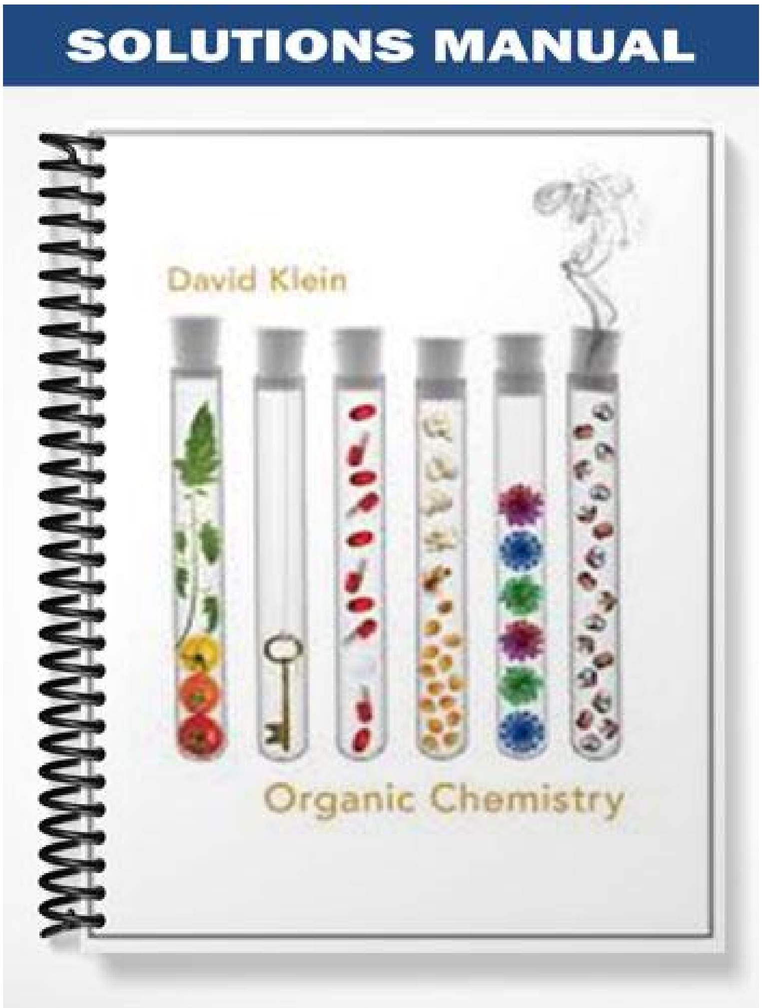

SOLUTIONS MANUAL
David Klein
Organic Chemistry

Chapter 2
Molecular Representations

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 2. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- In **bond-line structures**, _______atoms and most ________ atoms are not drawn.
- A ________________ is a characteristic group of atoms/bonds that show a predictable behavior.
- When a carbon atom bears either a positive charge or a negative charge, it will have ___________, rather than four, bonds.
- In bond-line structures, a **wedge** represents a group coming ______ the page, while a **dash** represents a group _________ the page.
- ___________ **arrows** are tools for drawing resonance structures.
- When drawing curved arrows for resonance structures, avoid breaking a _______ bond and never exceed _____________ for second-row elements.
- There are three rules for identifying significant resonance structures:
    1. Minimize ____________.
    2. Electronegative atoms can bear a positive charge, but only if they possess an ________ of electrons.
    3. Avoid drawing a resonance structure in which two carbon atoms bear _____________ charges.
- A ______________ lone pair participates in resonance and is said to occupy a ____ orbital.
- A _____________ lone pair does not participate in resonance.

Review of Skills

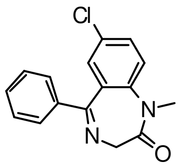
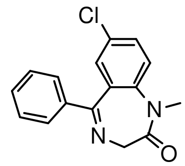
Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 2. The answers appear in the section entitled *SkillBuilder Review*.

SkillBuilder 2.1 Converting Between Different Drawing Styles

DRAW THE LEWIS STRUCTURE OF THE FOLLOWING COMPOUND

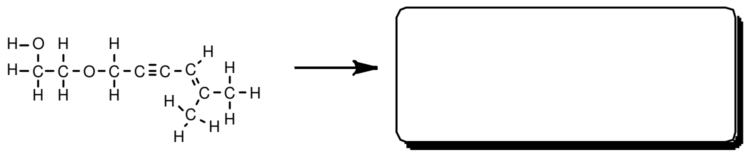
$(CH_3)_3COCH_3$ →

SkillBuilder 2.2 Reading Bond-Line Structures

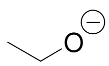
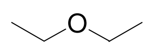
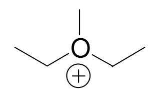
CIRCLE ALL CARBON ATOMS IN THE COMPOUND BELOW	DRAW ALL HYDROGEN ATOMS IN THE COMPOUND BELOW
	

SkillBuilder 2.3 Drawing Bond-Line Structures

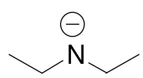
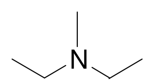
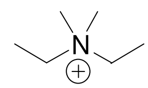
DRAW A BOND-LINE DRAWING OF THE FOLLOWING COMPOUND:



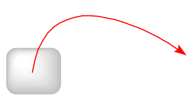
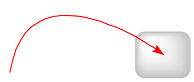
SkillBuilder 2.4 Identifying Lone Pairs on Oxygen Atoms

AN OXYGEN ATOM WITH A NEGATIVE CHARGE WILL HAVE ____ LONE PAIR(S) 	AN OXYGEN ATOM WITH NO FORMAL CHARGE WILL HAVE ____ LONE PAIR(S) 	AN OXYGEN ATOM WITH A POSITIVE CHARGE WILL HAVE ____ LONE PAIR(S) 

SkillBuilder 2.5 Identifying Lone Pairs on Nitrogen Atoms

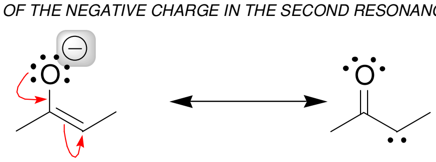
A NITROGEN ATOM WITH A NEGATIVE CHARGE WILL HAVE ____ LONE PAIR(S) 	A NITROGEN ATOM WITH NO FORMAL CHARGE WILL HAVE ____ LONE PAIR(S) 	A NITROGEN ATOM WITH A POSITIVE CHARGE WILL HAVE ____ LONE PAIR(S) 

SkillBuilder 2.6 Identifying Valid Resonance Arrows

RULE 1: THE TAIL OF A CURVED ARROW CANNOT BE PLACED ON A ______________  TAIL	RULE 2: THE HEAD OF A CURVED ARROW CANNOT RESULT IN ____________________ ____  HEAD

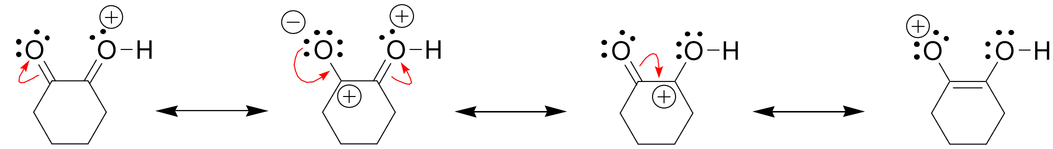
SkillBuilder 2.7 Assigning Formal Charges in Resonance Structures

INDICATE THE LOCATION OF THE NEGATIVE CHARGE IN THE SECOND RESONANCE STRUCTURE BELOW



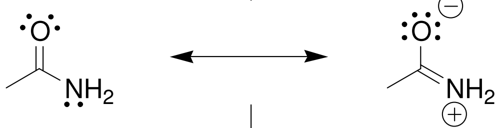
SkillBuilder 2.8 Drawing Significant Resonance Structures

IDENTIFY WHICH RESONANCE STRUCTURES BELOW ARE SIGNIFICANT AND WHICH ARE INSIGNIFICANT



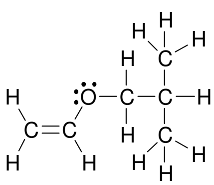
SkillBuilder 2.9 Identifying Localized and Delocalized Lone Pairs

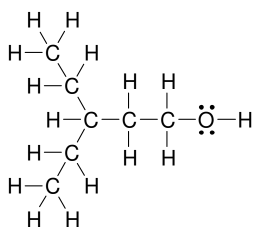
IDENTIFY WHETHER THE LONE PAIR ON THE NITROGEN ATOM BELOW IS DELOCALIZED	IDENTIFY THE HYBRIDIZATION STATE OF THE NITROGEN ATOM

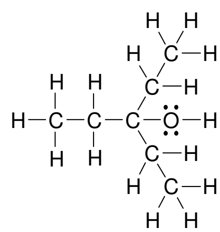


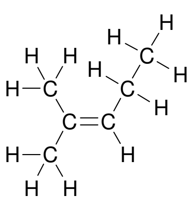
Solutions

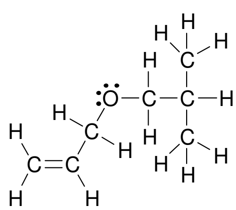
2.1.

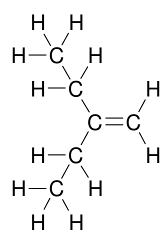
a) 

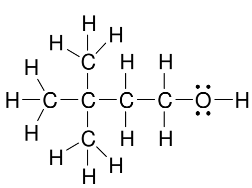
b) 

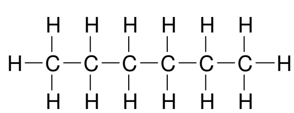
c) 

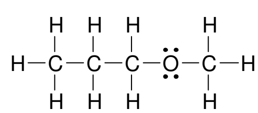
d) 

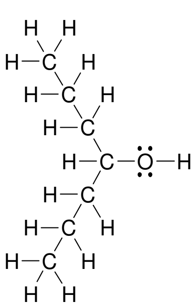
e) 

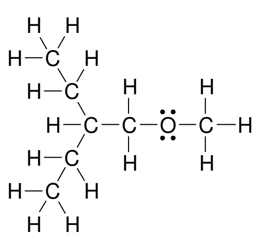
f) 

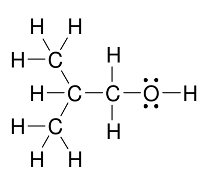
g) 

h) 

i) 

j) 

k) 

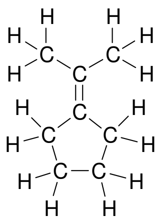
l) 

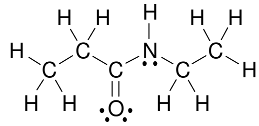
2.2 $(CH_3)_3COCH_3$ and $(CH_3)_2CHOCH_2CH_3$

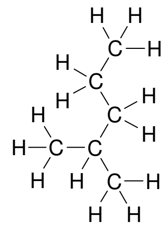
2.3 Six

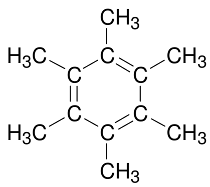
2.4 $H_2C{=}CHCH_3$

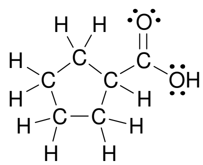
2.5.

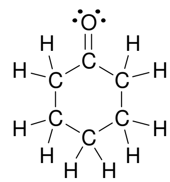
a) 

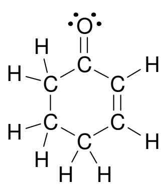
b) 

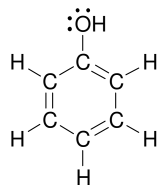
c) 

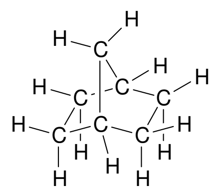
d) 

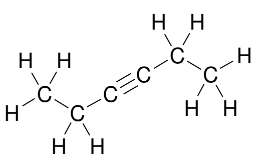
e) 

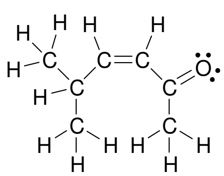
f) 

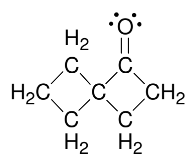
g) 

h) 

i) 

j) 

k) 

l) 

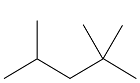
2.6

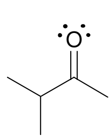
a) decrease (7→6) b) no change (8→8)
c) no change (8→8) d) increase (5→7)

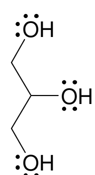
2.7

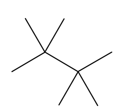
a) increase (12→14) b) decrease (8→6)

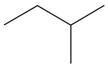
2.8.

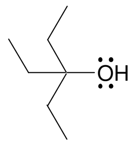
a) 

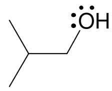
b) 

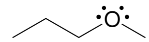
c) 

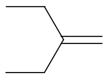
d) 

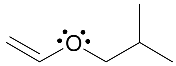
e) 

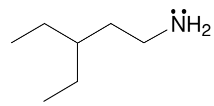
f) 

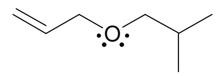
g) 

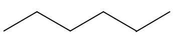
h) 

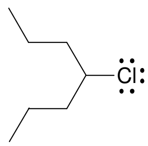
i) 

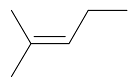
j) 

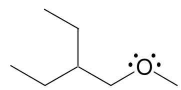
k) 

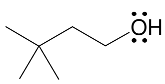
l) 

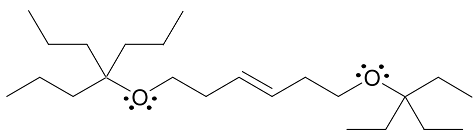
m) 

n) 

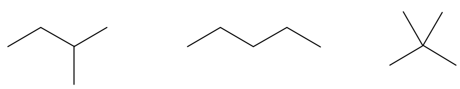
o) 

p) 

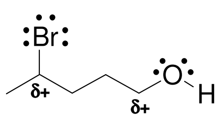
q) 

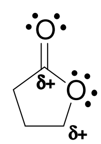
r) 

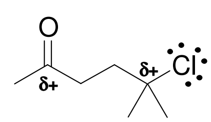
2.9.



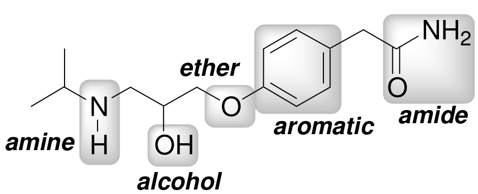
2.10.

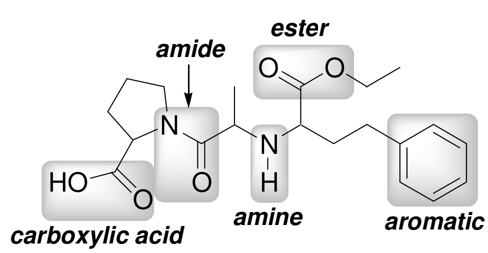
a) 

b) 

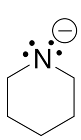
c) 

2.11.

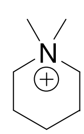




2.12.

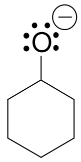
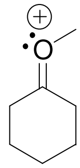
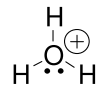
a) 

b) No charge

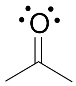
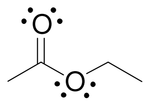
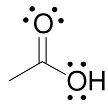
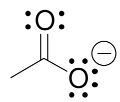
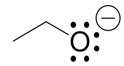
c) 

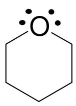
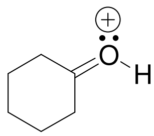
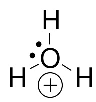
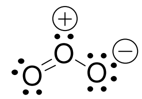
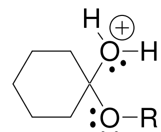
d) No charge

2.13.

a) 
b) 
c) No charge
d) 

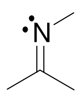
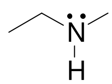
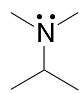
2.14.

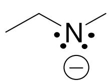
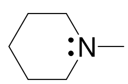
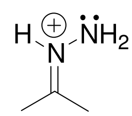
a) 
b) 
c) 
d) 
e) 

f) 
g) 
h) 
i) 
j) 

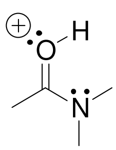
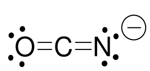
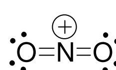
2.15. There are no hydrogen atoms attached to the central carbon atom. The carbon atom has four valence electron. Two valence electrons are being used to form bonds, and the remaining two electrons are a lone pair. This carbon atom is using the appropriate number of valence electrons.

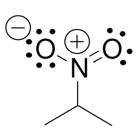
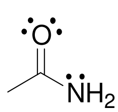
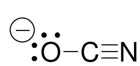
2.16.

a) 
b) 
c) 
d) no lone pairs

e) 
f) 
g) no lone pairs
h) 

2.17.

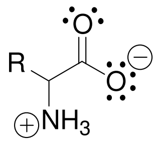
a) 
b) 
c) 

d) 
e) 
f) 

2.18.

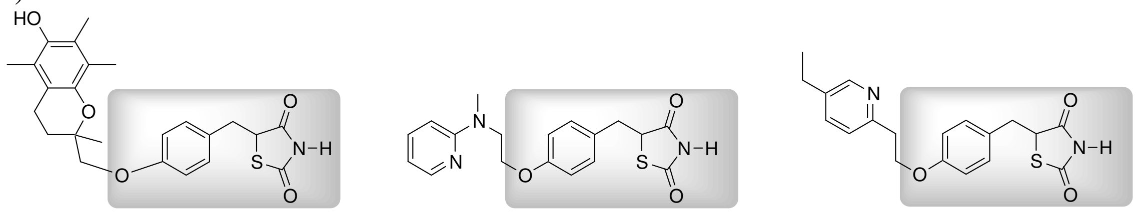
a) one b) zero c) one d) five

2.19 Five lone pairs:



2.20

a)



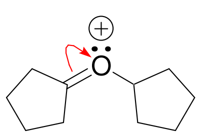
Troglitazone ***Rosiglitazone*** ***Pioglitazone***

b) Yes, it contains the likely pharmacophore highlighted above.

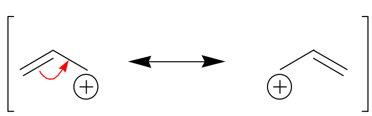
2.21

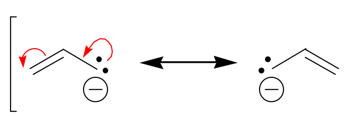
a) Violates second rule by giving a fifth bond to a nitrogen atom.
b) Does not violate either rule.
c) Violates second rule by giving five bonds to a carbon atom.
d) Violates second rule by giving three bonds and two lone pairs to an oxygen atom.
e) Violates second rule by giving five bonds to a carbon atom.
f) Violates second rule by giving five bonds to a carbon atom.
g) Violates second rule by giving five bonds to a carbon atom, and violates second rule by breaking a single bond.
h) Violates second rule by giving five bonds to a carbon atom, and violates second rule by breaking a single bond.
i) Does not violate either rule.
j) Does not violate either rule.
k) Violates second rule by giving five bonds to a carbon atom.
l) Violates second rule by giving five bonds to a carbon atom.

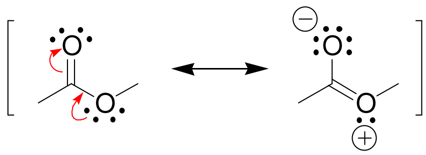
2.22.



2.23.

a) 

b) 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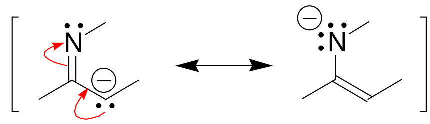
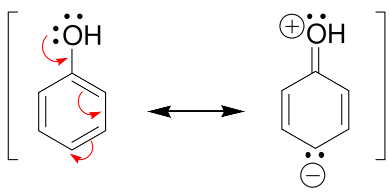

d)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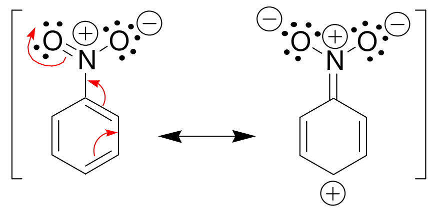
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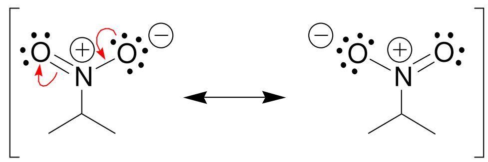
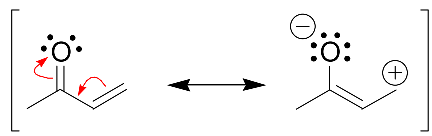
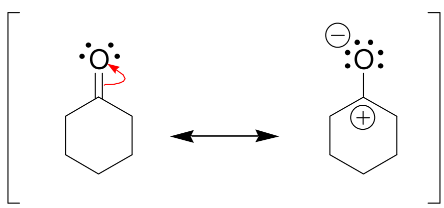
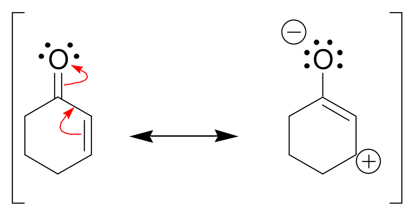

g)


h)

2.24.


a)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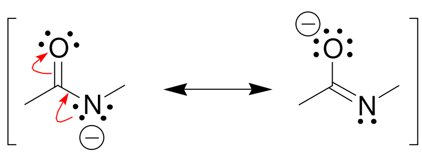
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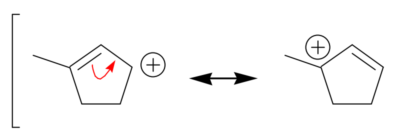
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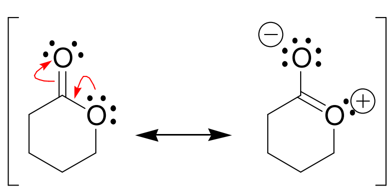
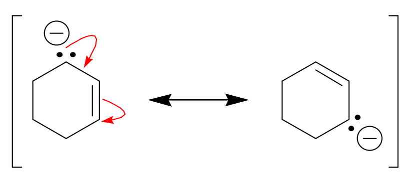
2.25.


a)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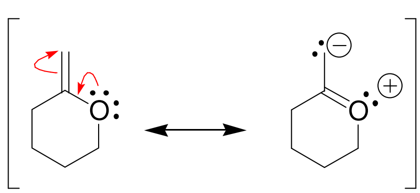
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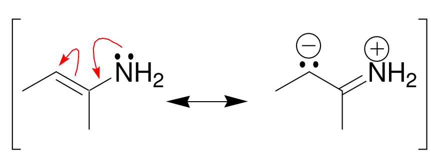
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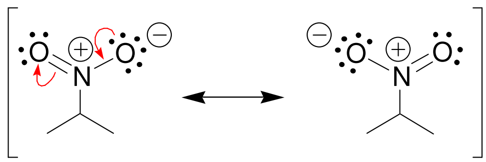

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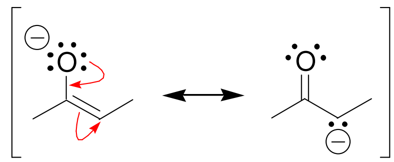

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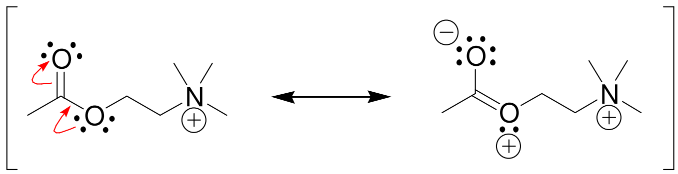

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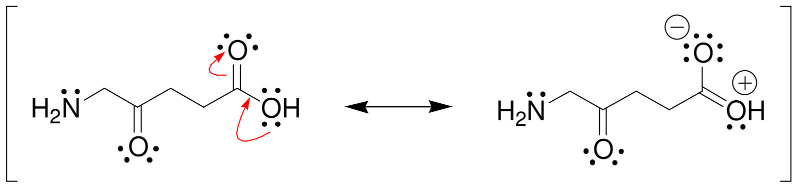

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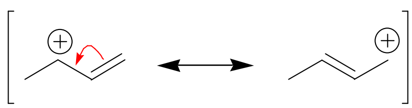
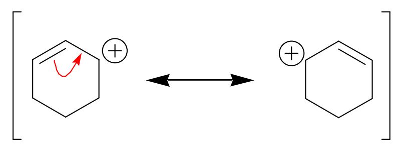
2.26.



a)



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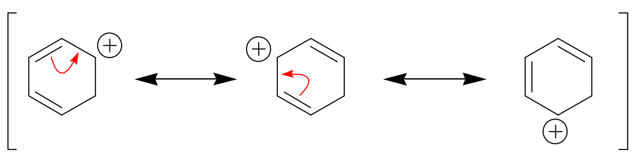

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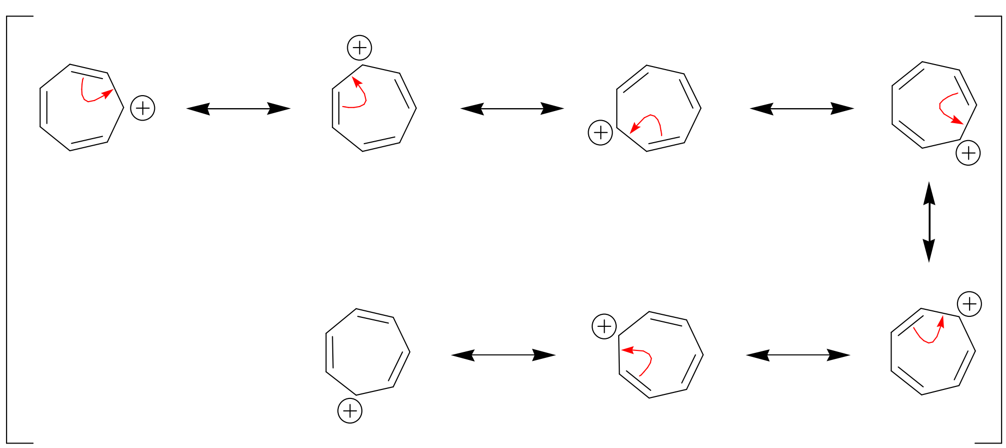

d)

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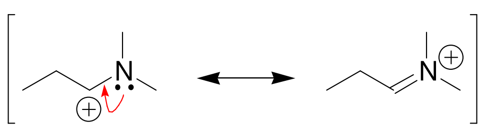
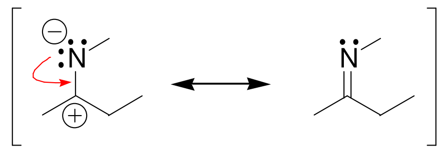
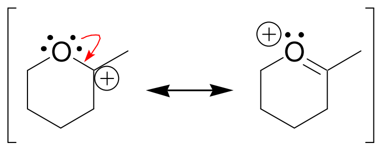
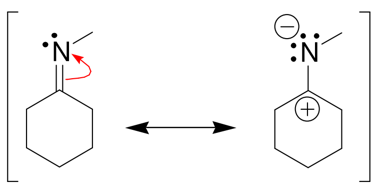
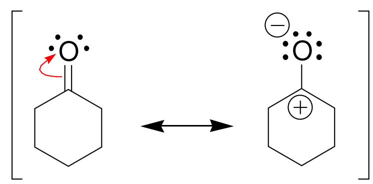
a) 

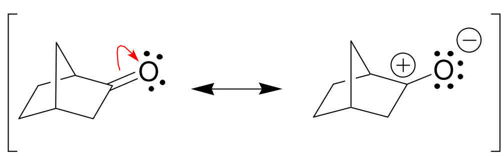
b) 

c) 

2.28.

a) 

b) 

c) 

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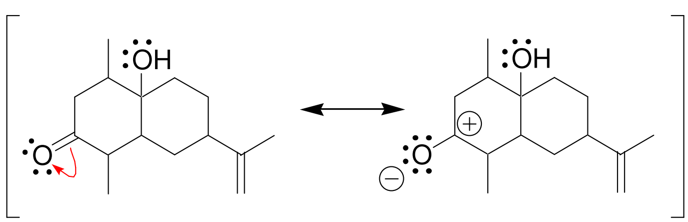

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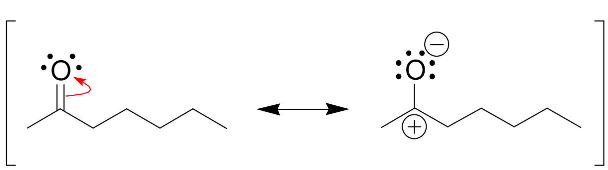

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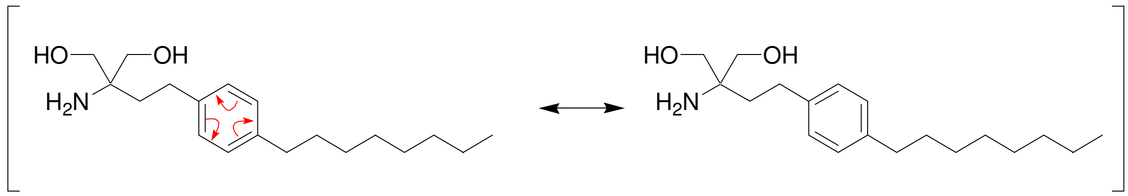

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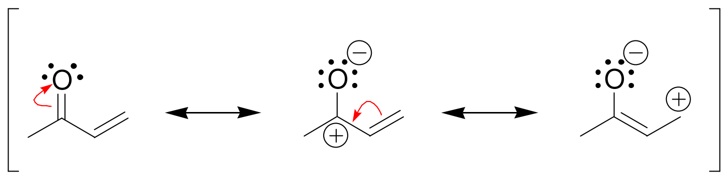
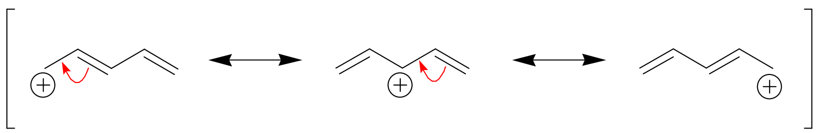
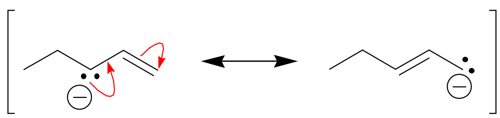
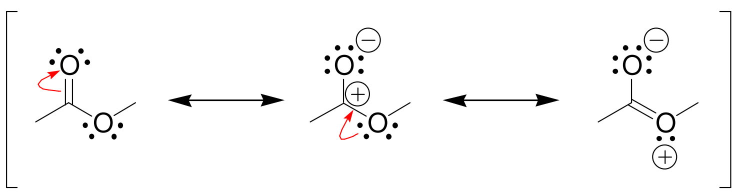
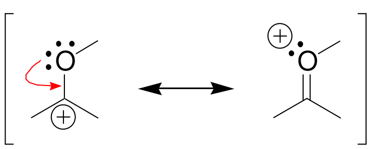
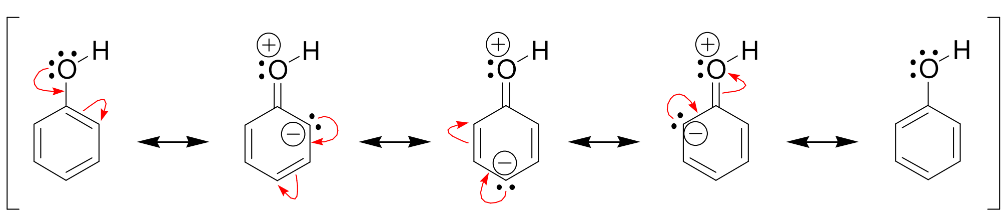
a) 

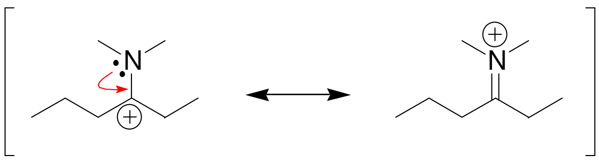
b) 

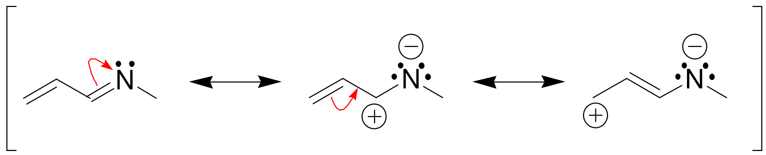
c) 

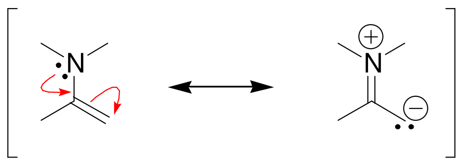
d) 

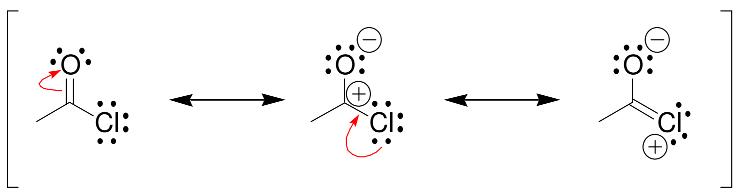
e) 

f) 

g) 

h) 

i) 

j) 

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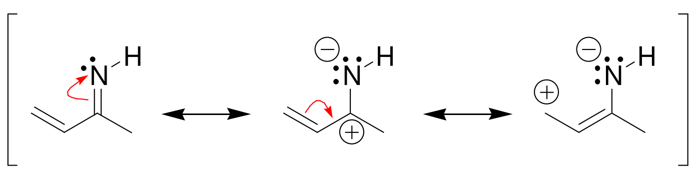
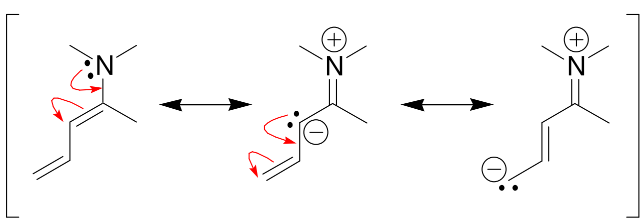
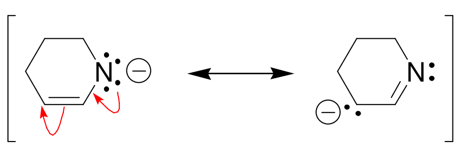
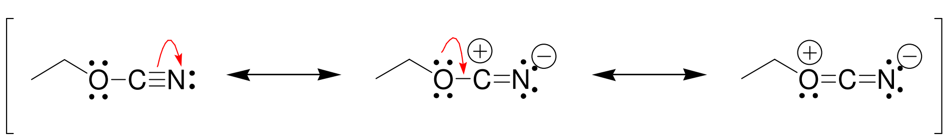
a) 

b) 

c) 

d) 

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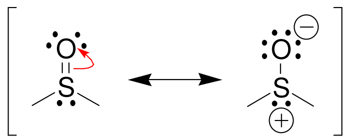

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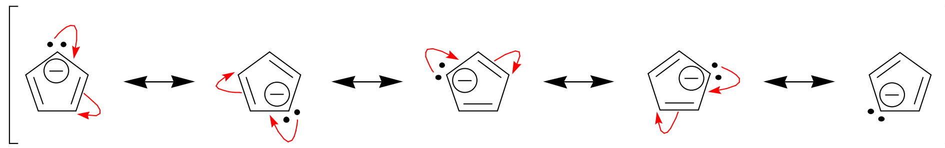

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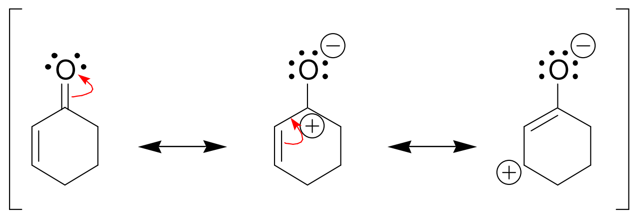

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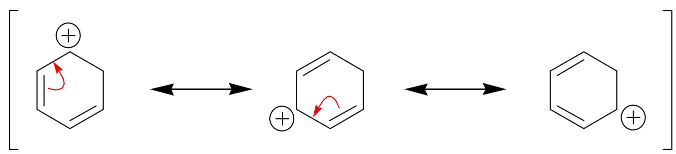

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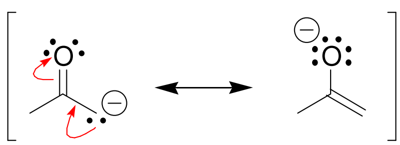

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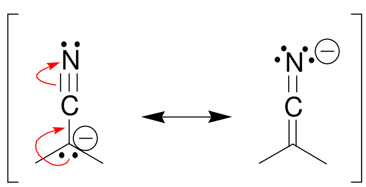

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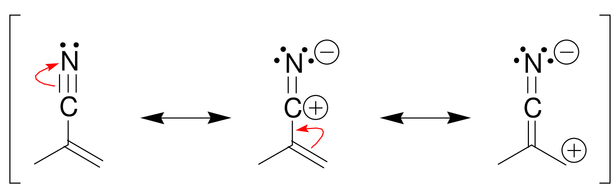

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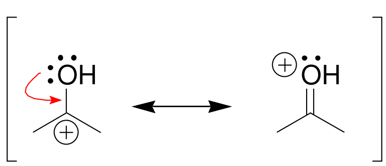
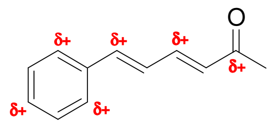


2.34.



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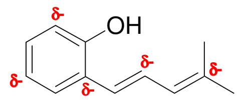
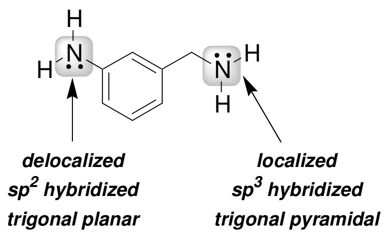
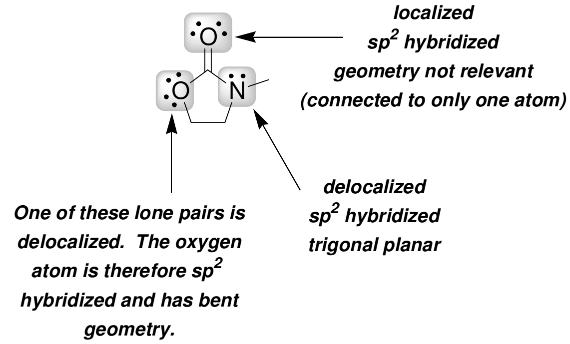
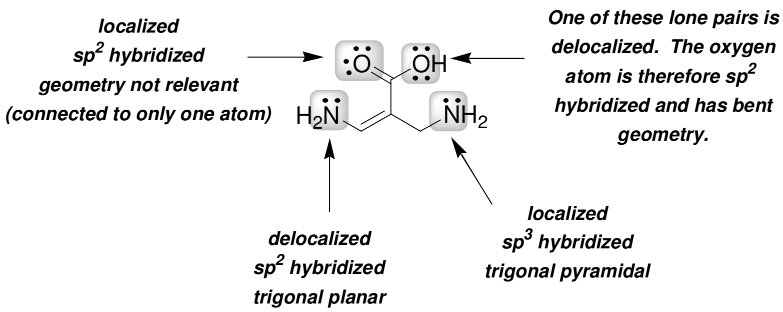
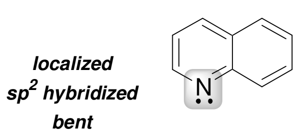


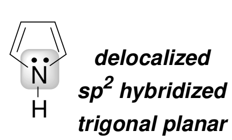
2.36.

a) 

b) 

c) 

d) 

e) 

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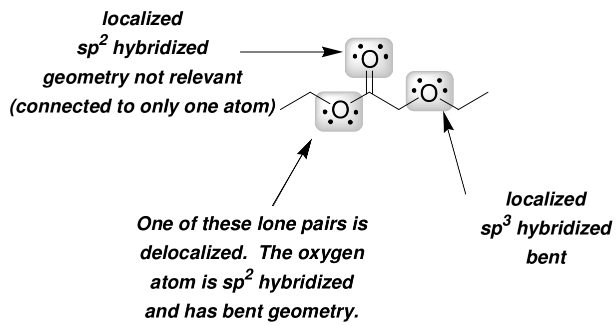
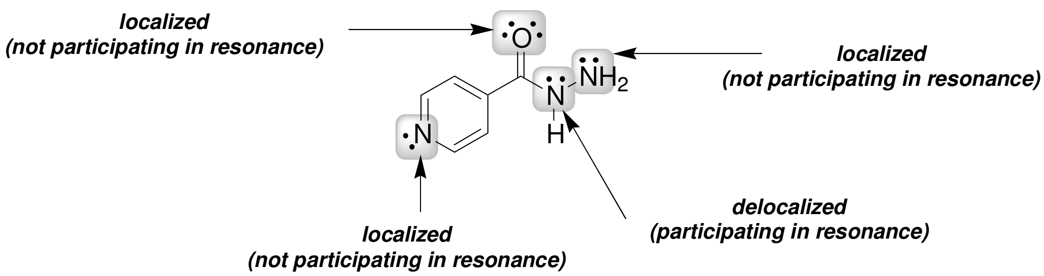
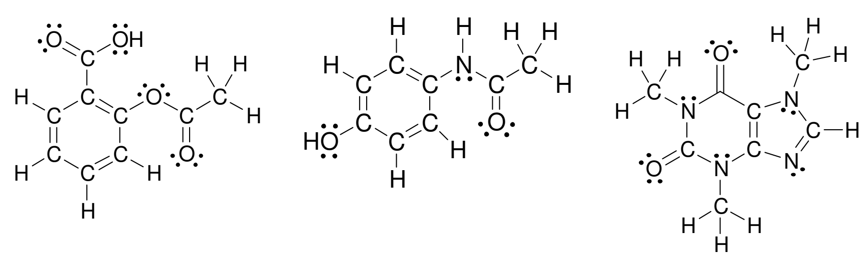


2.37. Both lone pairs are localized and, therefore, both are expected to be reactive.

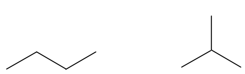
2.38.



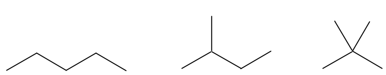
2.39.



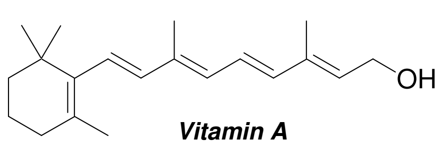
2.40.



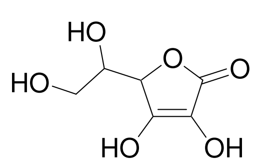
2.41.



2.42.



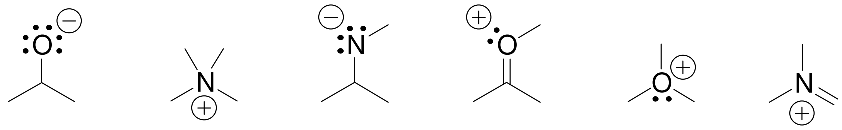
Vitamin A



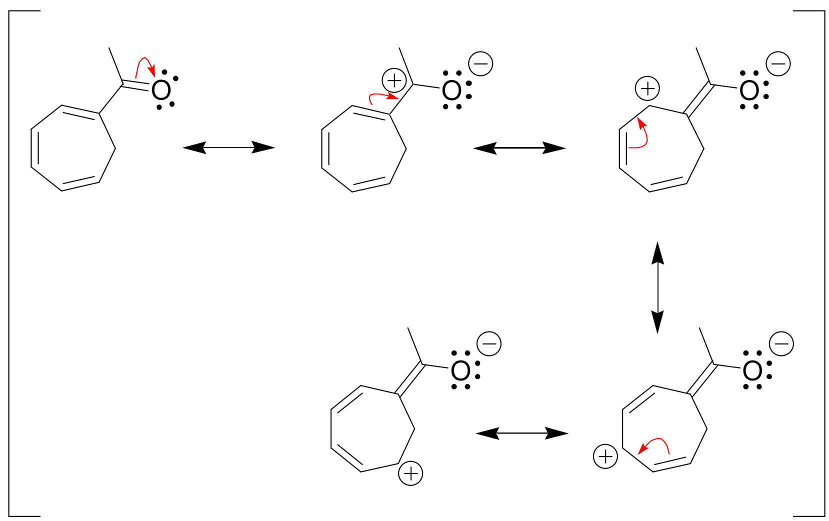
Vitamin C

2.43. Twelve (each oxygen atom has two lone pairs)

2.44.

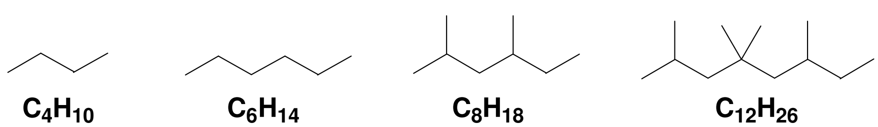


2.45.



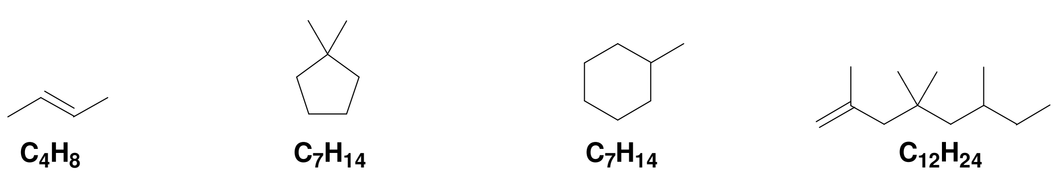
2.46.

a)



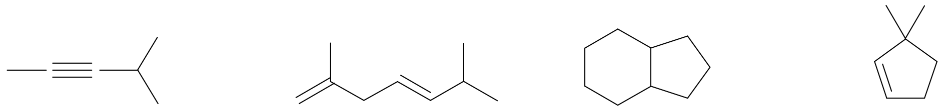
In each of the compounds above, the number of hydrogen atoms is equal to two times the number of carbon atoms, plus two.

b)



In each of the compounds above, the number of hydrogen atoms is two times the number of carbon atoms.

c)

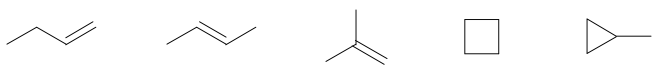


C_6H_{10} C_9H_{16} C_9H_{16} C_7H_{12}

In each of the compounds above, the number of hydrogen atoms is two times the number carbon atoms, minus two.

d) A compound with molecular formula $C_{24}H_{48}$ must have either one double bond or one ring. It cannot have a triple bond, but it may have a double bond.

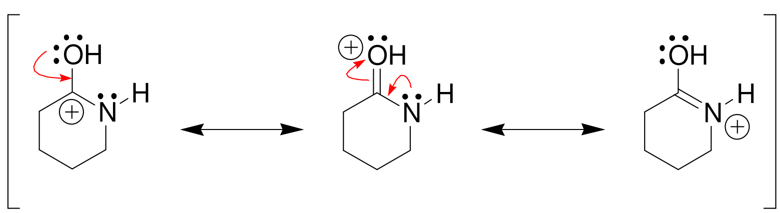
e)

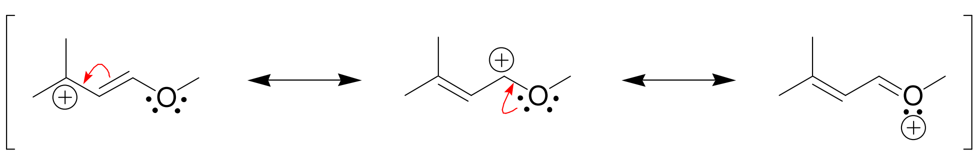


2.47.

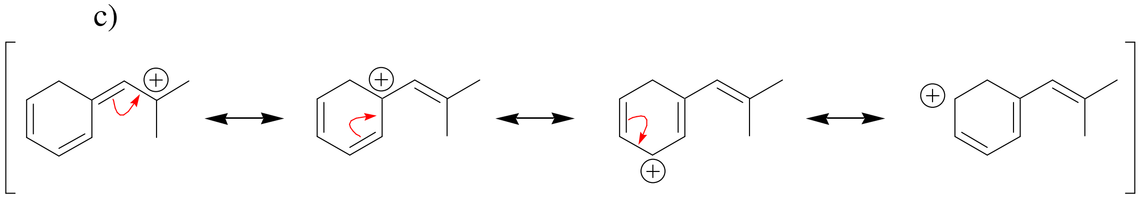
a) an sp^2 hybridized atomic orbital
b) a *p* orbital
c) a *p* orbital

2.48.

a) 

b) 

c)



2.49.

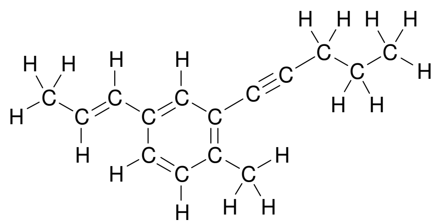
a) $(CH_3)_3CCH_2CH_2CH(CH_3)_2$
b) $(CH_3)_2CHCH_2CH_2CH_2OH$
c) $CH_3CH_2CH{=}C(CH_2CH_3)_2$

2.50.

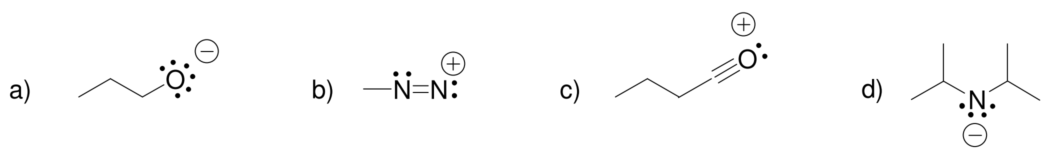
a) C_9H_{20}
b) $C_6H_{14}O$
c) C_8H_{16}

2.51.
(d) is not a valid resonance structure, because it violates the octet rule. The nitrogen atom has five bonds in this drawing, which is not possible, because the nitrogen atom only has four orbitals with which it can form bonds.

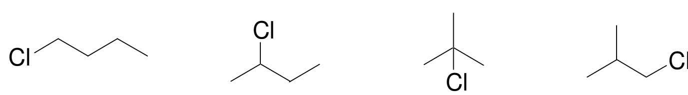
2.52. 15 carbon atoms and 18 hydrogen atoms:



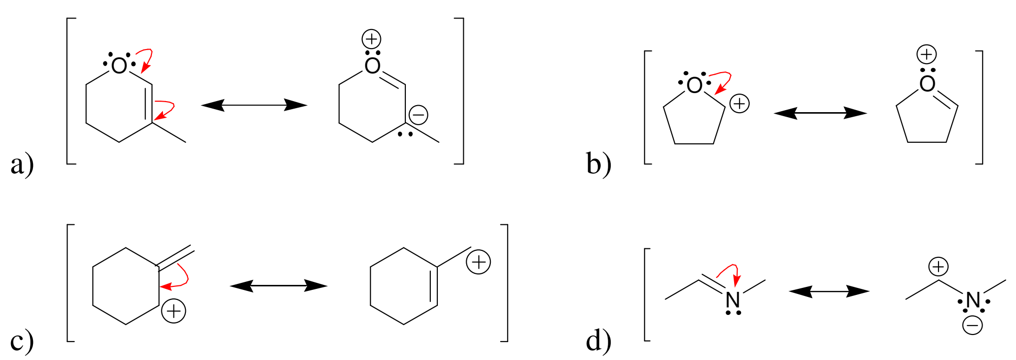
2.53.



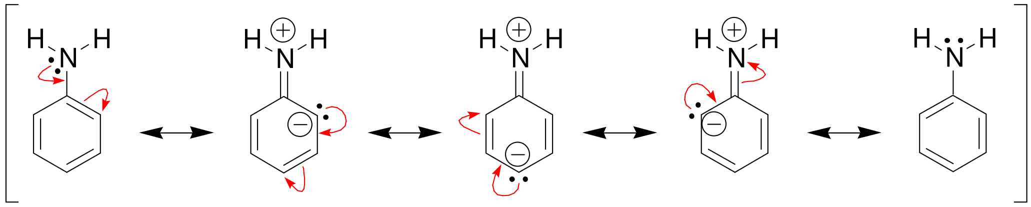
2.54.



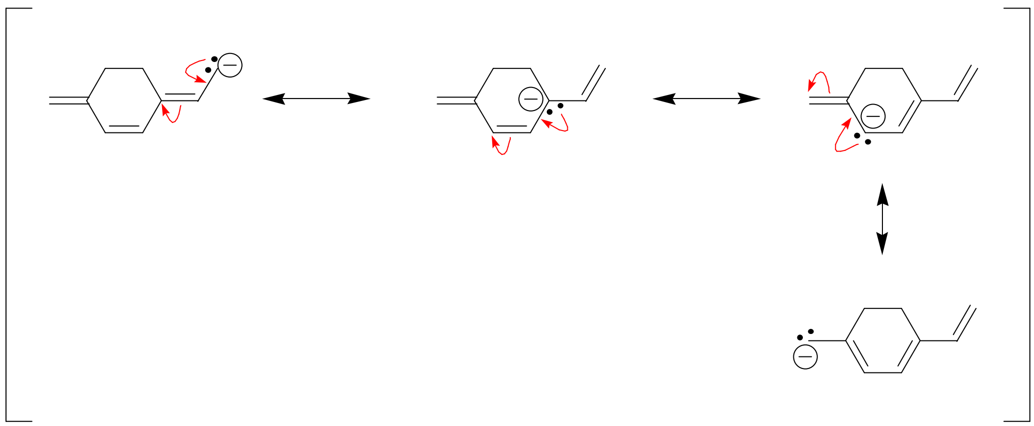
2.55.



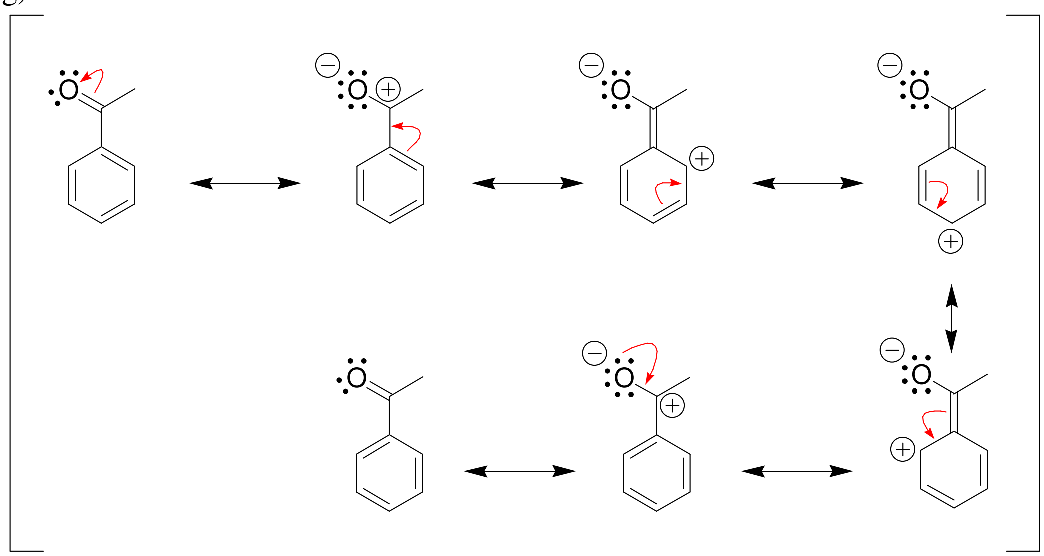
e)



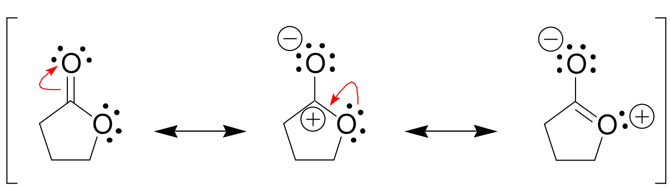
f)



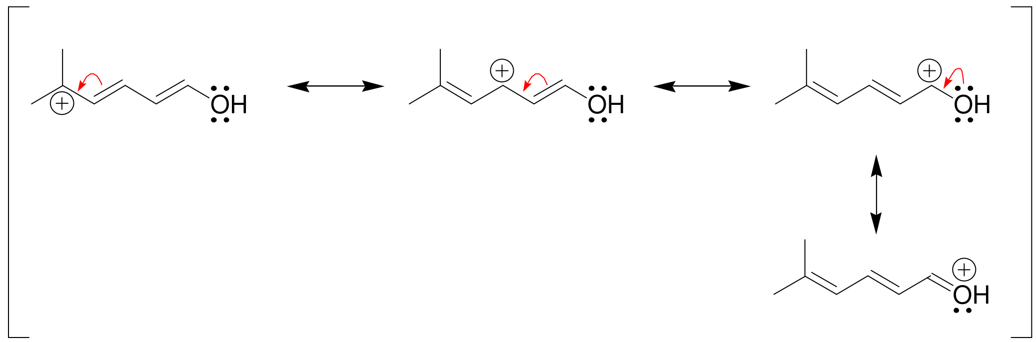
g)



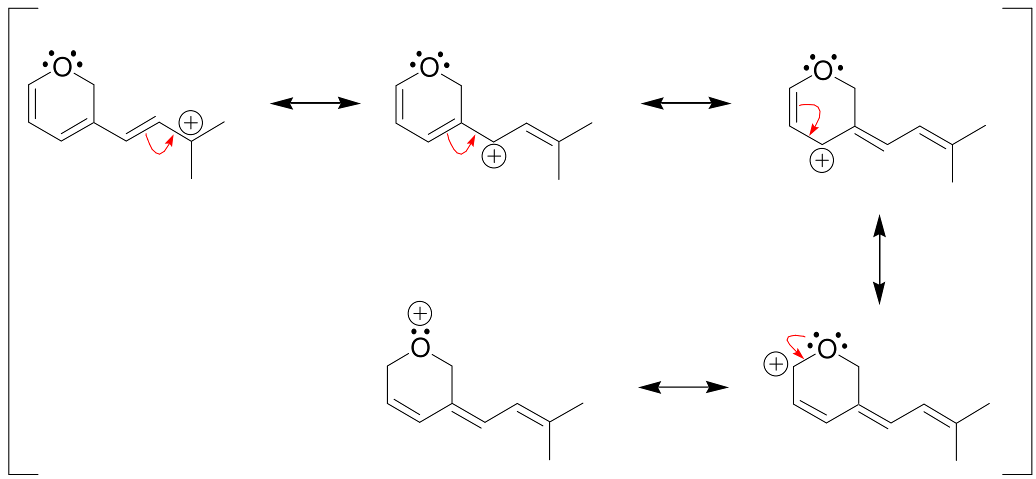
h)



i)



j)

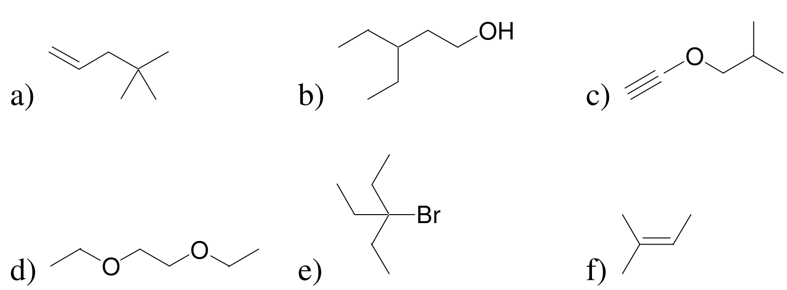


2.56. These structures do not differ in their connectivity of atoms. They differ only in the placement of electrons, and are therefore resonance structures.

2.57.

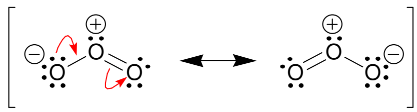
a) constitutional isomers
b) same compound
c) different compounds that are not isomeric
d) constitutional isomers

2.58.



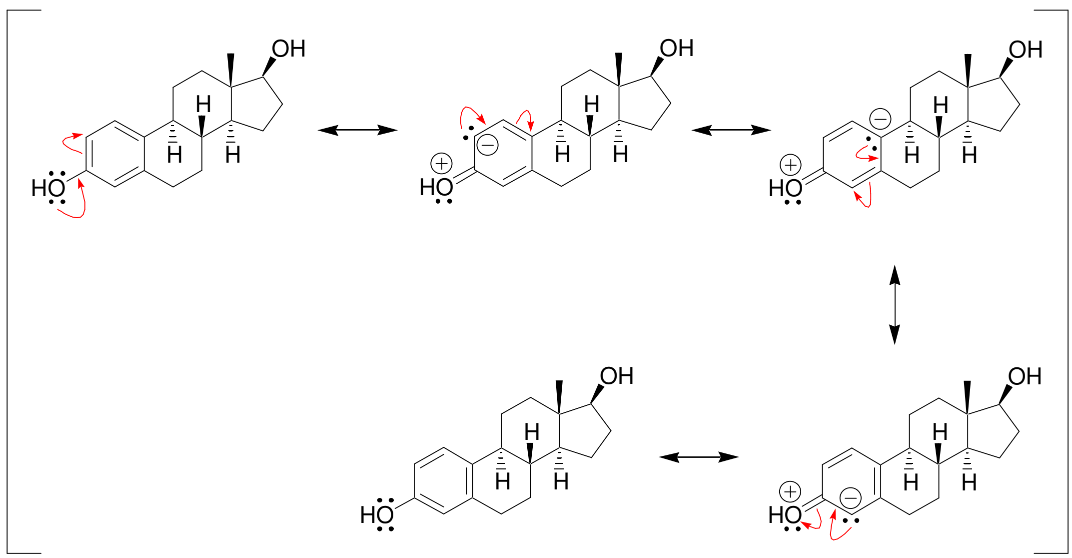
2.59. The nitronium ion does *not* have any significant resonance structures because any attempts to draw a resonance structure will either 1) exceed an octet for the nitrogen atom or 2) generate a nitrogen atom with less than an octet of electrons, or 3) generate a structure with three charges. The first of these would not be a valid resonance structure, and the latter two would not give significant resonance structures.

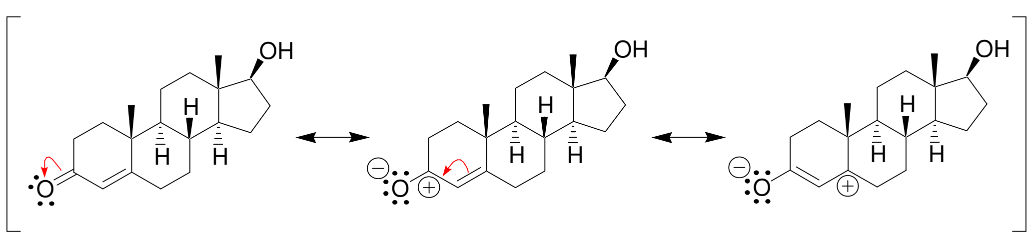
2.60.



2.61. Both nitrogen atoms are sp^2 hybridized and trigonal planar, because in each case, the lone pair participates in resonance.

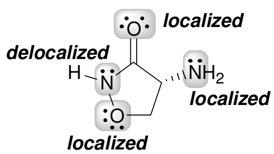
2.62.



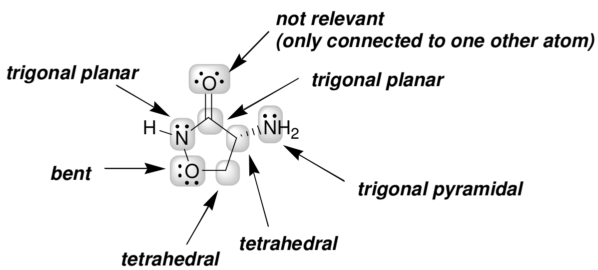


2.63.

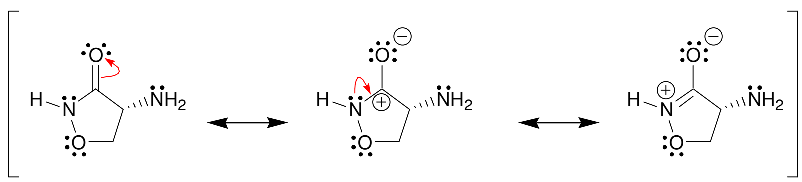
a) The molecular formula is $C_3H_6N_2O_2$
b) There are two *sp*^{3} hybridized carbon atoms
c) There is one *sp*^{2} hybridized carbon atom
d) There are no *sp* hybridized carbon atoms
e) There are six lone pairs (each nitrogen atom has one lone pair and each oxygen atom has two lone pairs)
f)



g)



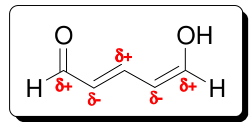
h)

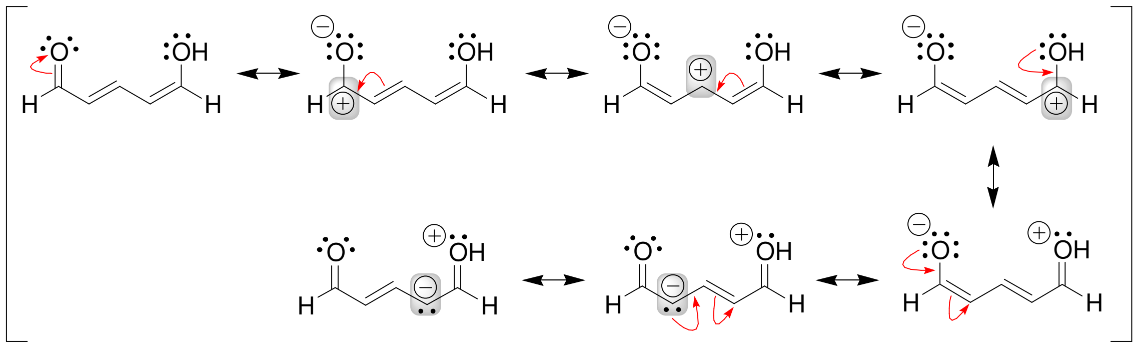


2.64.

a) The molecular formula is $C_{16}H_{21}NO_2$
b) There are nine *sp*^{3} hybridized carbon atoms
c) There is seven *sp*^{2} hybridized carbon atoms
d) There are no *sp* hybridized carbon atoms
e) There are five lone pairs (the nitrogen atom has one lone pair and each oxygen atom has two lone pairs)
f) The lone pairs on the oxygen of the C=O bond are localized. One of the lone pairs on the other oxygen atom is delocalized. The lone pair on the nitrogen atom is delocalized.
g) All *sp*^{2} hybridized carbon atoms are trigonal planar. All *sp*^{3} hybridized carbon atoms are tetrahedral. The nitrogen atom is trigonal planar. The oxygen atom of the C=O bond does not have a geometry because it is connected to only one other atom, and the other oxygen atom has bent geometry.

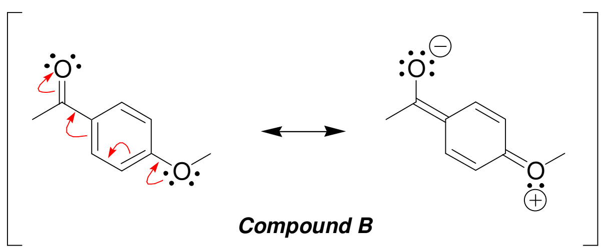
2.65.





2.66.

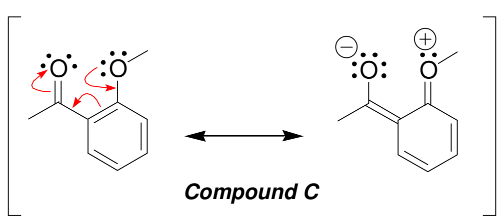
a) Compound B has one additional resonance structure that Compound A lacks, because of the relative positions of the two groups on the aromatic ring. Specifically, Compound B has a resonance structure in which one oxygen atom has a negative charge and the other oxygen atom has a positive charge:



Compound B

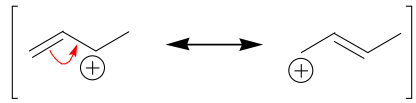
Compound A does *not* have a resonance structure in which one oxygen atom has a negative charge and the other oxygen atom has a positive charge. That is, Compound A has fewer resonance structures than Compound B. Accordingly, Compound B has greater resonance stabilization.

b) Compound C is expected to have resonance stabilization similar to that of Compound B, because Compound C also has a resonance structure in which one oxygen atom has a negative charge and the other oxygen atom has a positive charge:

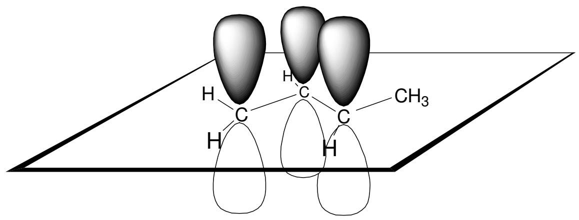


Compound C

2.67.
The single bond mentioned in this problem has some double bond character, as a result of resonance:



Each of the carbon atoms of this single bond uses an atomic p orbital to form a conduit (as described in Section 2.7):



Rotation about this single bond will destroy the overlap of the p orbitals, thereby destroying the resonance stabilization. This single bond therefore exhibits a large barrier to rotation.