

Final Exam – CHM 1321 – B**Prof. Sandro Gambarotta****Date: Apr 2019****Length: 3 hours****Last Name:** _____
Name: _____**First****Student #** _____**Seat #****Instructions:**

- Calculator permitted (Faculty approved or non-programmable)
- Closed book
- No remarking for exam written in pencil
- **Do not un-staple this booklet**

Read carefully:

Cellular phones, unauthorized electronic devices or course notes (unless an open-book exam) are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: academic fraud allegations will be filed which may result in your obtaining a **0** (zero) for the exam.

By signing below, you acknowledge that you have read and ensured that you are complying with the above statement.

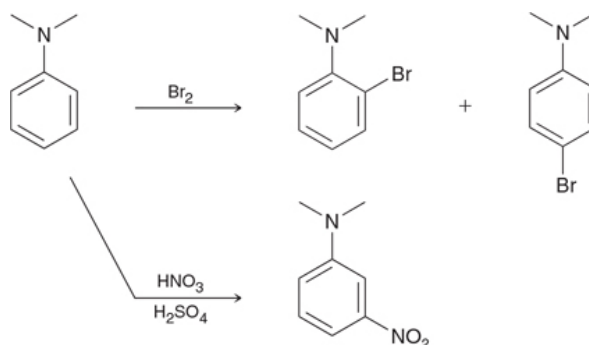
Signature: _____

Please put your INITIALS IN THE BOX when you have verified that there are **11 pages in this exam.**

Question #					
1	../3	10	../2	19	../1
2	../5	11	../2	20	../5
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4	../2	13	../1	22	../1
5	../4	14	../2	23	../1
6	../2	15	../1	24	../2
7	../3	16	../2	25	../2
8	../4	17	../2	26	../2
9	../3	18	../4	27	../3
			Total.	../67	
			Total	../45	
			Total	../70	

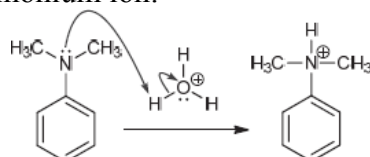
1. (3 points)

When *N,N*-dimethylaniline is treated with bromine, *ortho* and *para* products are observed. Yet, when *N,N*-dimethylaniline is treated with a mixture of nitric acid and sulfuric acid, only the *meta* product is observed. Explain these results.

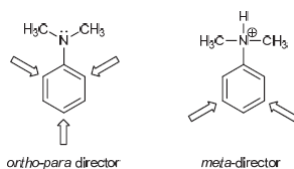


Answ.

The amino group in *N,N*-dimethylaniline is a strong activator, and therefore, an *ortho-para* director. For this reason, bromination occurs at the *ortho* and *para* positions. However, in acidic conditions, the amino group is protonated to give an ammonium ion:

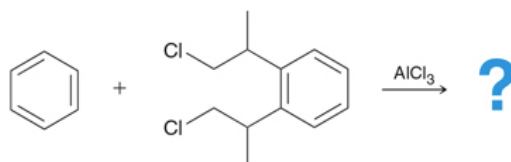


Unlike the amino group, an ammonium ion is a strong deactivator and a *meta* director. Under these conditions, nitration occurs primarily at the *meta* position.



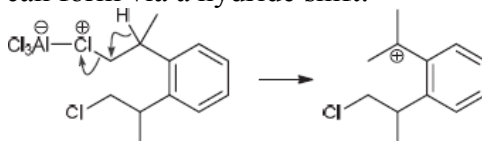
2. (5 points)

Predict the major product of the following reaction:

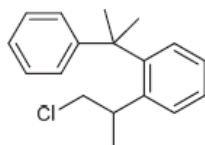


Answ.

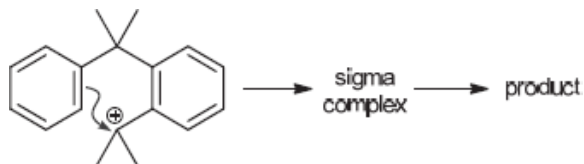
Each of the chlorine atoms in the dichloride can interact with AlCl_3 and initiate a Friedel-Crafts alkylation process. During the first alkylation process, a tertiary benzylic carbocation can form via a hydride shift:



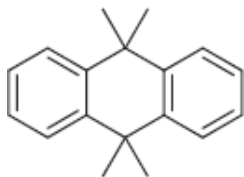
This carbocation is then attacked by benzene in an electrophilic aromatic substitution reaction, giving the following:



This compound still has one more chlorine atom, allowing for the second alkylation process. Once again, the second alkylation occurs in a similar fashion (via a tertiary, benzylic carbocation), but this time, the electrophilic aromatic substitution reaction proceeds in an intramolecular fashion:

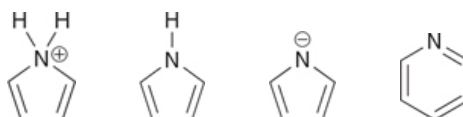


The following product is therefore expected:



3. (2 points)

Which of the following structures is not aromatic?



Answ.

In structure (a), the nitrogen atom has four sigma bonds, so it must be sp^3 hybridized. It does not have a p orbital, so the ring is NOT a continuous system of overlapping p orbitals. Therefore, structure (a) is nonaromatic. Structures (b), (c), and (d) are all aromatic.

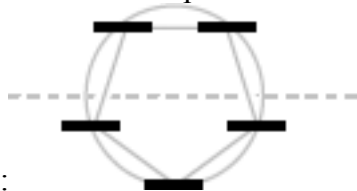
4. (2 points)

Draw a Frost circle for the following cation and explain the source of instability of this cation:



Answ.

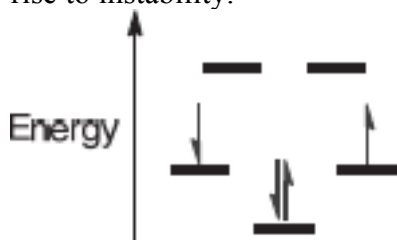
In order to draw a Frost circle, we begin by drawing a circle, and then we place a pentagon inside the circle, with all five corners touching the circle, such that one of the corners points to the bottom of the circle, as shown



here:

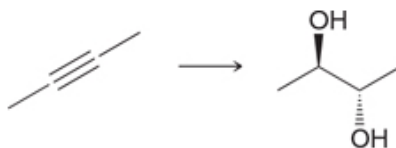
Each position where a corner touches the circle represents the relative energy level of a molecular orbital. If we draw a horizontal line through the center of the circle, we see that there are three MOs in the bottom half of the circle, and

two MOs in the top half. The former represent the bonding MOs, while the latter represent the antibonding MOs. With three bonding MOs, we expect that six π electrons are required in order to achieve aromaticity. This cation only has four π electrons. Two of them occupy the lowest energy MO (at the bottom of the circle), but the remaining are split between the two degenerate bonding MOs. As such, this system is not a closed-shell electron configuration, giving rise to instability.



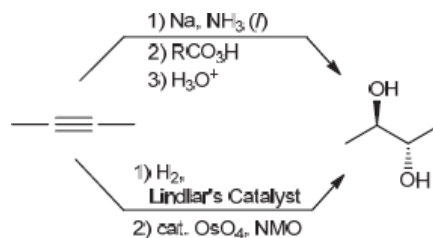
5. (4 points)

Identify the reagents necessary to achieve the transformation below. Be aware of the stereochemical outcome:



Answ.

This transformation requires two processes: 1) reduction of the alkyne to give an alkene, and 2) dihydroxylation to give a diol. In order to achieve the desired stereochemical outcome, we must either perform each process in an *anti* fashion (as shown in the first answer below), or we must perform each process in a *syn* fashion (as shown in the second answer below). Both answers are acceptable



6. (2 points)

Which reagents will achieve the following transformation?

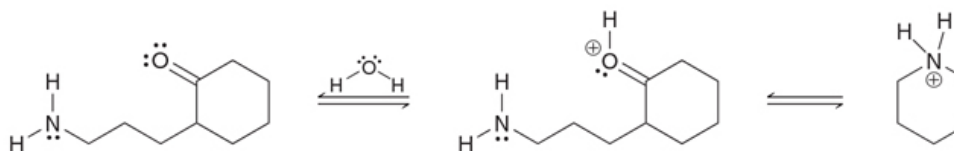
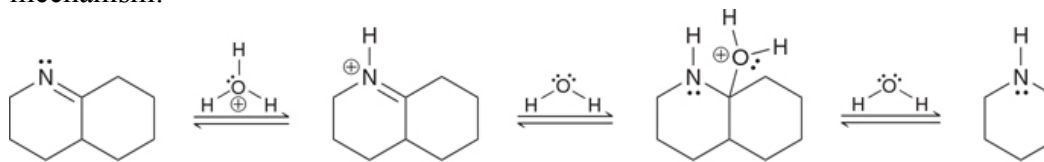


Answ.

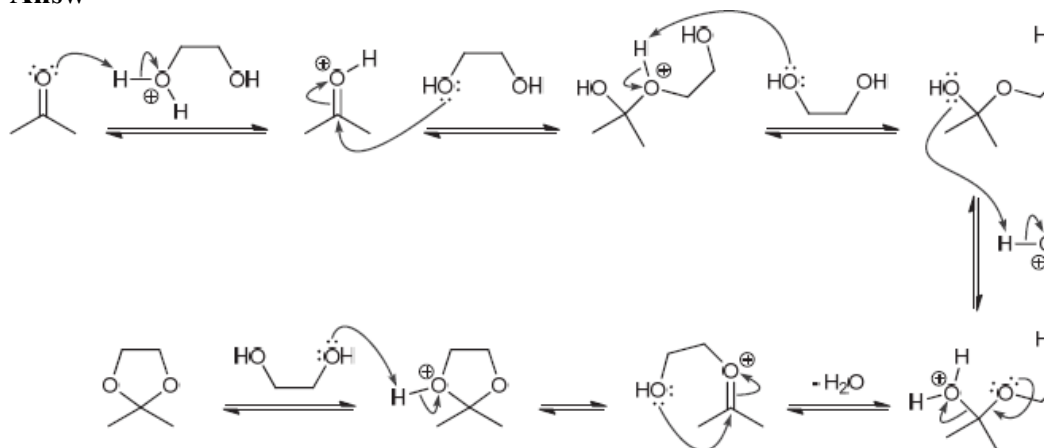
The reaction shows the conversion of an internal alkyne into a *trans* alkene. This can be accomplished via a dissolving metal reduction, which employs sodium in liquid ammonia.

7. (3 points)

Draw curved arrows for each step of the following mechanism:

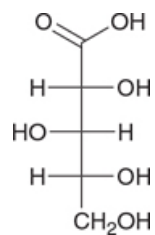


Answ

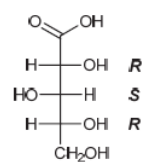


8. (4 points)

Determine the configuration for every chiral center in each of the following compounds:



Answ



9. (3 points)

Identify whether each of the following compounds is chiral or achiral:



Answ.

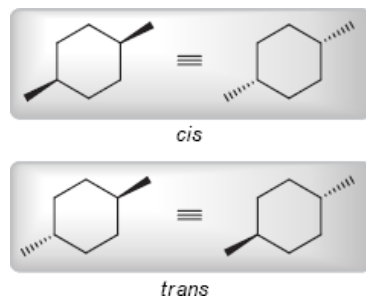
- (a) This compound has a non-superimposable mirror image, and therefore it is chiral.
- (b) This compound has a non-superimposable mirror image, and therefore it is chiral.
- (c) This compound lacks a chiral center and is therefore achiral.
- (d) This compound has a non-superimposable mirror image, and therefore it is chiral.

10. (2 points)

There are only two stereoisomers of 1,4-dimethylcyclohexane. Draw them.

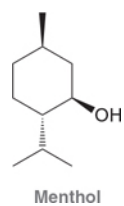
Answ.

As shown below, there are only two stereoisomers (the *cis* isomer and the *trans* isomer).



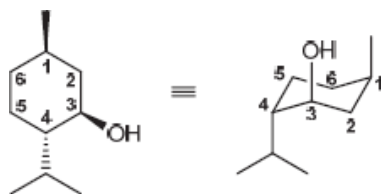
11. (2 points)

Draw the two chair conformations of menthol.



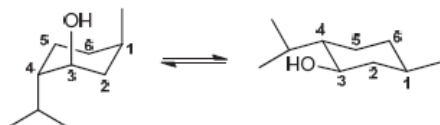
Answ.

In order to draw the first chair conformation, begin by assigning a numbering system, and then determine the location and three-dimensional orientation of each substituent:

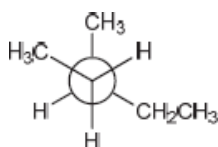


When assigning the numbers to the chair drawing, the first number can be placed anywhere on the ring (as long as the numbers go clockwise).

Once we have drawn the first chair conformation, we then draw the second chair conformation, again using a numbering system. Notice that a ring flip causes all equatorial groups to become axial groups, and vice versa.

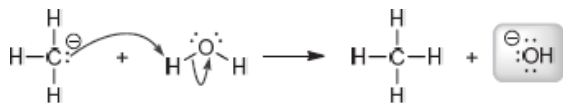
**12. (1 points)**

Use a Newman projection to draw the most stable conformation of 3-methylpentane, looking down the C2—C3 bond.

Answ**13. (1 points)**

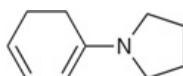
What is the strongest base that is present after methyl magnesium bromide (CH_3MgBr) is treated with water?

Answ.



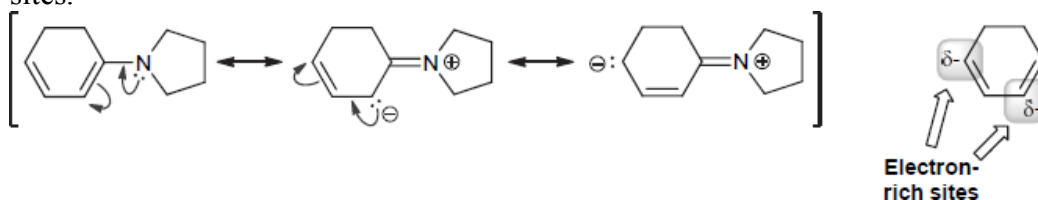
14. (2 points)

Enamines, compounds with an amino group attached to a double bond, are electron-rich alkenes. Draw the major resonance contributors for the enamine shown and determine which site(s) on the structure are most electron-rich.

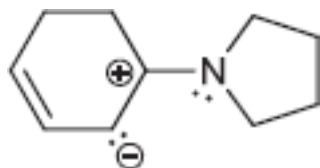


Answ.

The only resonance pattern evident in the enamine is an allylic lone pair. After that pattern is applied, however, another allylic lone pair results so the resonance can ultimately involve both π bonds. There are a total of three major resonance forms that all have filled octets. Consideration of the hybrid of these resonance forms predicts two electron-rich sites.



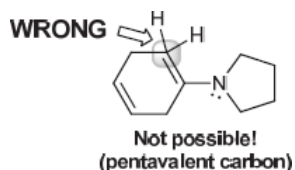
Did you draw the following additional structure (or something similar, with C+ and C-) and wonder why it was not shown in this solution?



Insignificant

This resonance form suffers from two major deficiencies: 1) it does not have filled octets, while the other resonance forms shown above all have filled octets, and 2) it has a negative charge on a carbon atom (which is not an electronegative atom). Either of these deficiencies alone would render the resonance form a minor contributor. But with both deficiencies together (C+ and C-), this resonance form is insignificant. The same is true for any resonance form that has both C+ and C-. Such a resonance form will generally be insignificant.

Also, note that the π bonds cannot be moved to other parts of the six-membered ring since the CH_2 groups are sp^3 hybridized. These carbon atoms cannot accommodate an additional bond without violating the octet rule.



15. (1 Points)

Isonitriles (**A**) can be converted to isonitrile dihalides (**B**), which represents a useful procedure for temporarily hiding the reactivity of an isonitrile.



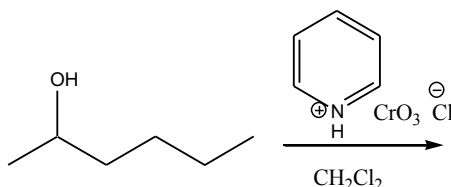
- Identify the hybridization state for each highlighted atom in **A**.
- One of the carbon atoms in **A** exhibits a lone pair. In what type of atomic orbital does this lone pair reside?
- Predict the C–N–C bond angle in compound **A**.

Answ.

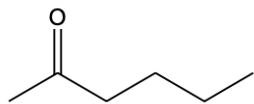
- sp hybridized.
- sp hybridized, so the lone pair occupies an sp hybridized orbital.
- linear geometry. As such, the C–N–C bond angle in **A** is expected to be 180° .

16. (2 points)

Predict the product for the following reaction. The reagent drawn above the arrow is a strong oxidizing agent

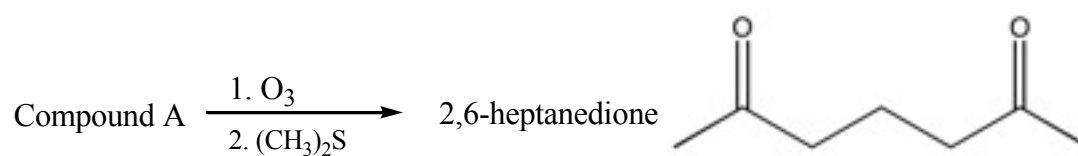


Answ.



17. (2 points)

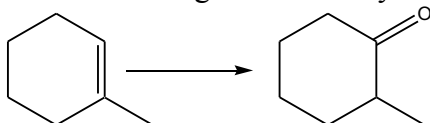
Compound A on ozonolysis yields 2,6-heptanedione. What is the structure of compound A?



Answ. 1,2-dimethylcyclopentene

18. (4 points)

Provide the reagents necessary to carry out the following conversion.

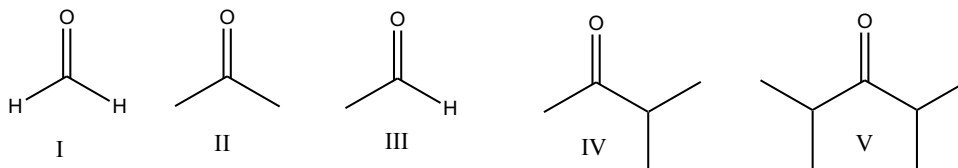


Answ:

BH_3 $\text{H}_2\text{O}_2/\text{NaOH}/\text{H}_2\text{O}$ followed by
 $\text{CrO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ (or $\text{PCC}/\text{CH}_2\text{Cl}_2$)

19. (1 point)

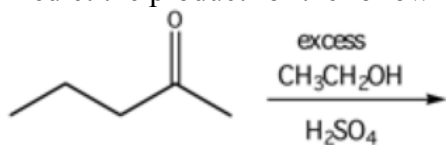
Which of the following compounds is least reactive towards nucleophilic addition reaction?



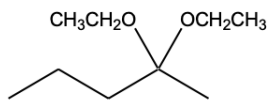
Answ. V

20. (5 point)

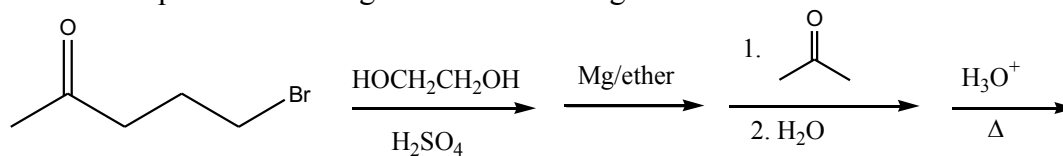
Predict the product for the following reaction and draw the complete mechanism.



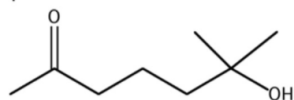
Answ:

**21. (5 points)**

Provide the product resulting from the following series of reactions

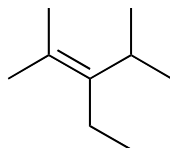
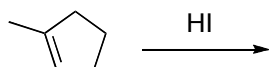
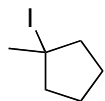
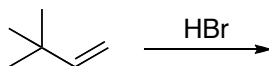
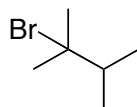


Answ



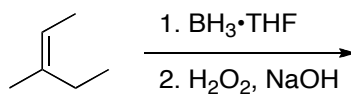
22. (1 point)

Name the following compound

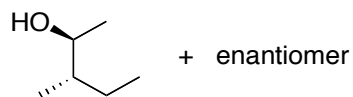
**Ans** . 3-ethyl-2,4-dimethyl-2-pentene**23. (1 point)**What is the *major* product for the following reaction?**Ans****24. (2 points)**Draw the structure of the expected *major* product(s) of HBr addition to the alkene shown below:**Ans**

25. (2 points)

What is the expected *major* product for the following reaction sequence? Specify whether enantiomers may be formed.

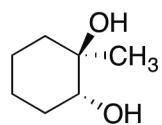
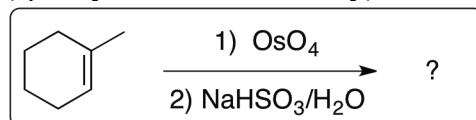


Answer



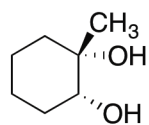
26. (2 points)

Draw the structure of the expected *major* organic product generated from the reaction sequence shown. (specify the stereochemistry)



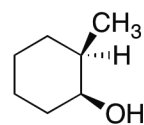
+ enantiomer

I



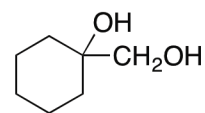
+ enantiomer

II



+ enantiomer

III

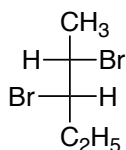
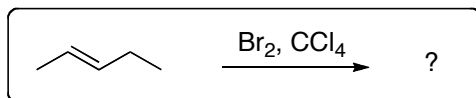


IV

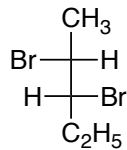
Answer: II

27. (3 points)

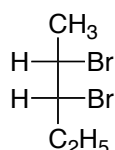
Which of the statements is most correct regarding the products expected from the halogenation reaction shown below?



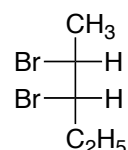
I



II



III



IV

- A) Equal amounts of I and II are produced.
 B) Equal amounts of III and IV are produced.
 C) Equal amounts of I and IV are produced.
 D) Equal amounts of II and III are produced.
 E) Equal amounts of I and III are produced.

Answer: B

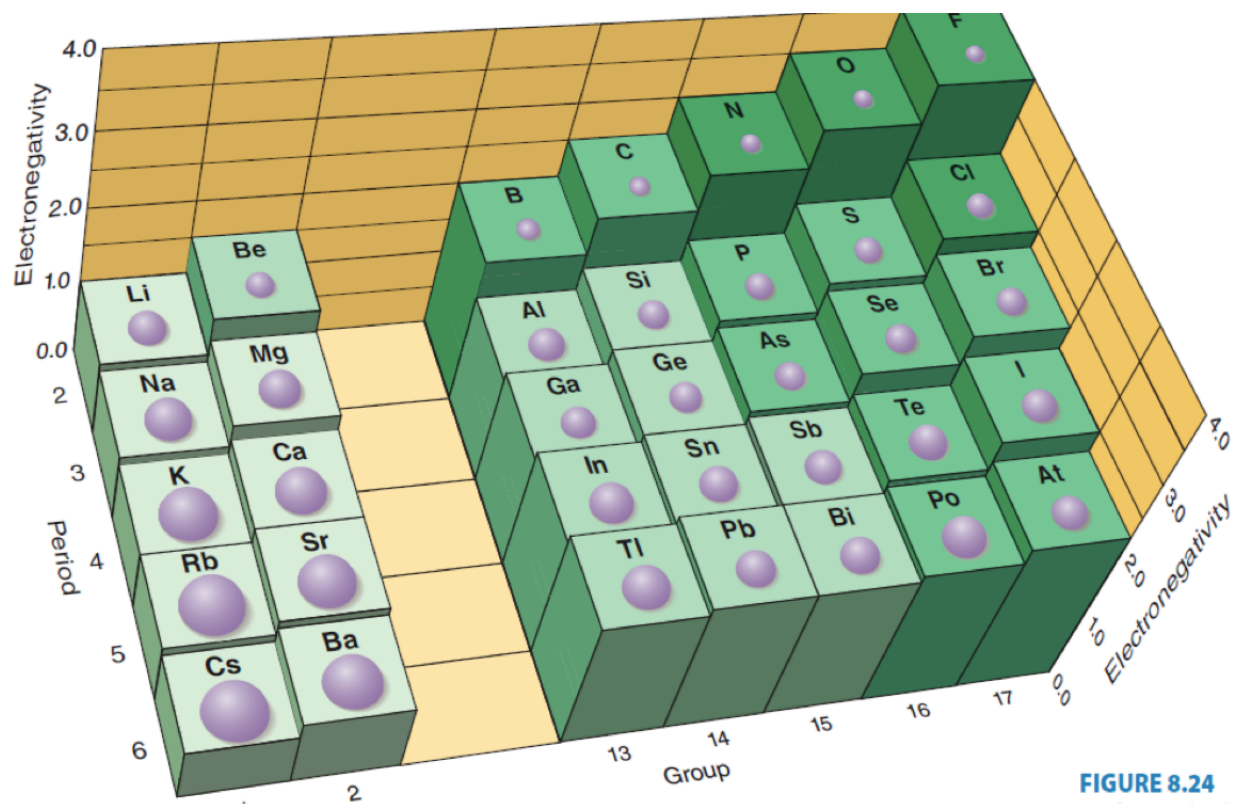


FIGURE 8.24

