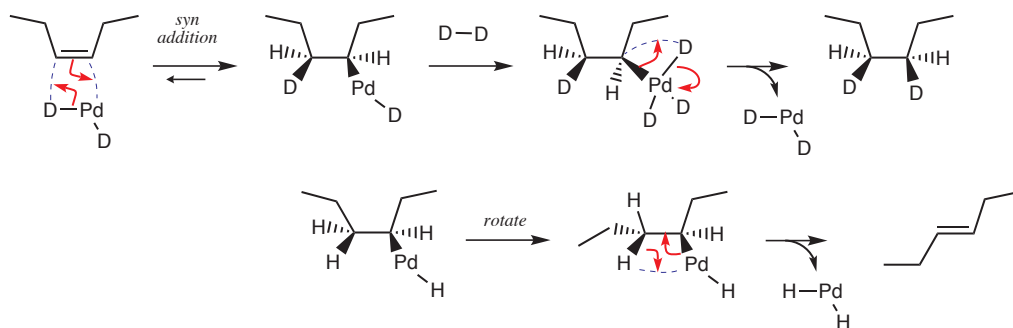
Acyclic Heck Reaction

1. Step 1, reduction of palladium (II) to zero valent palladium with propene. (See *Notes*.)



Catalytic Reduction of an Alkene (See *Notes*.)

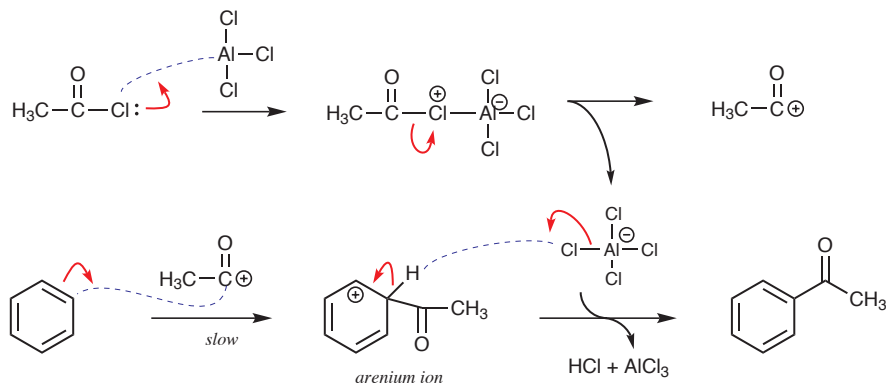
3. Catalytic hydrogenation of *cis*-3-hexene to hexane.



14 — Aromatic Substitution Reactions

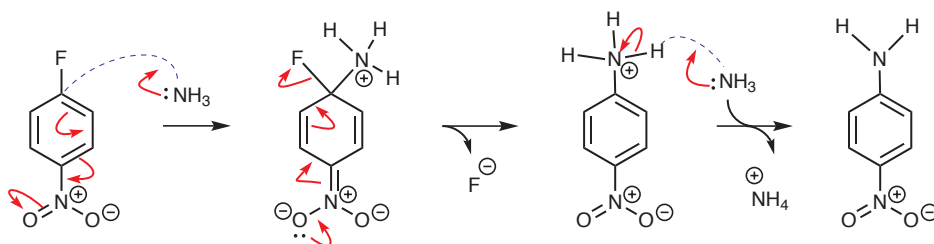
Electrophilic Aromatic Substitution of Benzene

1. Friedel Crafts acylation of benzene.

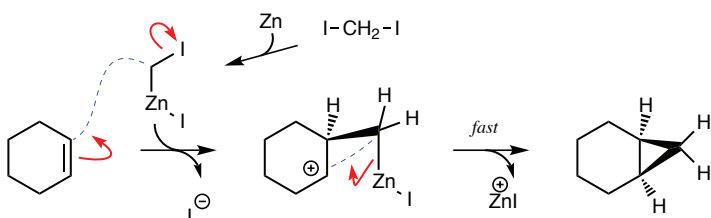


Nucleophilic Aromatic Substitution

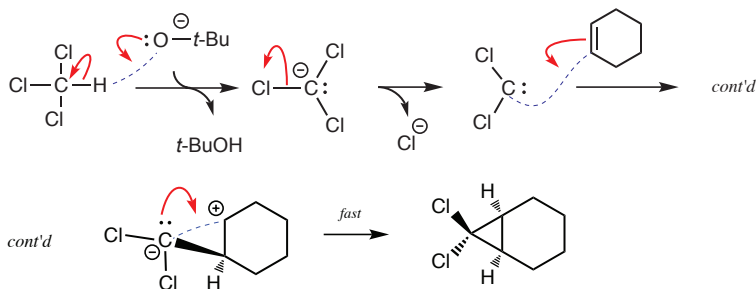
11. Nucleophilic aromatic substitution of 1-fluoro-4-nitrobenzene with ammonia to give 4-nitroaniline. (See *Notes*.)

**15 — Carbene and Nitrene Reactions****Carbene Reactions**

1. Simmons-Smith carbene addition to cyclohexene to give a bicyclo[4.1.0]heptane. (See *Notes*.)

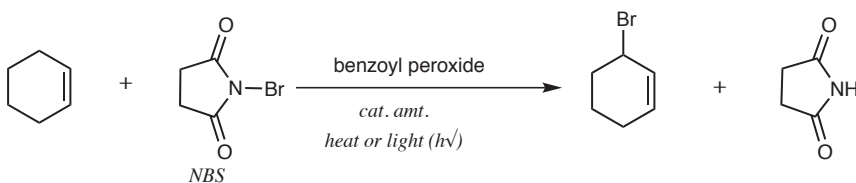


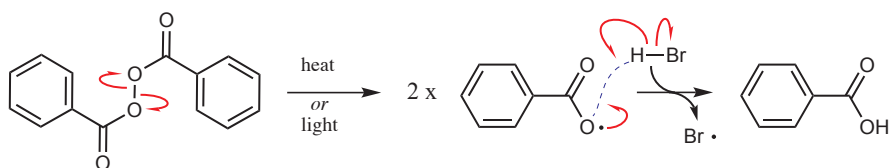
3. Dihalocarbene addition to cyclohexene to give 7,7-dichlorobicyclo[4.1.0]heptane.

**16 — Radical Reactions****Allylic Bromination with NBS**

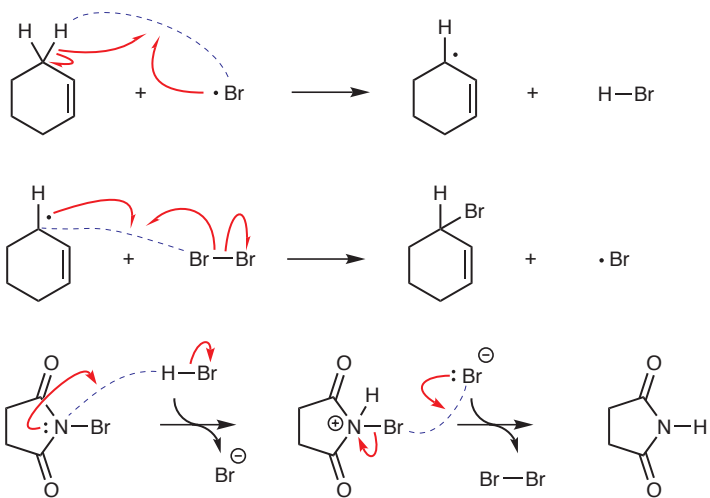
2. Free radical bromination of cyclohexene with *N*-bromosuccinimide, an allylic bromination.

Overall reaction

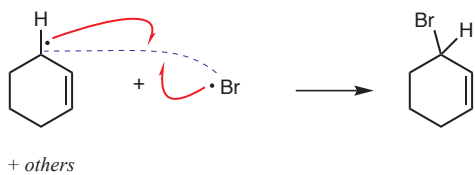


2. Free radical bromination of cyclohexene with *N*-bromosuccinimide, an allylic bromination -- continued.Initiation (See *Notes*.)

Propagation



Termination



To the Instructor

The examples contained in *A Guide to Organic Chemistry Mechanisms* are designed to supplement a standard organic chemistry textbook. They were also designed by how I perceived how our brains work and how teaching can make the best use of that model.

A quotation that guided my teaching is credited to Confucius, “I hear and I forget. I see and I remember. I do and I understand.” I believed the greater the intellectual contribution a student made to their learning, the more they would understand. Therefore I sought ways to ask students to make the intellectual connections required for learning organic chemistry. Herein lies a maxim, “One cannot imagine the unimaginable.” If you wish to lead a donkey with a carrot, the carrot must be within sight but still out of reach of the donkey. I think students lose sight of the connection between a mechanism they are given and the steps necessary to solve a problem from an assignment. This book connects the missing steps by changing the complexity of each mechanism. By simplifying the mechanisms, the solutions remain within intellectual reach of students. As students master the steps, they can repeat the problems in which they must add more information.

When used in a class, *A Guide to Organic Chemistry Mechanisms* can be used in large classes with transparencies of a worksheet or in smaller classes in a guided inquiry style with students working in small groups. This works well with examples from Part A. Because students can solve the problems on their own, you may also use Parts B or C if previously assigned.

To the Student

If *A Guide to Organic Chemistry Mechanisms* is being used in your class, your instructor should assign the examples that correspond with your textbook. If you are using *A Guide to Organic Chemistry Mechanisms* on your own, then you should find relevant examples by examining the index or table of contents. *A Guide to Organic Chemistry Mechanisms* will make it easy to learn the steps in a reaction mechanism. I recommend you work your way through Parts A, B, and C. Commonly, students need to repeat most mechanisms several times before they can apply that mechanism to a new problem. After you have succeeded in writing a mechanism from this book, you should test yourself with a new example from your class assignment or textbook. If you have difficulty, you may return to an example from *A Guide to Organic Chemistry Mechanisms*.

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Functional Group Index

By Preparation

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Aldehyde			aldehyde		9.1, 9.3
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alkene		12.9	alcohol	8.13-16, 8.20, 8.31, 10.8	
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diol		12.12	carboxylic acid	8.13-16, 8.20, 8.31, 10.8	
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Amine			alkyne		5.20-21
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amide	11.6-7, 11.9, 11.13		dihalide		4.20-23
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ketone		9.13	Nitrile		
nitrile		8.28	amide		10.1
Carboxylic acid amide			halide		3.8-9
carboxylic acid		8.17-19	ketone		8.10
ester		8.27	nitrile		9.12
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Functional Group Index By Preparation

<i>Preparation of</i>	<i>Starting Material</i>	<i>Chapter</i>	<i>Preparation of</i>	<i>Starting Material</i>	<i>Chapter</i>
Phenol			Sulfur containing		
amine		14.14	halide		3.3, 3.6
aryl ketone		6.11-12	alcohol		10.3
ether		3.15			
α -Substituted carbonyl compound			¹ Requires an additional reduction reaction		
aldehyde		9.1	² Step one of a two step Gabriel amine synthesis. It requires an additional hydrolysis reaction.		
ester		3.11, 9.5, 9.7-8, 9.10	³ A diol will result if methanol is replaced with water.		
ketone		3.19, 9.2-4, 9.6, 9.8, 9.15-17	⁴ See <i>Notes.</i> , p. 22.		
nitrile		9.12			

Functional Group Index By Reaction

<i>Reaction of</i>	<i>Preparation of</i>	<i>Chapter</i>	<i>Reaction of</i>	<i>Preparation of</i>	<i>Chapter</i>
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alkene		4.13-14, 4.16	alkyne		3.10, 3.17
carboxylic acid		12.2	halide		5.20-21
ester		8.20, 10.8	ketone		5.22-23
ether		3.2 ⁵ , 3.14 ⁵ , 3.16	Amine		
halide		3.5, 3.22, 3.25, 3.27, 10.2, 10.6-7	alkene		4.17-18
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ketone		6.12 ⁶ , 12.1, 12.5, 12.8	carboxylic acid amide		8.27
sulfonate		10.3	enamine		9.17
Aldehyde			halide		14.14
alcohol		8.2-3, 8.12, 9.1-2, 11.1	ketone		9.4, 9.15
alkene		8.5-6	Aromatic compound, Substituted		
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carboxylic acid		6.3, 6.7, 12.2, 12.4	amine		14.10 ⁷ , 14.11, 14.13
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ester		8.12	ether		14.12
ketone		9.4	halide		14.3, 14.5-6, 14.14
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Alkene			Carboxylic acid amide		
alcohol		5.2, 5.16-19	amine		8.24-25, 11.6-7, 15.5
aldehyde		12.9	carboxylic acid		8.24-25
alkane		15.1-3	carboxylic acid amide		3.12
alkene		13.1-2	nitrile		10.1
alkyne		4.20-21	Carboxylic acid		
carboxylic acid		12.9	alcohol		11.8
diol		12.10-11	amine		15.4 ⁸
epoxide		12.6	carboxylic acid amide		8.17-19 ⁸
ester		5.3	carboxylic acid chloride		10.4-5
halide		5.1, 5.4-9, 5.12-15, 16.2, 16.3	ester		3.4, 8.13-16 ⁸ , 8.20, 8.31, 10.8
ketone		12.9	ketone		13.6 ⁸ , 14.1 ⁸

Functional Group Index

By Reaction

<i>Reaction of</i>	<i>Preparation of</i>	<i>Chapter</i>	<i>Reaction of</i>	<i>Preparation of</i>	<i>Chapter</i>
Diene, Diels Alder Rxn			alcohol	6.10, 8.1, 8.4, 9.2, 11.2-4	
cyclohexene		7.1-15	alkane		11.12
halide		5.10-11	alkene		9.3
Diol			alkyne		8.4
aldehyde		12.12	amine		9.4
ketone		6.8-9	carboxylic acid	6.10, 9.13	
Enone and unsat'd ester			enamine		9.17
amine		9.15	enone		9.3
cyclohexene	7.1-2, 7.4, 7.6-15		ester	6.1-2, 6.4-6	
ester		9.16	halide		9.14
ketone	9.15-16, 13.5		ketal		8.7
Ester and lactone			ketone	9.2-4, 9.6, 9.14, 9.17	
alcohol	8.12, 8.26, 11.5		nitride		8.10
alcohol	8.21, 8.23, 11.10		oxime		8.9
aldehyde		11.10	Nitrile		
alkene		8.22	amine		8.28-29
carboxylic acid	8.21-23		carboxylic acid		8.28-29
carboxylic acid amide	8.27		carboxylic acid amide		8.29
ester	3.11, 8.12, 9.5-12		ketone		8.30
ketone	9.5-8, 9.10		nitride		9.12
Ether and epoxide			Organometallic		
alcohol		3.17-19	alcohol		8.1-4, 8.26
alkyne		3.17	alkane		13.3
halide		3.15	alkene		13.1-2, 13.4
ketone		3.19	ketone		13.5-6
phenol		3.15	Phenol		
Halide			ether		3.13
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alkylbenzene		14.2	aldehyde		9.1
alkyne	3.10, 4.20-23		alkane		9.8-10, 9.17
amine	3.7, 3.12		amine		9.4, 9.15
enone		4.10	carboxylic acid		9.13
epoxide		3.16	enone		9.1, 9.3
ester	3.4, 3.11, 9.8-10		ester	3.11, 8.12, 9.5, 9.7-11, 9.16	
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ketone		9.8-10	nitride		9.12
nitride	3.8-9, 9.12		Sulfonate		
Haloalkene or arene			nitride		3.8
alkene		13.1-2, 13.4	sulfide		3.6
alkyne		4.20-23			
amine		14.11, 14.13			
ether		14.12			
halide	(3.6), 5.20-21				
Imine, oxime, hydrazone					
alkylbenzene		11.12			
Ketal					
ketone		8.8			
Ketone					

⁵ An alcohol must first be converted to an alkoxide, see Chapter 9.7, ethoxide propagation. Also prepared with sodium metal.

⁶ An alcohol must first be converted to a peroxide with hydrogen peroxide and acid.

⁷ A benzamide conversion to an aniline.

⁸ A carboxylic acid must first be converted to an acid chloride or anhydride.

Preface

About the Book

This book is a guide for learning organic chemistry reaction mechanisms. How should you use this book? Since I believed that I could always adapt a reaction to a new problem, I just need to know at least one example. This book is designed to teach that example. This book will help you to learn reactions in small portions making it easier for you to understand and remember.

However, before you start with the reactions, there are some things you should review. Therefore, Chapters 1 and 2 go over some fundamentals. In Chapter 1, I discuss some chemical principles that you can use to predict electron reactivity. This is followed by resonance structures. The problems are designed to be easy and illustrate patterns. This should appeal to our brains ability to find patterns that we can repeat. Therefore, you should succeed in completing all of these problems.

Resonance structures show how electrons move without forming any bonds to new atoms. In Chapter 2, you will do acid-base reactions. You will learn how to predict the equilibrium of a reaction and you will learn how to use the curved arrow. I have added an exercise to write English sentences with the curved arrows. I want to connect the logic of a curved arrow to a sentence as well as the graphical representation.

Now, start with any of the reactions or chapters and start with the Part A problems. Fill in the missing curved arrows. Everything you need to know is present in Part A. This shows the logic of a reaction. **You must write the correct curved arrows for each step before you go to Part B.** Go to that same reaction in Part B and repeat that reaction. Now you must add any missing 'pre-bonds', curved arrows, and structures. While I have removed some information from the reaction, the basic logic of the reaction remains. Finally, complete Part C. This is similar to problems in an organic chemistry textbook. I have retained the same number of reaction arrows as the original mechanism as additional hints. In addition, the reagents are written with their complete formulae and solvents are added but noted in italic type. You should strive to write out the complete mechanism. You may wish to photocopy a reaction or write it on a blank sheet of paper so you can go back and repeat an exercise. Once you have succeeded in writing a mechanism, you can move on to problems from your text.

The reactions are grouped by reaction type because it is easier to learn a series of related reactions. If your book is not organized in that manner, then select similar examples from the table of contents or from the index.

If you are able to write a mechanism for a problem in this book, you should be able to write a mechanism for other problems of the same mechanism. You should use this approach to solve the problems in your textbook. Clearly, you must be able to solve at least one problem if you are to solve another problem using that same mechanism.

Your objective in studying should be to learn the *patterns* of the reaction mechanisms. The first problem always takes the greatest amount of time because you must learn the most to solve it. The more problems you solve, the less time it will take to solve them.

Writing Style (and Meaning)

I also wrote this book in the first person. Why write in the first person? First of all, it is a format that I am comfortable with. I like how it sounds. I also want to write in the first person because science can be gray. A scientific proof may not be as strong as we would like it to be. I think we are too frequently willing to accept *something as true simply because it is written in a book*. By writing in the first person, you will have a natural sense that an idea is my idea and other scientists may not accept it. As some of the mechanisms, topics and models contained in this text are different; I

will leave it to you to determine whether they are useful or true.* I hope by doing so, you may go back to your regular textbook and measure the thoughts of that author in the same manner. †

The Curved Arrow

The ‘curved arrow’ is the symbol that represents how electrons move. They indicate which bonds are being made and broken AND which atoms are being joined. They are the language of organic chemistry and their use is also referred to as ‘pushing electrons’.

In this book, I use a simple modification of pushing electrons. The traditional curved arrows are ambiguous if the curved arrow starts with a pair of electrons shared by two atoms AND indicate indicate a new bond being formed. This ambiguity can be avoided if a curved arrow does not indicate formation of a new bond. Therefore, a “pre-bond” or dashed line has been added to indicate where new bonds will be formed. It is used with the curved arrow to show which electrons move to make or break bonds and makes pushing electrons consistent and unequivocal in meaning. ‡

Curved arrows are fundamental to understanding chemistry. The curved arrows are a **required element** in describing what is happening in a reaction. They describe the only electronic changes that can be made in any step in a reaction. If there is a curved arrow, that change **must** be made, and unless there is another curved arrow, **no other changes can be made**. Here is where students make a very common error. A student may write a curved arrow believed to lead to the formation of a product. However, the product they write will not be consistent with the curved arrows. *Any difference between a curved arrow and the predicted result is an error of critical importance.*

Another error is to fail to start the curved arrow with a pair of electrons. Some students may start a curved arrow at a proton to show its movement. However, the curved arrow represents a movement of electrons, not protons. A useful device I often use and encourage students to use, especially initially, is to circle the electrons being moved.

Rules for Pushing Electrons

To Make a Bond or Increase the Bond Order	
Two Electrons	One Electron
<i>A curved arrow must start with a pair of electrons on an atom or connecting two atoms and end between two atoms. It may point toward a pre-bond to indicate a new bond or to a single, or a double bond for a change in bond order. A bond will form to the common atom of the starting material and product.</i>	<i>Two half-headed curved arrows must end between two atoms and point toward a pre-bond, single, or double bond to indicate a new bond or a change in bond order. Each atom donating an electron are part of the new bond.</i>
To Break a Bond or Reduce the Bond Order	
Two Electrons	One Electron
<i>A curved arrow must start with a pair of electrons connecting two atoms. That bond will be broken or reduced in bond order. If a curved arrow ends between two different atoms, a new bond is formed to the common atom. If not, no new bond is formed.</i>	<i>Two half-headed curved arrow must start with a pair of electrons connecting two atoms. That bond will be broken or reduced in bond order. The curved arrows may end on an atom or connect to new atoms to form new bonds..</i>

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* What is the difference? Models are never true, but they can be useful. If a model were true, then it wouldn't be a model for something.

† Ideas presented in peer-reviewed journals will contain a reference to their source. Therefore, a reader understands that the idea belongs to the source. If authors accept the principles first laid out, then they may become commonly accepted. However, in the strictest use of logic, it does not become more true. It will remain only as true as the original proof or proofs.

‡ Many books use this convention, especially with Diels-Alder reactions. I have added the term ‘pre-bond’.