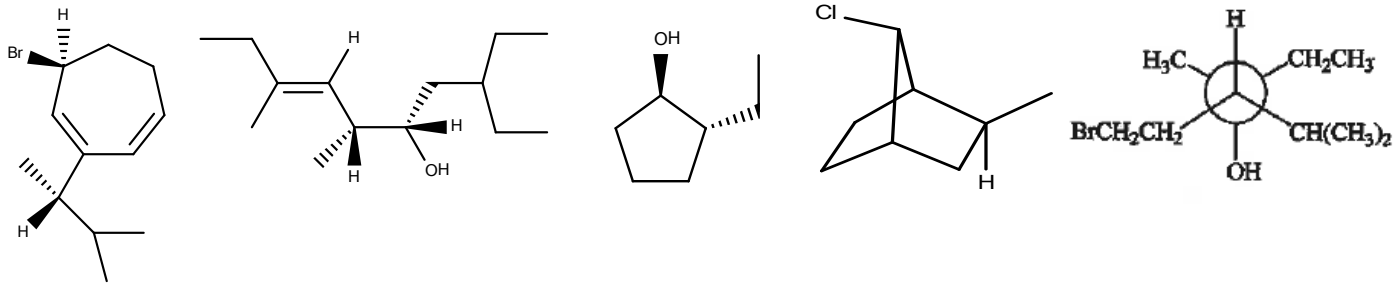
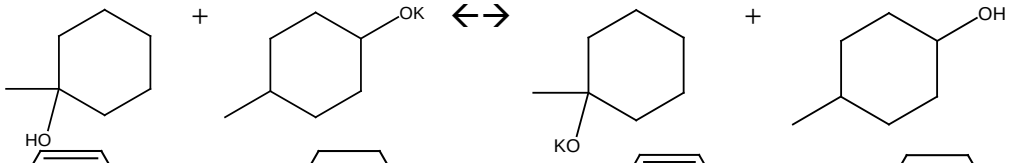
Organic Chemistry Practice Problems

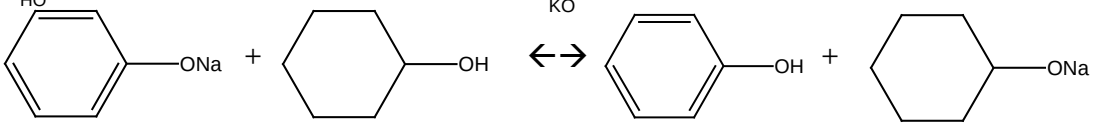
Organic Chemistry I Practice Set #12 (Cumulative – Carey)

1. For each of the following compounds, provide a name. ***Each compound is a single pure stereoisomer.*** Be sure to name stereoisomers properly.

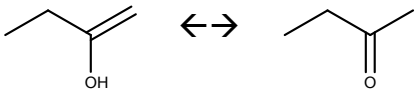


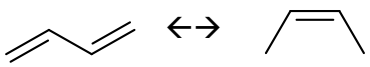
2. For each of the following, provide a structural formula. Be sure to identify stereoisomers properly.
   (a) a Fischer projection of (3R,4S)-3,4-dichloro-2,4-dimethylhexane
   (b) the more stable chair conformation of (1S, 3R)-1-*tert*-butyl-3-isopropylcyclohexane
   (c) viewing down the C2-C3 bond, give the Newman projection of the lowest energy staggered conformation of hexane
3. For each of the following, does the equilibrium lie to the ***left*** or to the ***right*** ?
   (a) $HBr + H_2O \leftrightarrow H_3O^+ + Br^-$
   (b) $CH_3CH_3 + NaC{\equiv}CH \leftrightarrow CH_3CH_2Na + HC{\equiv}CH$

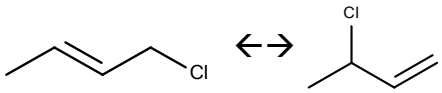
(c) 

(d) 

(e) $CH_3CH_2CH_2NHNa + CH_3CH_2CH_2OH \leftrightarrow CH_3CH_2CH_2NH_2 + CH_3CH_2CH_2ONa$

(f) 

(g) 

(h) 

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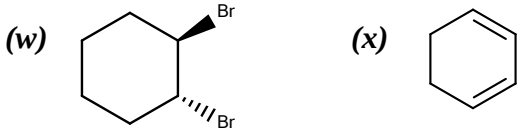
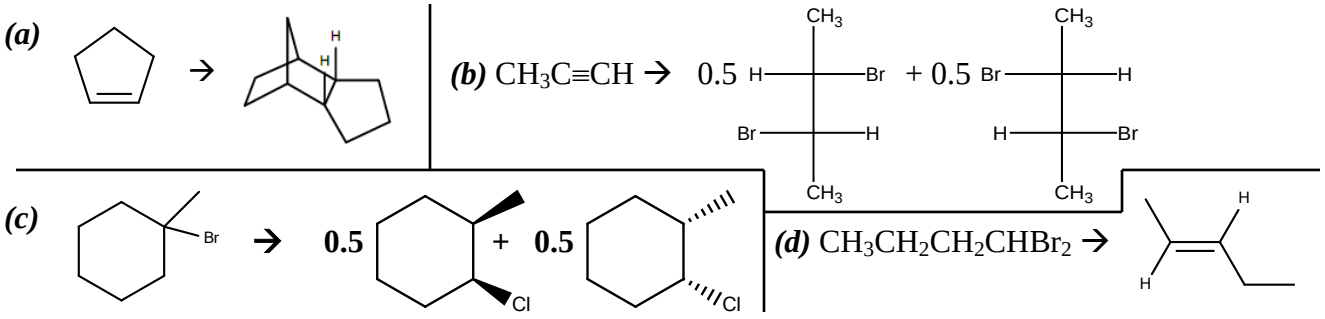
4. For each of the following, ***choose the best answer; give the letter – unless otherwise noted.***
   (a) Which compound has the higher boiling point: ***(w)*** $CH_3(CH_2)_3CH_3$ or ***(x)*** $(CH_3)_4C$
   (b) Which compound is more soluble in water: ***(w)*** $CH_3(CH_2)_3CH_2OH$ or ***(x)*** $CH_3(CH_2)_2CH_2Br$
   (c) Which compound is more soluble in water: ***(w)*** $CH_3CH_2CH_2CH_2OH$ or ***(x)*** $CH_3CH_2CH_2OH$
   (d) Which one is more oxidized: ***(If they are the same; give both letters)***



   (e) Which one is more oxidized: ***(w)*** cyclohex-2-enol or ***(x)*** cyclohexanol ***(If the same; give both letters)***
   (f) Which one has the higher pK_a: ***(w)*** phenol or ***(x)*** cyclohexanol
   (g) Which one has the lower pK_a: ***(w)*** $CH_3CH_2CH_2CH_2OH$ or ***(x)*** $(CH_3)_3COH$
   (h) Which one is the stronger base: ***(w)*** ethoxide ion or ***(x)*** *tert*-butoxide ion
   (i) Which reaction of 1-chloropropane is faster: ***(w) NaN_3 in ethanol*** or ***(x) NaN_3 in DMSO***
   (j) Which reaction with sodium azide is faster:
   (w) 1-methylpropyl tosylate in DMSO or ***(x) butyl tosylate in DMSO***
   (k) Which reacts faster via S_N1: ***(w) 2-bromo-4-methylhexane*** or ***(x) 2-bromo-2-methylhexane***
   (l) Which reaction of 1-bromohexane proceeds via an E2 mechanism to give the major product:
   (w) $KOC(CH_3)_3$ in $(CH_3)_3COH$ or ***(x) $NaOCH_3$ in CH_3OH***
   (m) Which one is thermodynamically more stable: ***(w) 1,4-pentadiene*** or ***(x) 1,3-pentadiene***
   (n) Which one has the smaller heat of hydrogenation to give pentane: ***(w)*** (E)-1,3- or ***(x)*** 1,4-pentadiene
   (o) Which one reacts with NaI in acetone faster: ***(w) 1-chlorobutane*** or ***(x) 2-iodopentane in DMSO***
   (p) Which rxn w/sodium azide is faster: ***(w) 1-iodopentane in DMSO*** or ***(x) 2-iodopentane in DMSO***
   (q) Which substrate reacts faster via an S_N1 mechanism:
   (w) 1-bromo-1-ethylcyclohexane or ***(x) trans-1-bromo-4-ethylcyclohexane***
   (r) By which mechanism does the reaction of bromocyclohexane with sodium ethynide in liquid ammonia give the major product: ***(w) S_N1 (x) S_N2 (y) E1*** or ***(z) E2***
   (s) Which one is thermodynamically more stable: ***(w) allyl radical*** or ***(x) propyl radical***

5. Provide an efficient multistep synthesis for each of the following conversions of the given starting material into product. For each transformation, give all necessary reagents and catalysts and give a structural formula of the organic product. Show stereochemistry appropriately when necessary.



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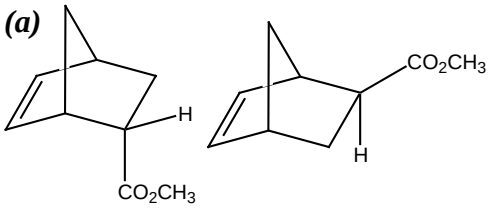
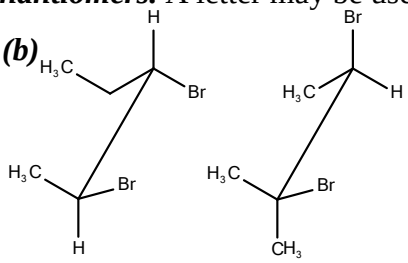
6. For each of the following pairs, give the best answer which best describes the relationship between the two molecules in the pair. Choose one from the following: ***(w) the same molecule; (x) constitutional isomers; (y) diastereomers;*** or ***(z) enantiomers.*** A letter may be used more than once or not at all.

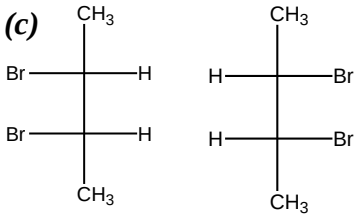
(a)



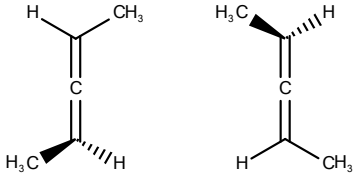
(b)



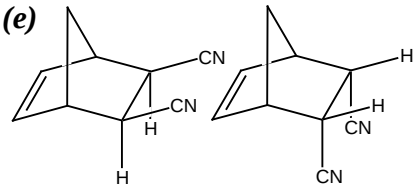
(c)



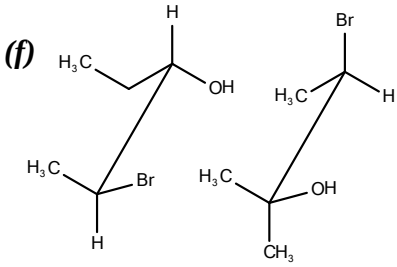
(d)



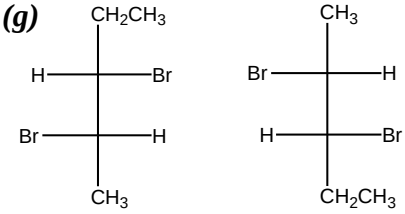
(e)



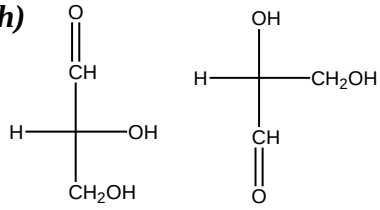
(f)



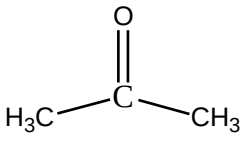
(g)



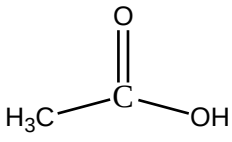
(h)



7. Consider the pair of molecules shown. Using Lewis structures for reactants and products and using curved arrows to show the flow of electrons for each molecule in the pair, give the chemical equation that shows the loss of the most acidic H to give H^+ and the corresponding conjugate base. Using structural considerations identify which of the molecules is the more acidic one and provide a clear, concise explanation why one is more acidic than the other. Use Lewis structures (and resonance structures when possible) in your explanation. For the Lewis structures you give you must show all atoms, all bonding valence electrons, all nonbonding valence electrons, and all nonzero formal charges.



acetone



acetic acid

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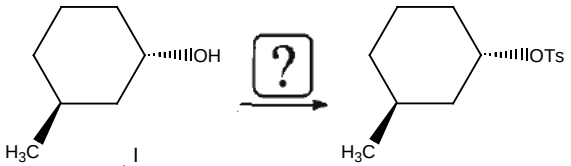
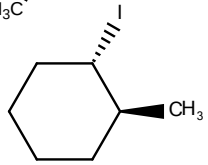
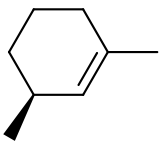
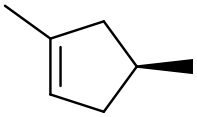
8. Fill in what is missing. Either give all of the missing reagents to complete the reaction or give a structural formula for the ***major organic product(s).*** Show stereoisomers properly if necessary. If no reaction occurs, write ***N.R. If the product is a racemic mixture, show both structures.***

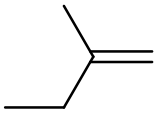
(a) 

(b) 

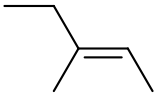
$KOC(CH_3)_3$, DMSO, ?

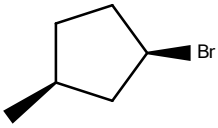

1. H_3B-THF
2. NaOH, H_2O_2
?


CH_3CO_3H, ?

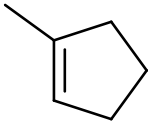

HBr, peroxides, ?

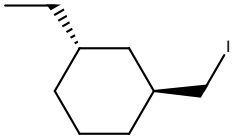
$CH_3C{\equiv}CCH_3$? 


HCl, ?

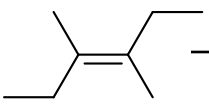


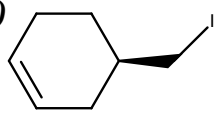
NaOH, DMSO, ?


1. O_3
2. H_2O, Zn
?

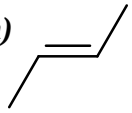


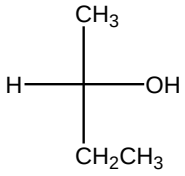
$NaC{\equiv}CH$, NH_3, ?


H_2, Lindlar Pd, ?

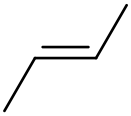
(l) 

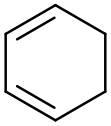
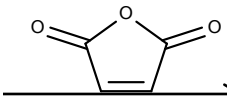
$NaOCH_3$, CH_3OH, ?

(m) 
Cl_2, ?



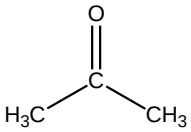
?

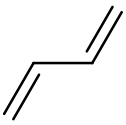


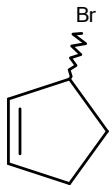
heat, ?

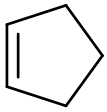
$CH_3C{\equiv}CH$?

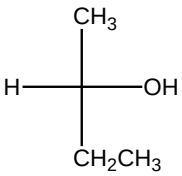



1 eq. HBr, 25°C, ?

$CH_3C{\equiv}CCH_3$ 1 eq. Br_2, ?




?



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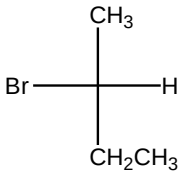
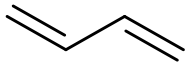


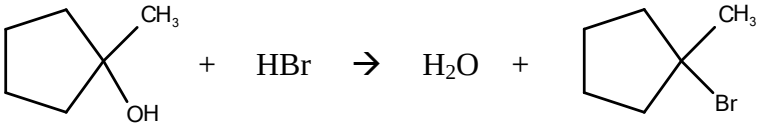
(u) 
1 eq. HBr, -80°C, ?

(v) **$CH_3CH_2CHBr_2$** 3 eq. $NaNH_2$, NH_3, ?

Organic Chemistry Practice Problems

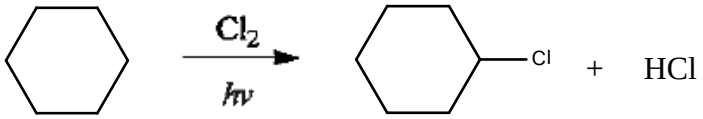
9. Consider the following reaction. Using arrows to show the flow of electrons, write a stepwise mechanism for this reaction.

(a)



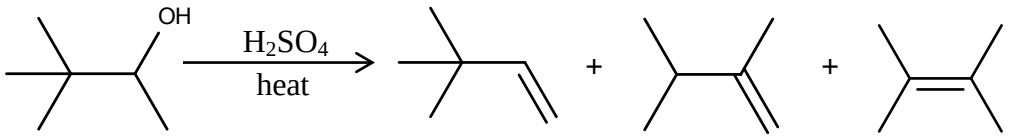
Using arrows to show the flow of electrons, write a stepwise mechanism for the following reaction. If the mechanism is a free-radical chain reaction, label each stem as either ***initiation, propagation, or termination***; ***also give three termination steps.***

(b)



Using arrows to show the flow of electrons, write a stepwise mechanism for the following reaction. Show how each product is formed.

(c)

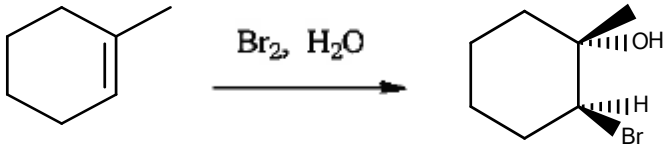


Using arrows to show the flow of electrons, write a stepwise mechanism for each of the following reactions. If the reaction proceeds via a free-radical mechanism, label the steps appropriately.

(i)

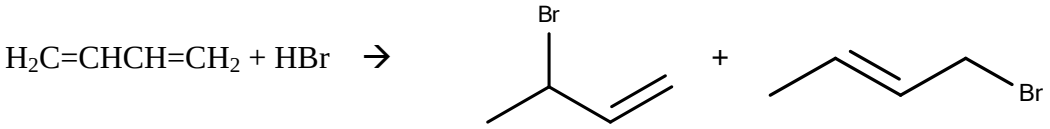
(d)

(ii)



Using arrows to show the flow of electrons, write a stepwise mechanism for the reaction shown below. For your mechanism, concisely explain why ***X = 81% yield and Y = 19% yield when the reaction is performed at -80℃*** and why ***X = 44% yield and Y = 56% yield when the reaction is performed at room temperature (25℃)***.

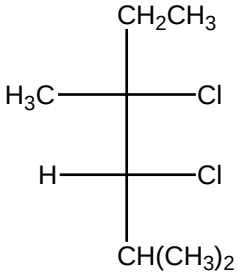
(e)

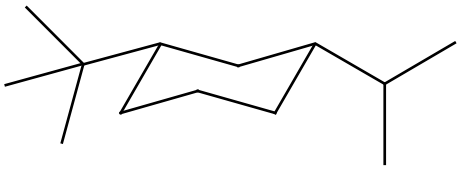


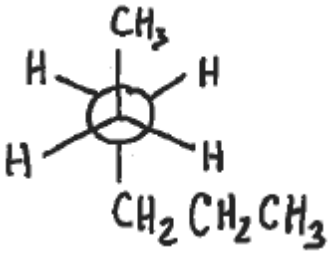
Organic Chemistry Practice Problems

Organic Chemistry I Answers to Practice Set #1 (Cumulative – Carey)

1a. (7S)-7-bromo-2-[(1S)-1,2-dimethylpropyl]cyclohepta-1,3-diene
1b. (5S, 6R, 7E)-3-ethyl-6,8-dimethyldec-7-en-5-ol
1c. (1R, 2R)-2-ethylcyclopentanol
1d. 7-chloro-2-isobutylbicyclo[2.2.1]heptane
1e. 6-bromo-4-isopropyl-3-methylhexan-3-ol

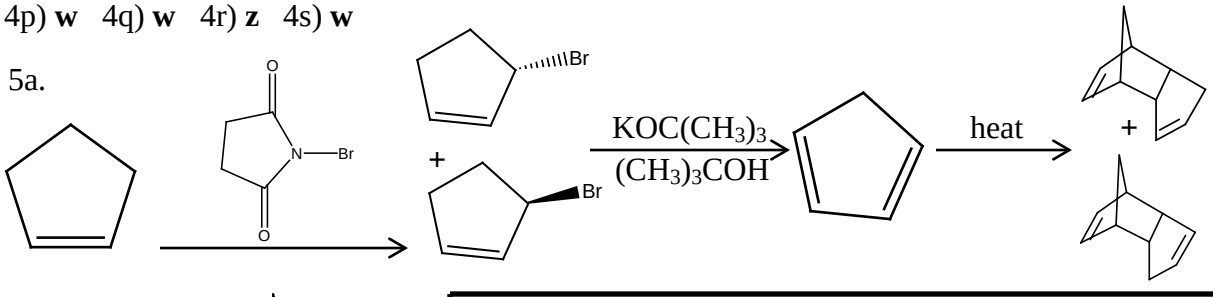
2a. 

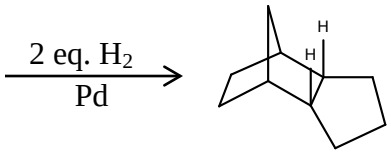
2b. 

2c. 

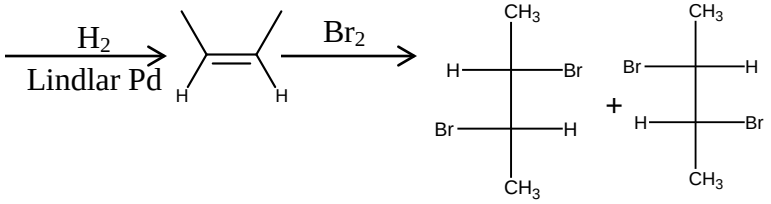
3a. right 3b. left 3c. left 3d. left 3e. right 3f. right 3g. left 3h. left

4a) **w** 4b) **w** 4c) **x** 4d) **w, x** 4e) **x** 4f) **x** 4g) **w** 4h) **x** 4i) **x** 4j) **x** 4k) **x** 4l) **w** 4m) **x** 4n) **w** 4o) **x** 4p) **w** 4q) **w** 4r) **z** 4s) **w**

5a. 



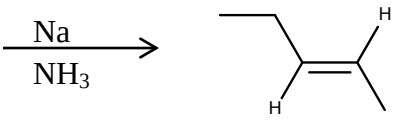
5b. **$CH_3C{\equiv}CH$** $\xrightarrow[NH_3]{NaNH_2}$ **$CH_3C{\equiv}CNa$** $\xrightarrow{CH_3Br}$ **$CH_3C{\equiv}CCH_3$**

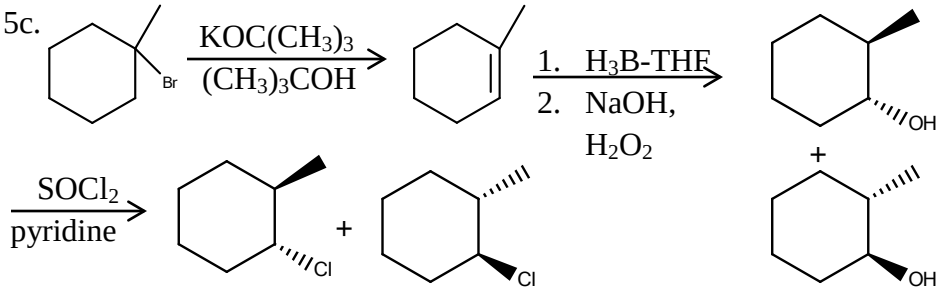


5d. **$CH_3CH_2CH_2CHBr_2$**

3 eq. $NaNH_2$, NH_3 → **$CH_3CH_2C{\equiv}CNa$**

CH_3Br → **$CH_3CH_2C{\equiv}CCH_3$**



5c. 

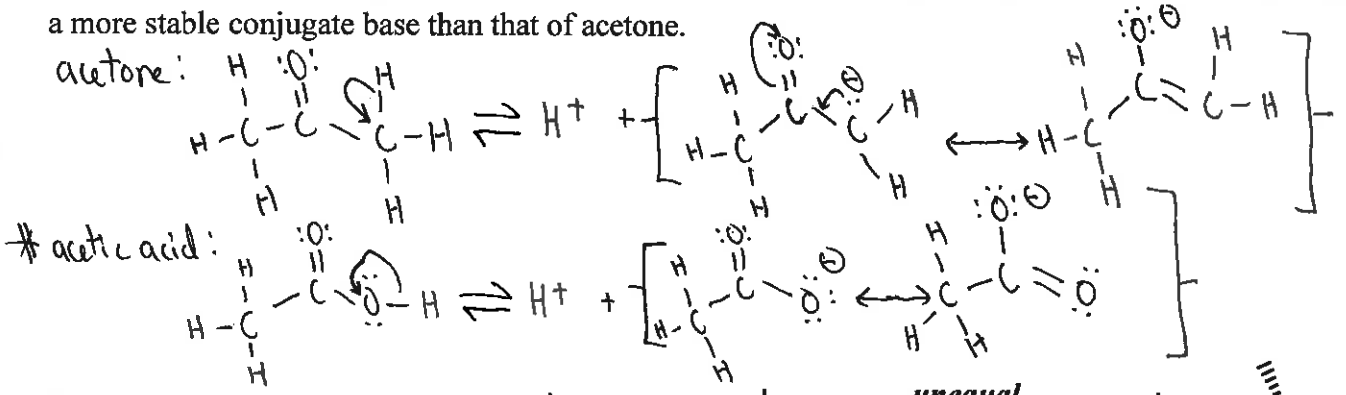
LEARNING COMMONS

Organic Chemistry Practice Problems

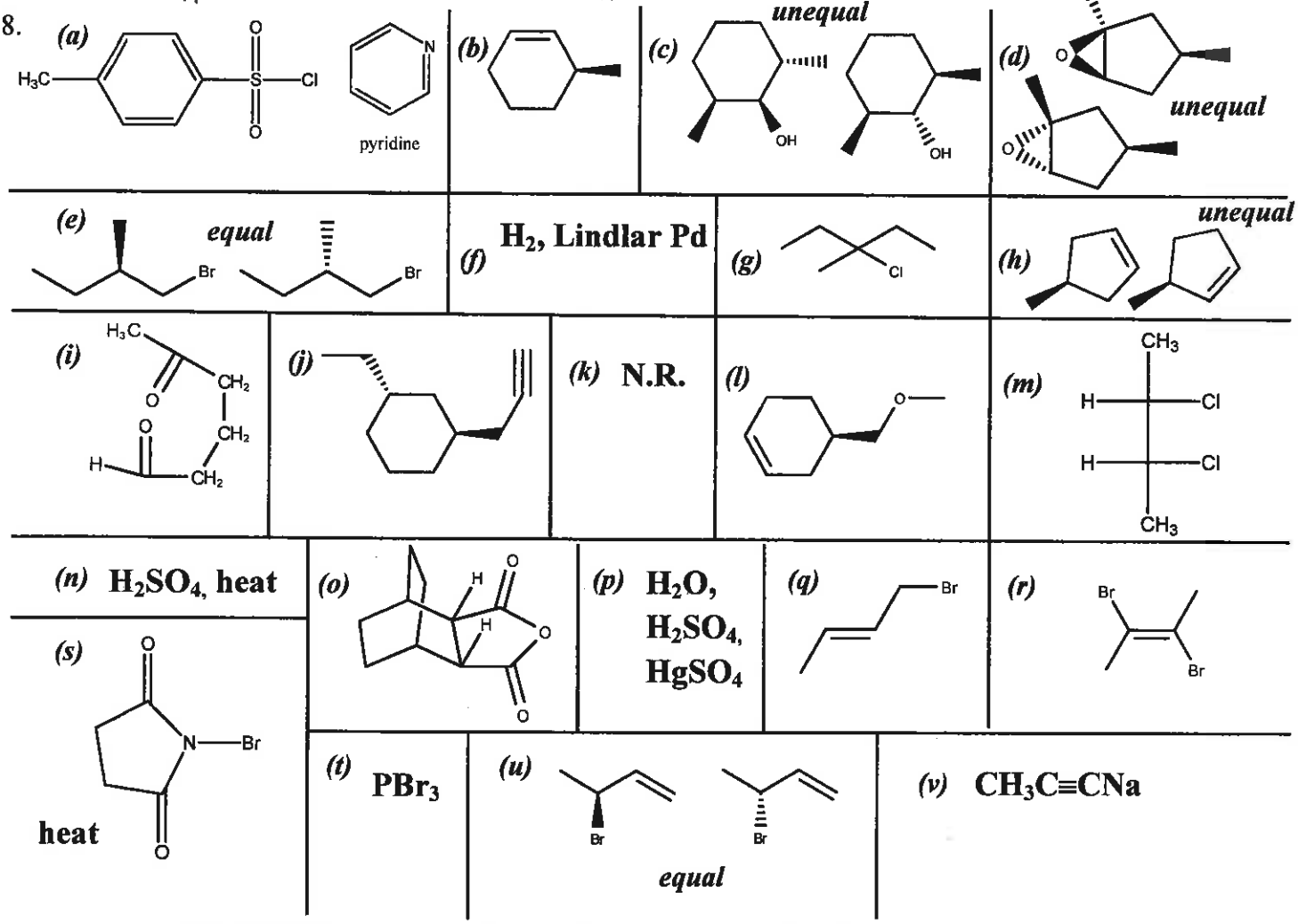
Organic Chemistry I Answers to Practice Set #12 (Cumulative – Carey)

6a. **y** 6b. **x** 6c. **w** 6d. **z** 6e. **y** 6f. **x** 6g. **z** 6h. **w**

7. Look for where the electron pair goes when the H^+ is lost to give the conjugate base. The most acidic of the H^+s is the one that produces the most stable conjugate base. For acetone, the electrons are delocalized over one O and one (less electronegative C). For acetic acid, the electrons are delocalized over ***two*** O's and therefore give a more stable conjugate base than that of acetone.



8.



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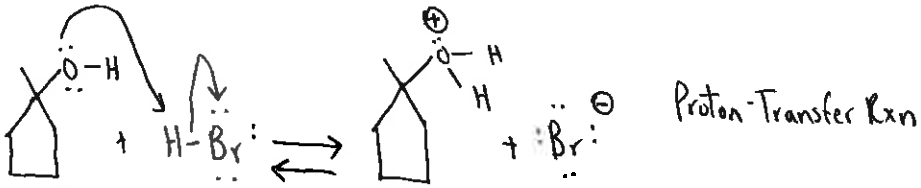
Organic Chemistry Practice Problems

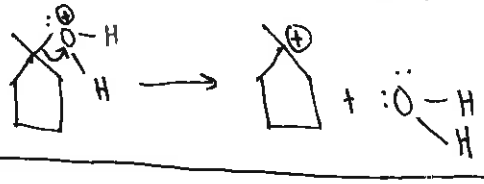
Organic Chemistry I Answers to Practice Set #12 (Cumulative – Carey)

9. a) S_N1

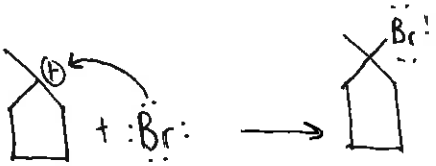
Step 1:



Step 2:



Step 3:



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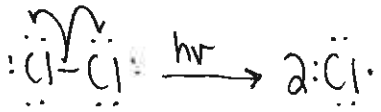
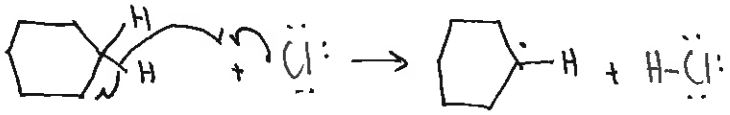
b) Free-Radical Halogenation

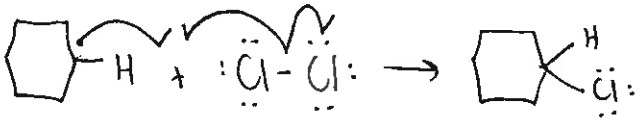
Initiation



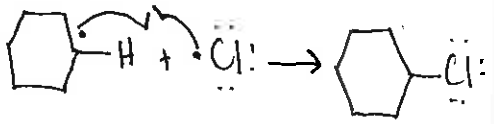
Propagation ①



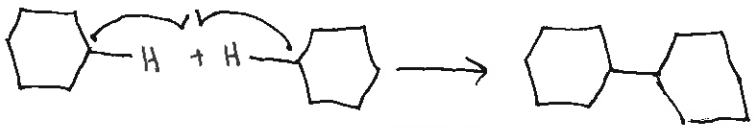
Propagation ②



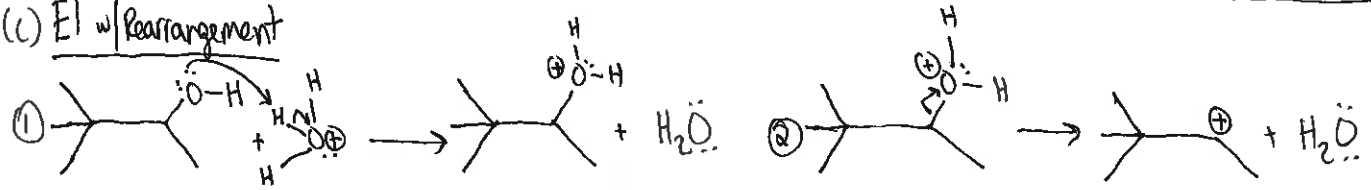
Termination ②

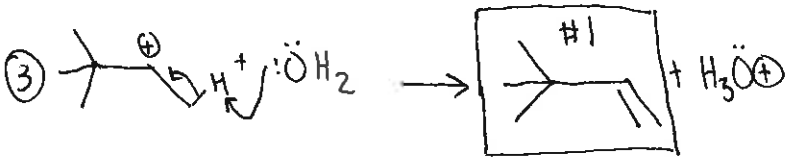


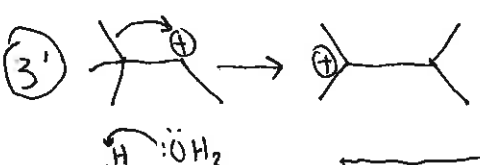
Termination ①

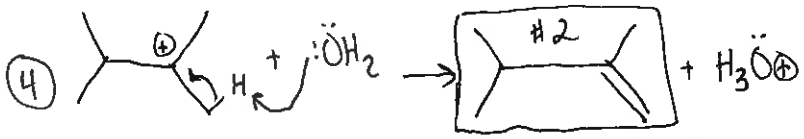


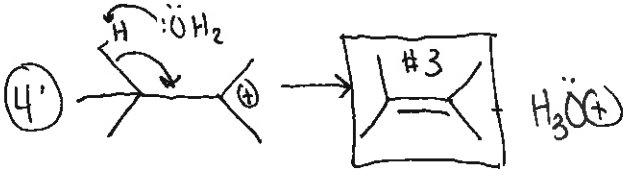
(c) E1 w/Rearrangement









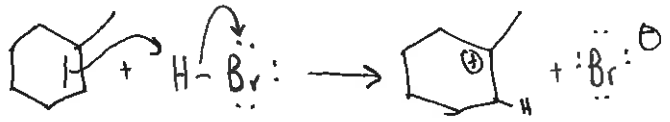


LEARNING COMMONS

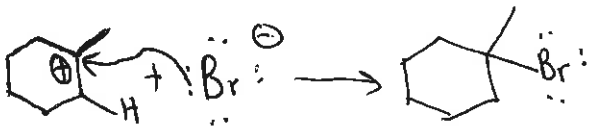
Organic Chemistry Practice Problems

Organic Chemistry I Answers to Practice Set #12 (Cumulative – Carey)

9. d) i)

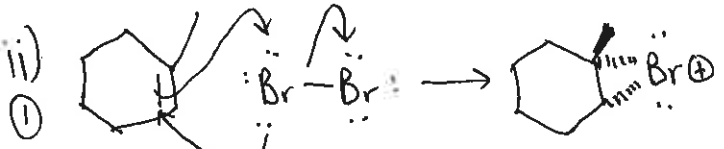


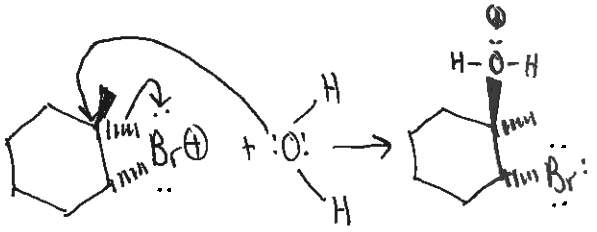
Step 1

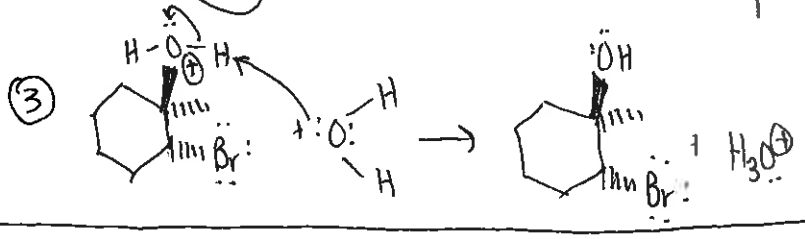


Step 2

ii)







e) $H_2C=CH-CH=CH_2 + H-\ddot{Br}: \longrightarrow [H_2C=CH-\overset{\oplus}{C}H-CH_3 \longleftrightarrow H_2C-CH=CH-CH_3] + :\ddot{Br}:^{\ominus}$

There is more $\delta^{\oplus}$ on the 2°C than the 1° C

At -80°C, 1-2 addition is favored - kinetically controlled

$H_2C=CH-\overset{\oplus}{C}H-CH_3 + :\ddot{Br}:^{\ominus} \longrightarrow H_2C=CH-\underset{\underset{:\ddot{Br}:}{|}}{CH}-CH_3$

X major product @ -80° C

At 25°C, conjugate 1,4 addition is favored → thermodynamically controlled. The double bond in Y is 1,2-disubstituted and therefore Y is more stable than X (monosubstituted)

$H_2\overset{\oplus}{C}-CH=CH-CH_3 + :\ddot{Br}:^{\ominus} \longrightarrow H_2C(Br)-CH=CH-CH_3$

Y major product @ 25° C