

Solutions

21.1.

a) IUPAC name = pentanedioic acid
Common name = glutaric acid

b) IUPAC name = butanoic acid
Common name = butyric acid

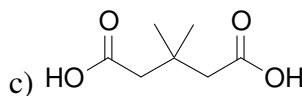
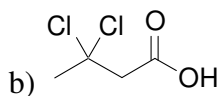
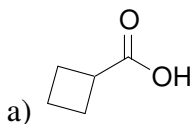
c) IUPAC name = benzene carboxylic acid
Common name = benzoic acid

d) IUPAC name = butanedioic acid
Common name = succinic acid

e) IUPAC name = ethanoic acid
Common name = acetic acid

f) IUPAC name = methanoic acid
Common name = formic acid

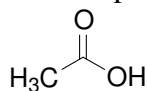
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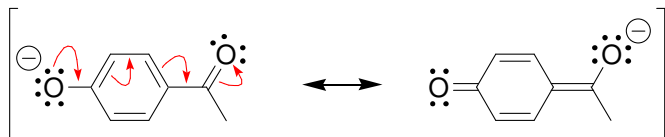
21.3.

- a) 3,3,4,4-tetramethylhexanoic acid
 b) 2-propylpentanoic acid
 c) (*S*)-2-amino-3-phenylpropanoic acid

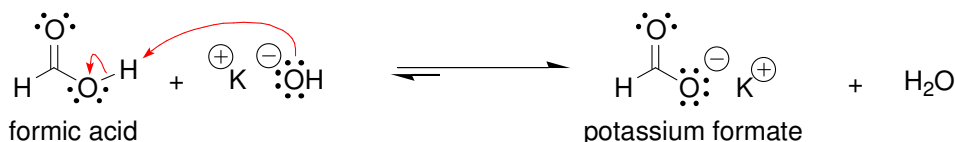
21.4. The compound below is more acidic because its conjugate base is resonance stabilized. The conjugate base of the other compound is not resonance stabilized.

**21.5.**

The conjugate base is resonance stabilized, with the negative charge spread over two oxygen atoms, just like with carboxylic acids:



21.6. *meta*-Hydroxyacetophenone should be less acidic than *para*-hydroxyacetophenone, because in the conjugate base of the former, the negative charge is spread over only one oxygen atoms (and three carbon atoms). In contrast, the conjugate base of *para*-hydroxyacetophenone has the negative charge spread over two oxygen atoms (more stable).

21.7.

21.8. The conjugate base predominates under these conditions:

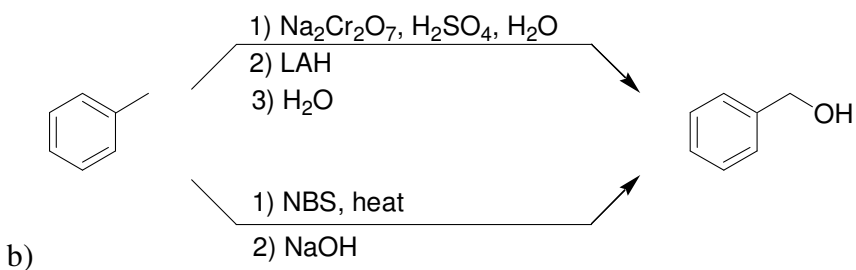
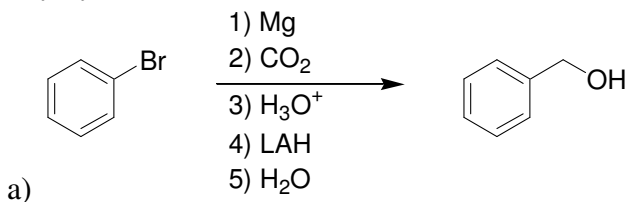
$$\frac{[\text{conjugate base}]}{[\text{acid}]} = 10^{(\text{pH} - \text{p}K_a)} = 10^{(5.76 - 4.76)} = 10^1 = 10$$

21.9.

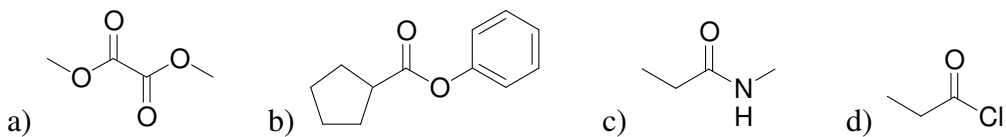
- a) 2,3-dichlorobutyric acid is the most acidic and 3,4-dimethylbutyric acid is the least acidic.
 b) 2,2-dibromopropionic acid is the most acidic and 3-bromopropionic acid is the least acidic.

21.10.

- a) $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , H_2O
 b) $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , H_2O
 c) CH_3Cl , AlCl_3 followed by $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , H_2O
 d) NaCN , followed by H_3O^+ , heat
 or Mg , followed by CO_2 , followed by H_3O^+
 e) $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , H_2O
 f) Mg , followed by CO_2 , followed by H_3O^+

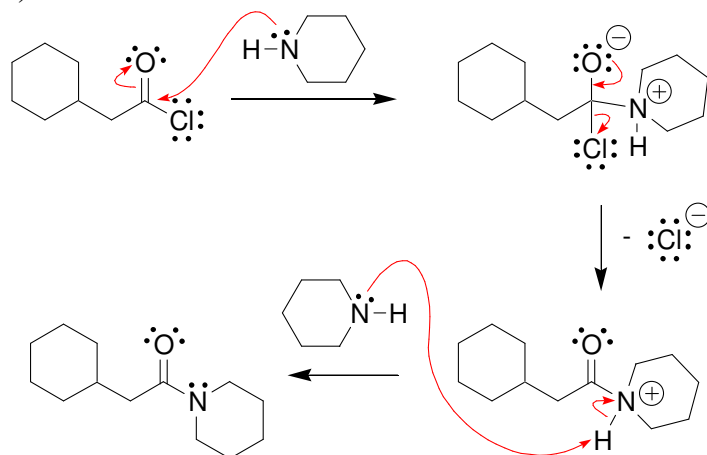
21.11.**21.12.**

- a) propionic anhydride
 b) *N,N*-diphenyl-propionamide
 c) dimethylsuccinate
 d) *N*-ethyl-*N*-methylcyclobutanecarboxamide
 e) butyronitrile
 f) propyl butyrate
 g) succinic anhydride
 h) methyl benzoate
 i) phenyl acetate

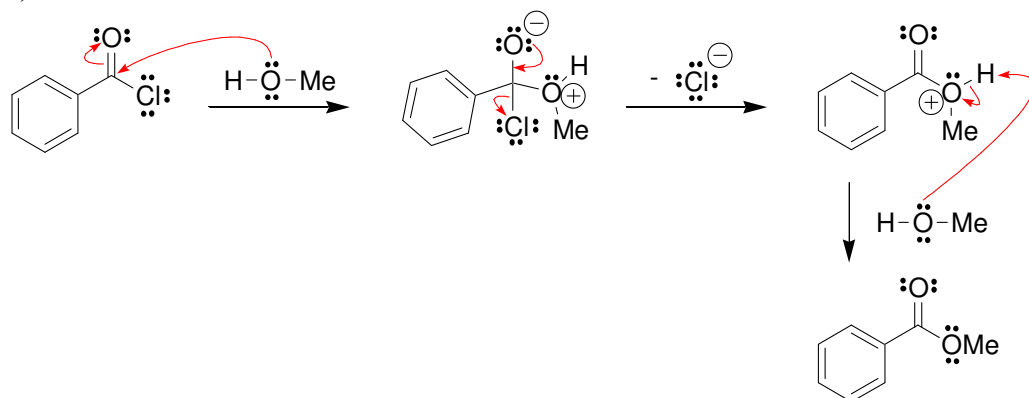
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21.14.

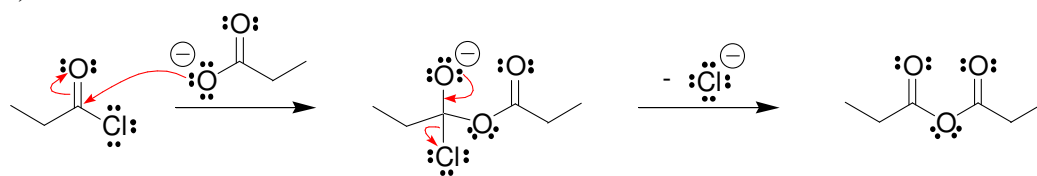
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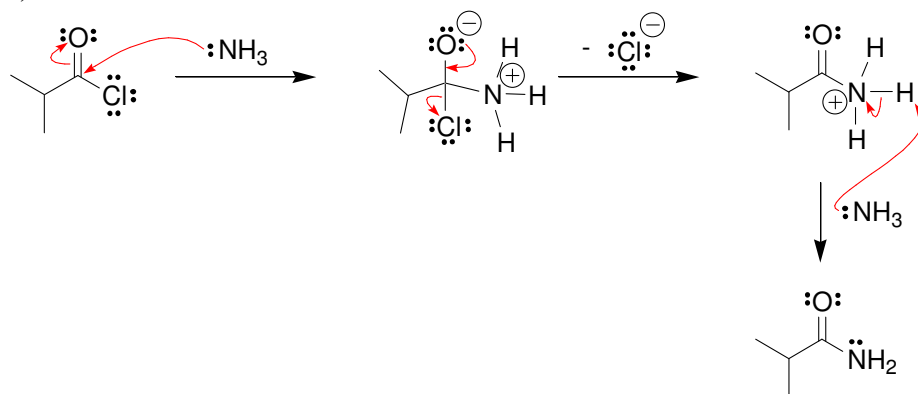
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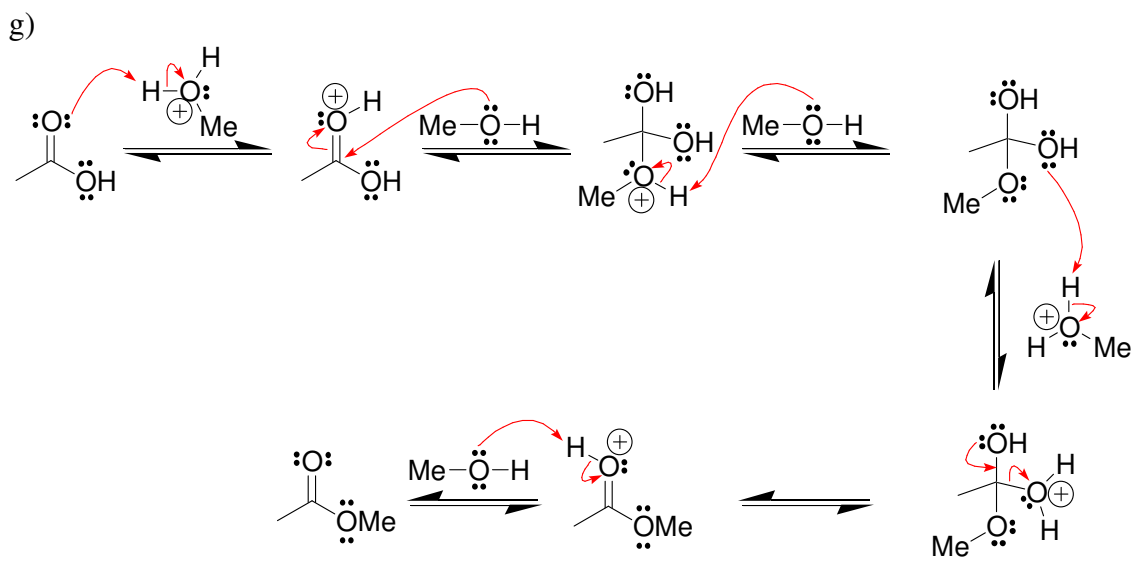
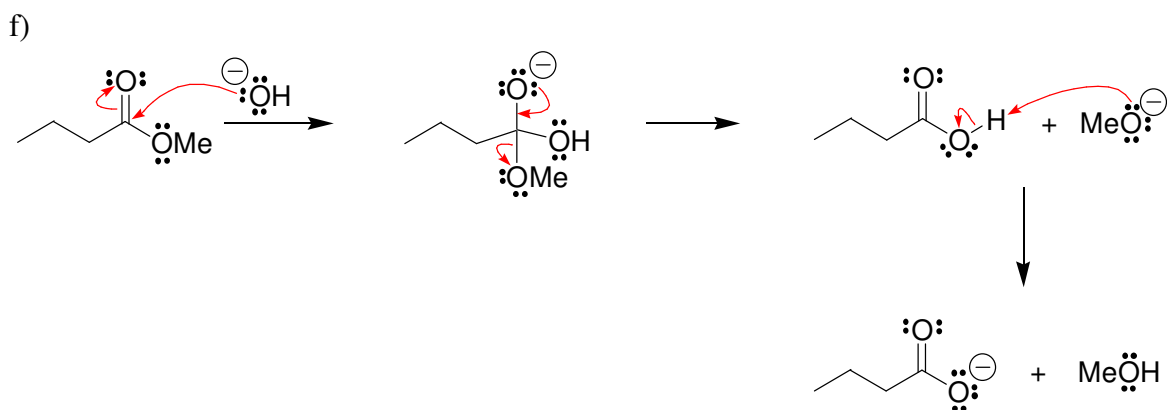
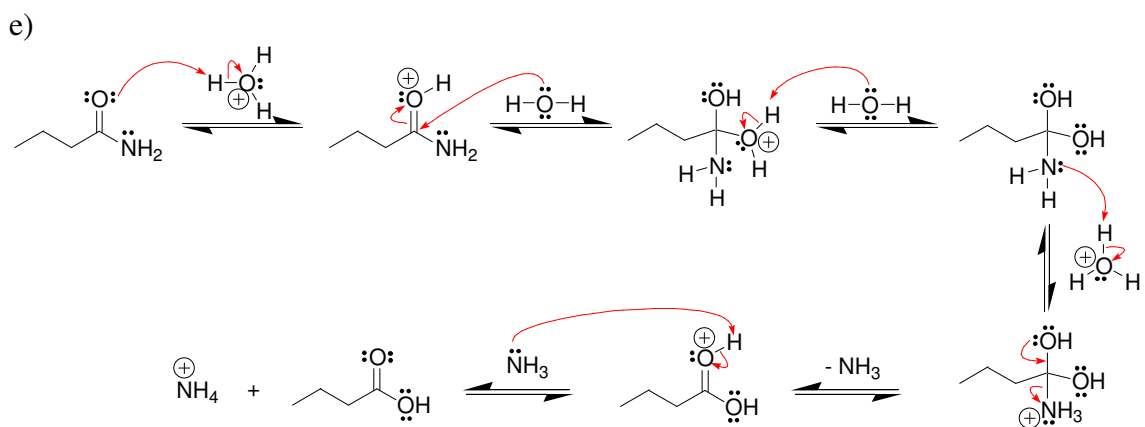


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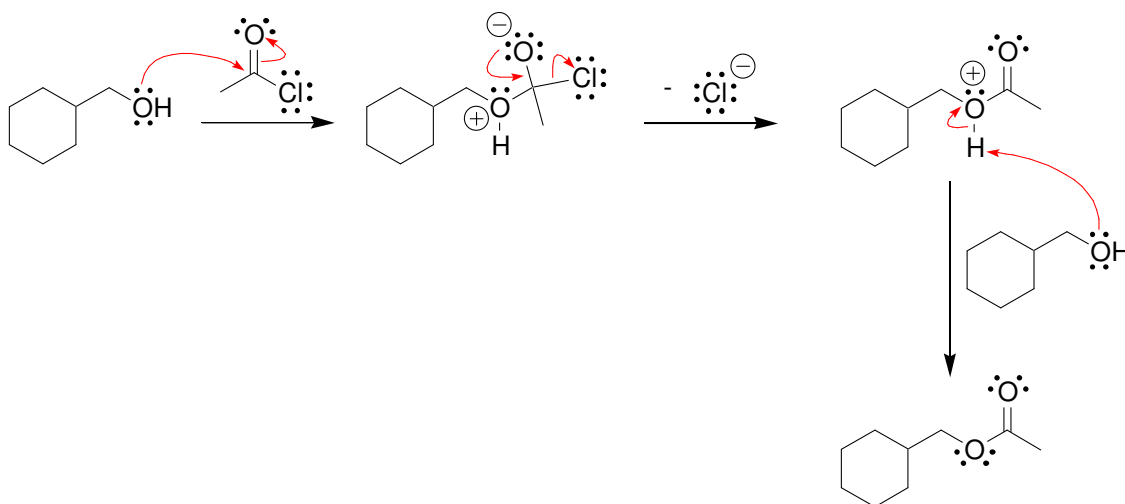


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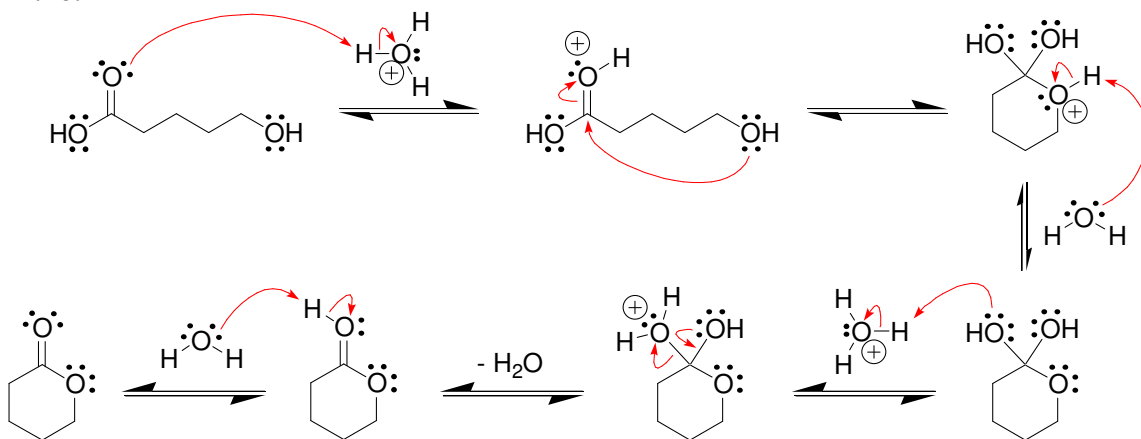




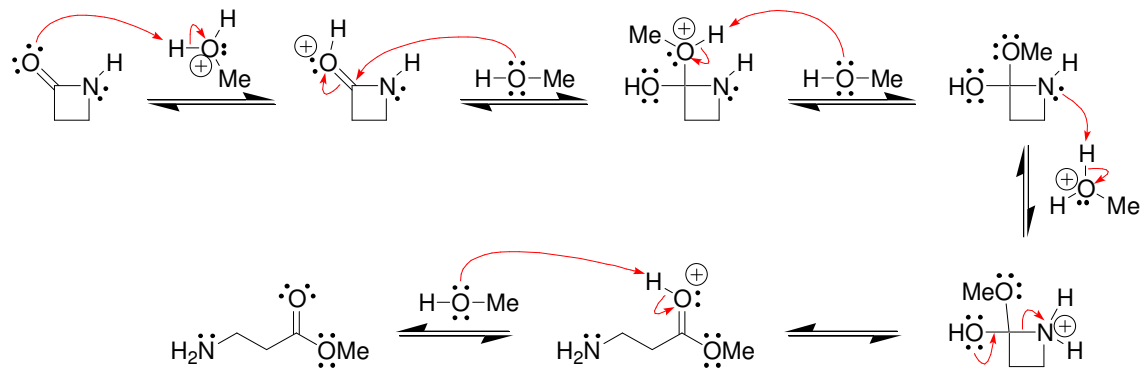
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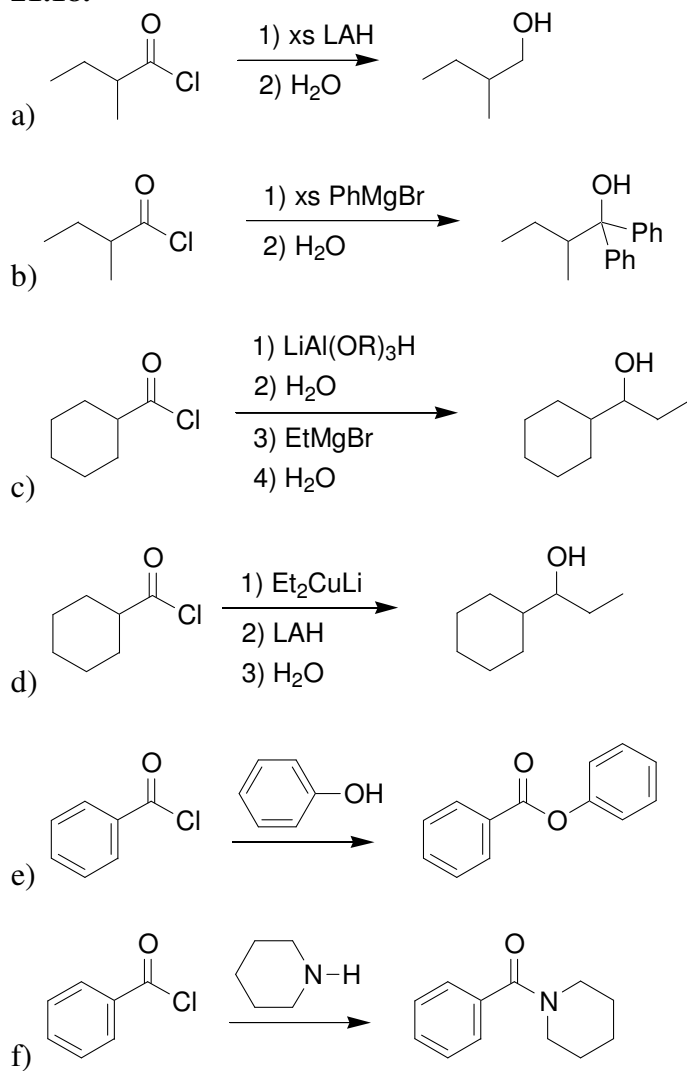
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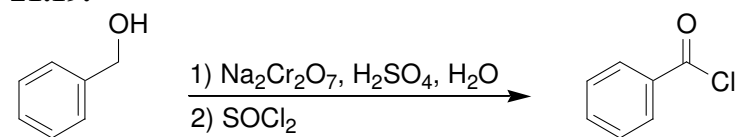
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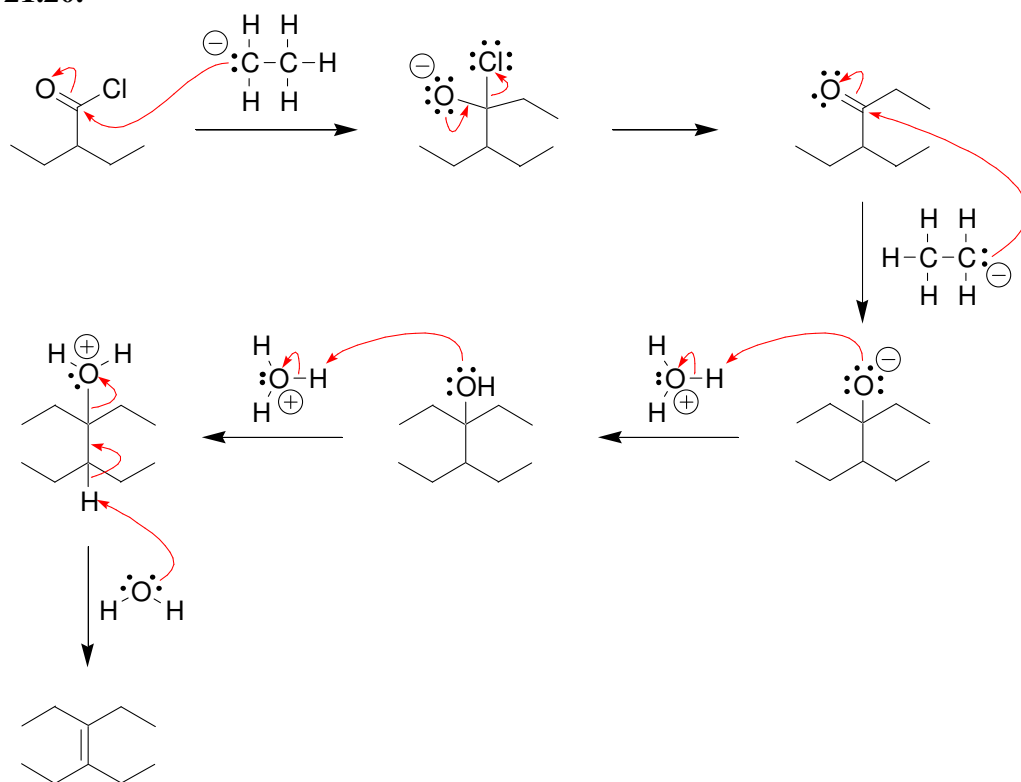
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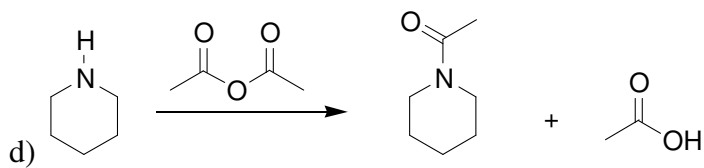
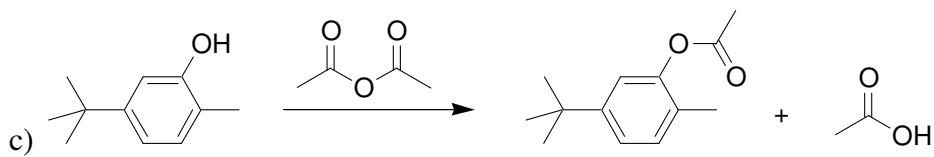
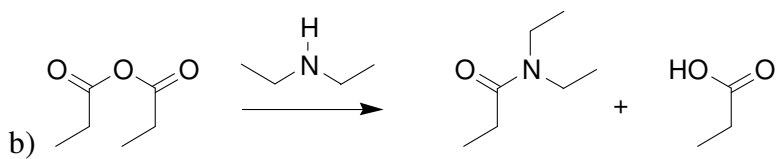
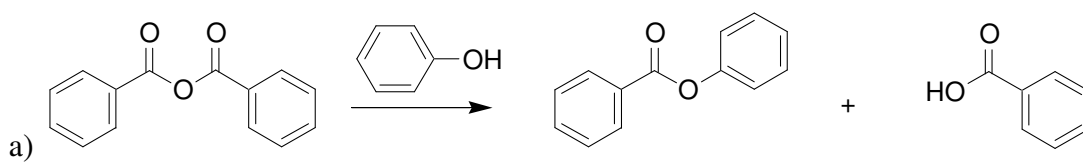
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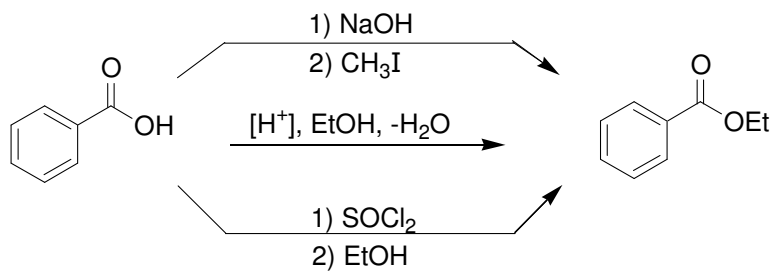
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21.21.

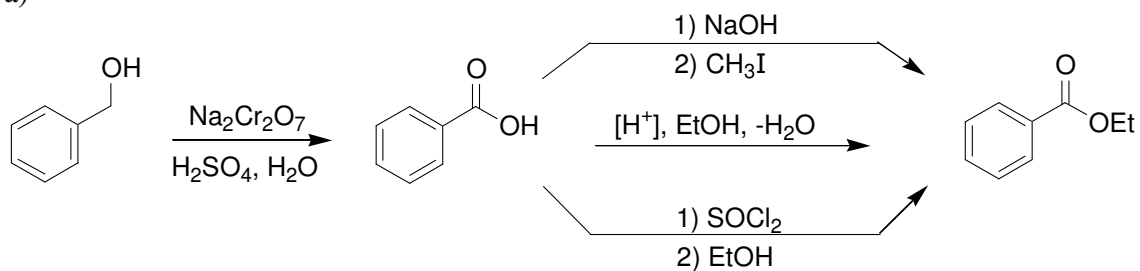


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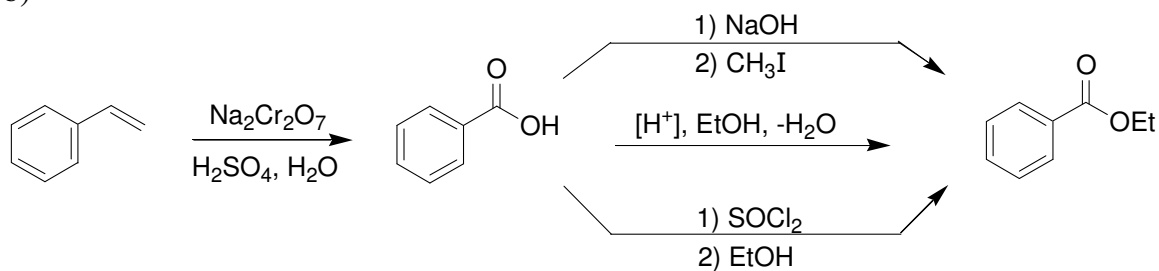


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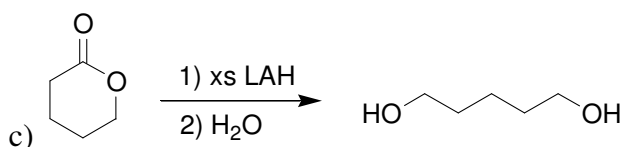
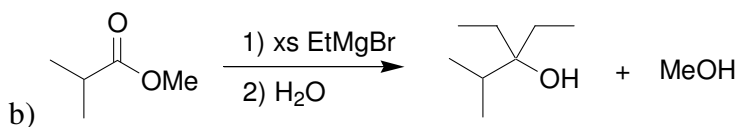
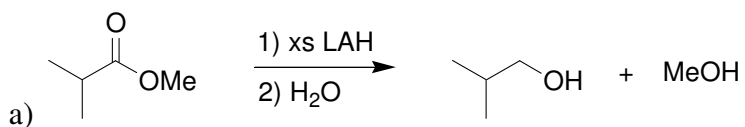
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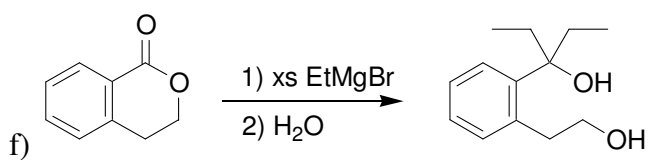
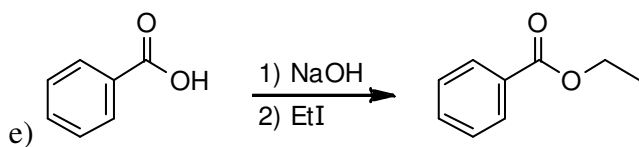
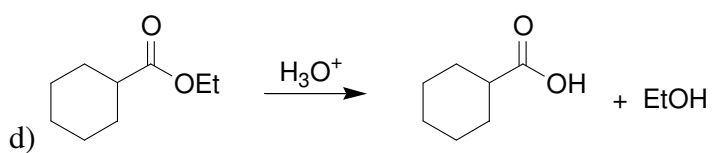


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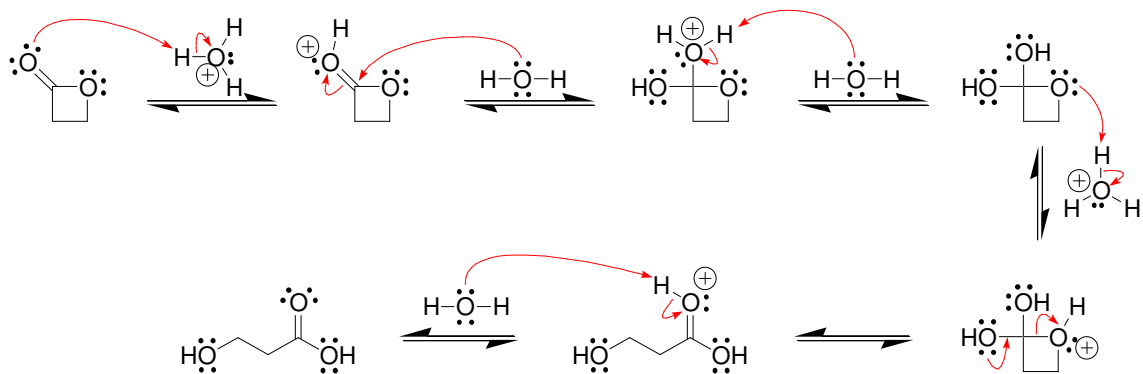


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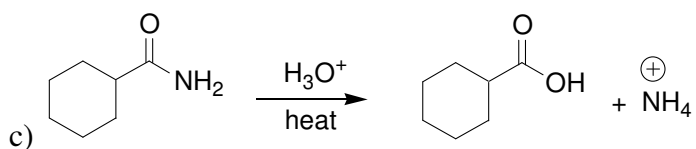
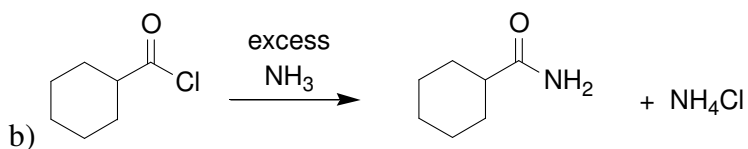
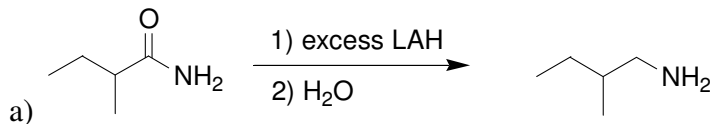




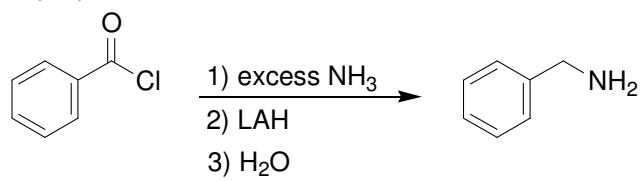
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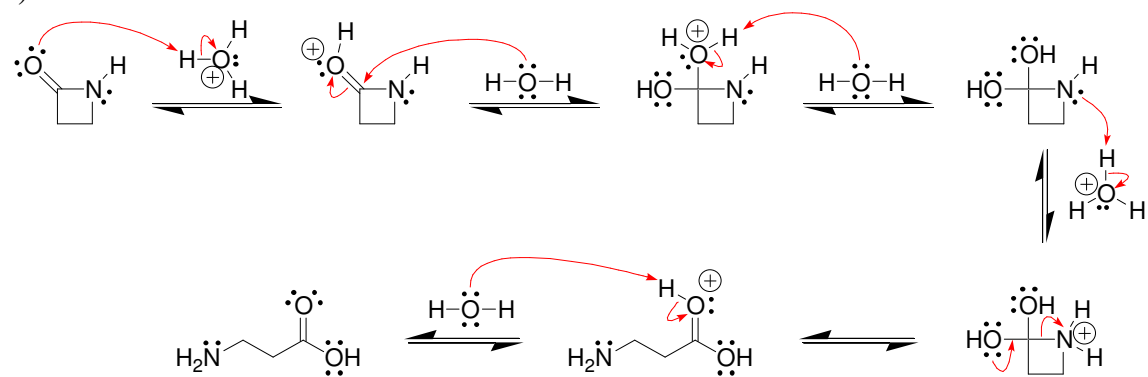


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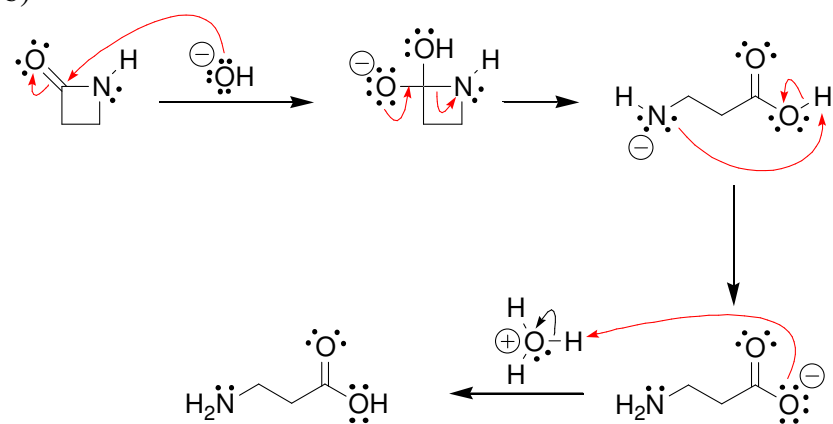


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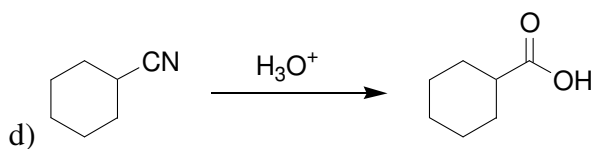
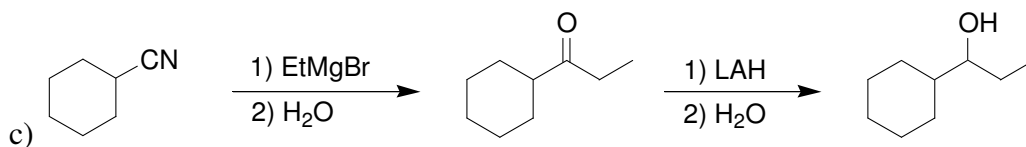
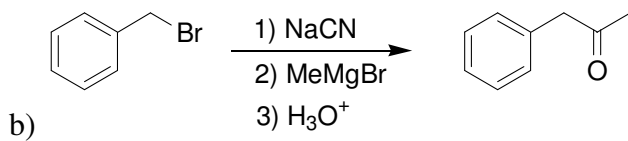
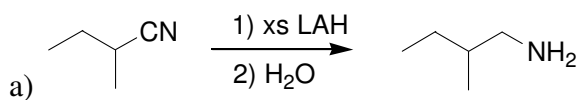
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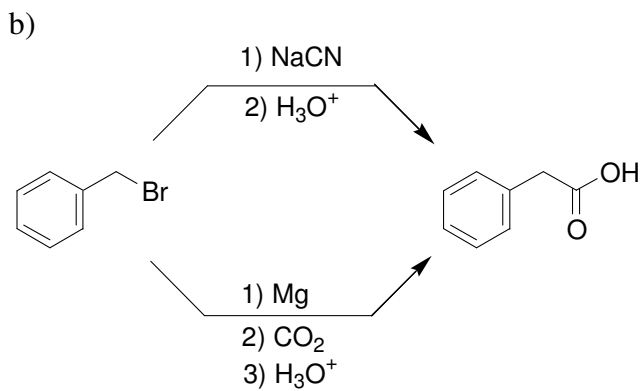
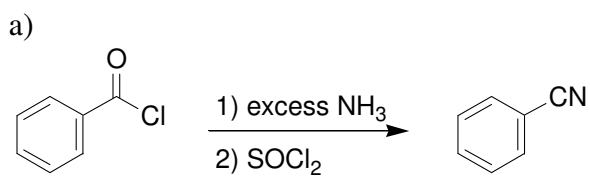
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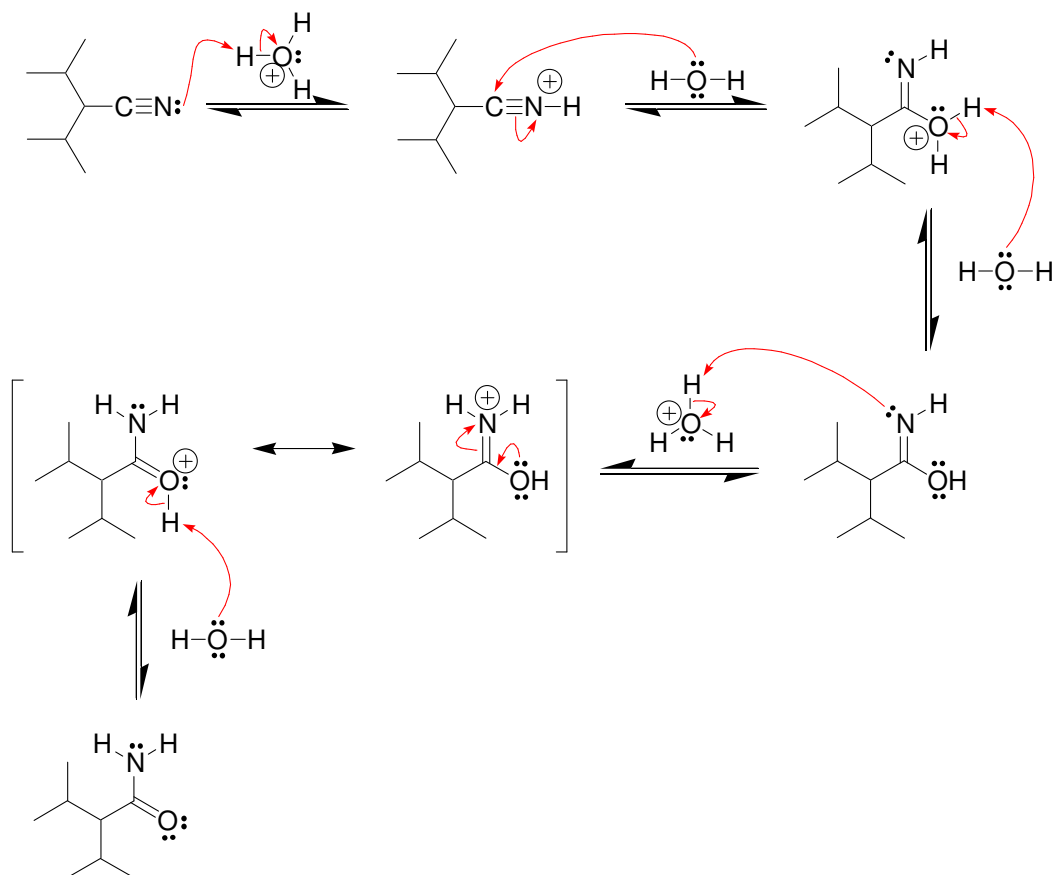
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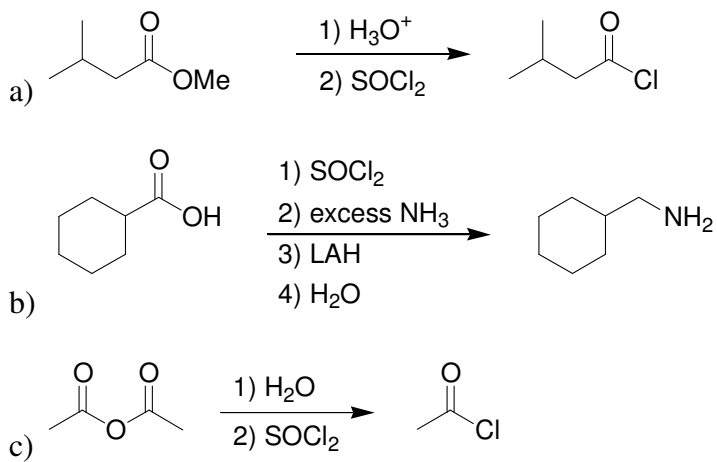
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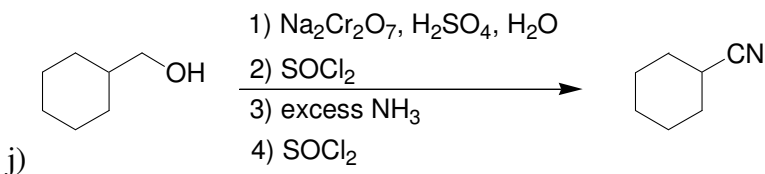
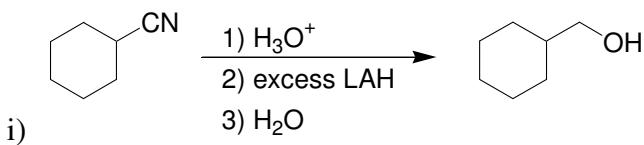
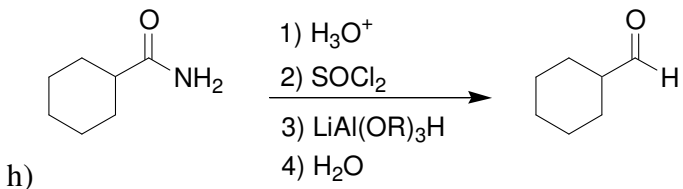
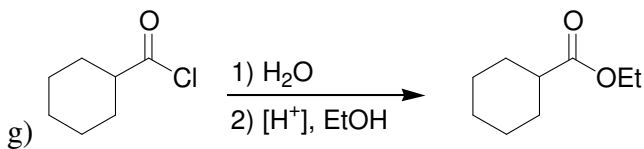
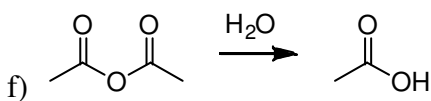
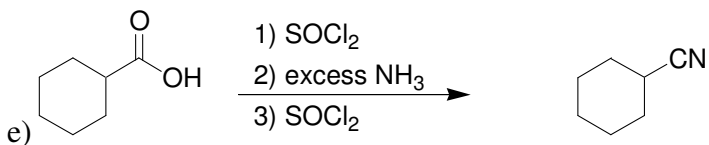
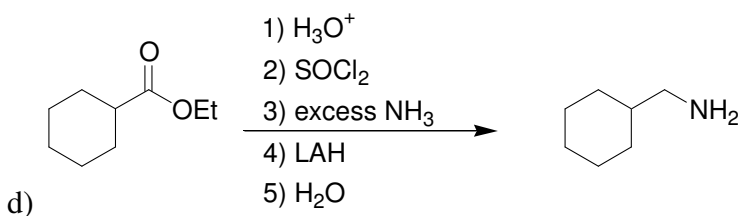


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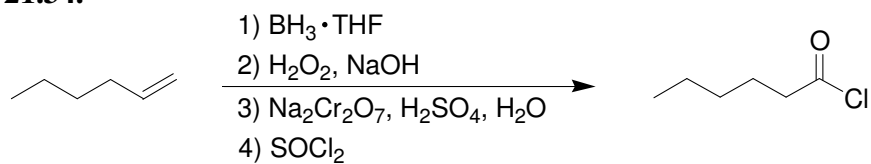
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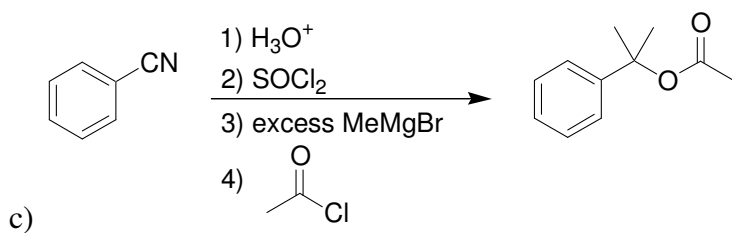
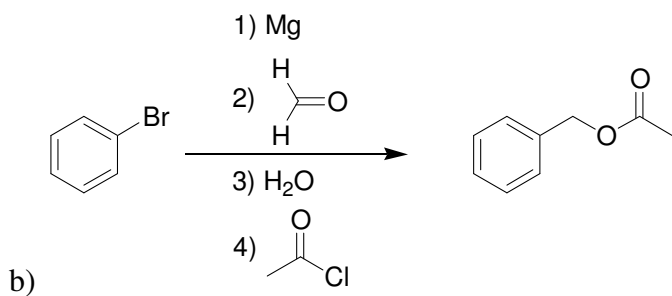
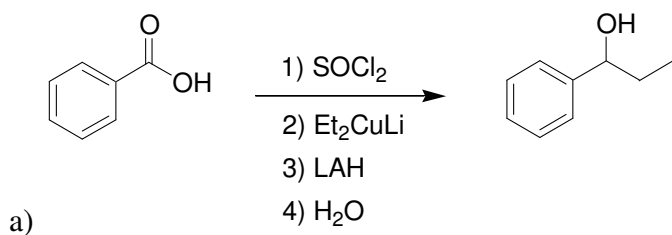


21.33. Four steps: 1) oxidize to a carboxylic acid, 2) convert into an acid halide, 3) convert into an amide, and 4) reduce to give an amine.

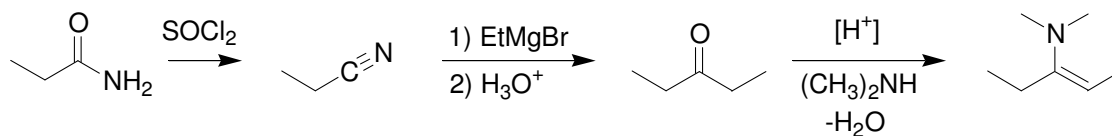
21.34.



21.35.

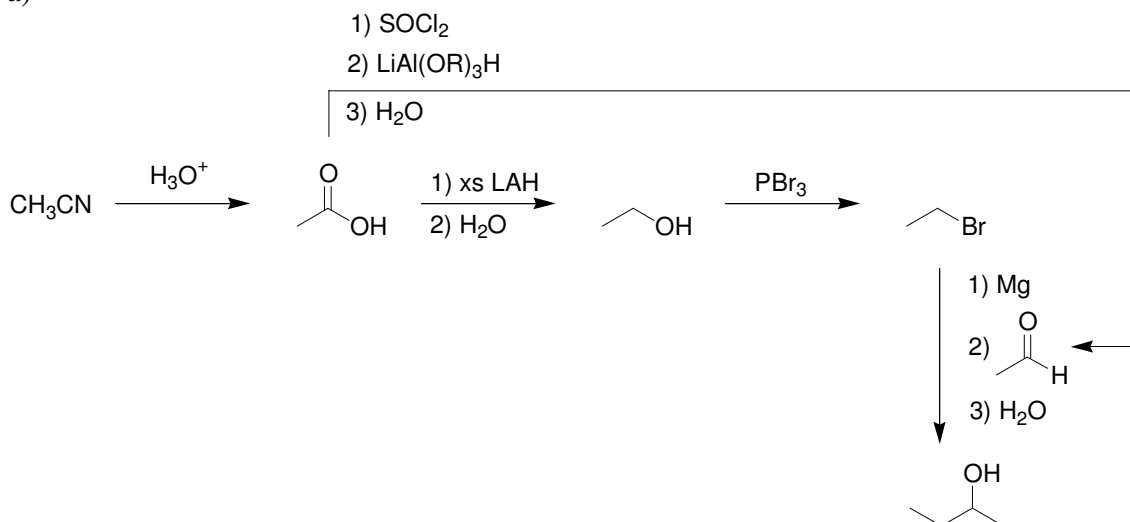


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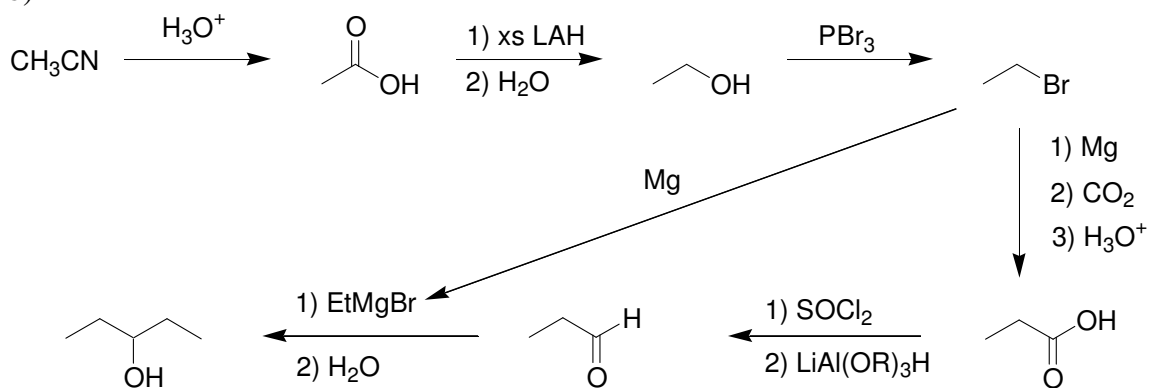


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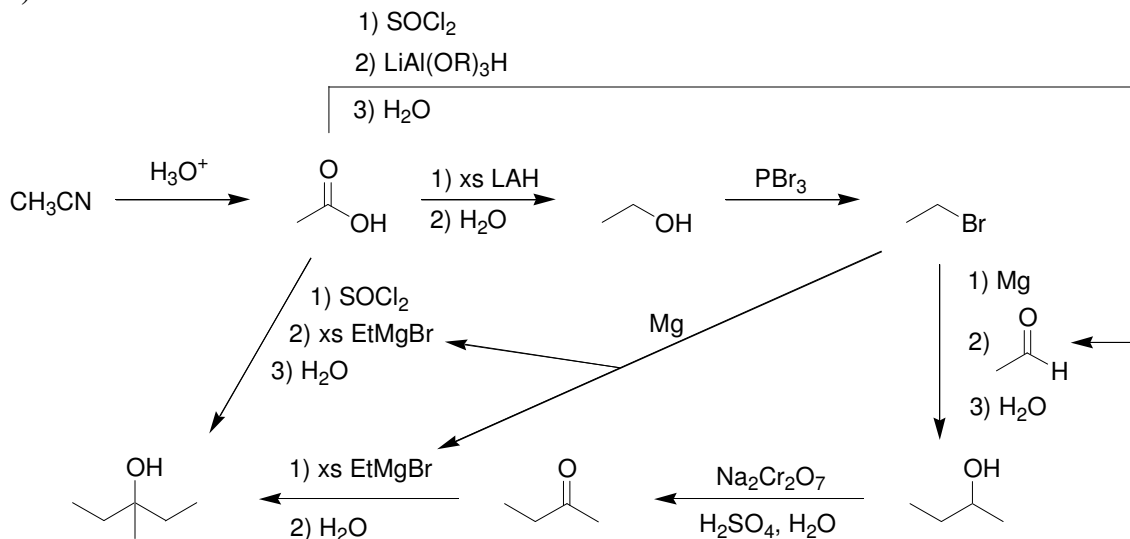
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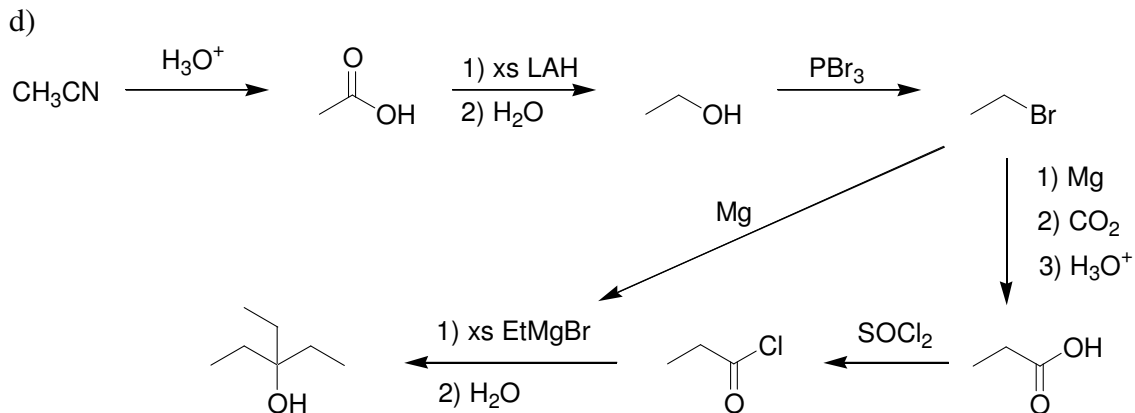


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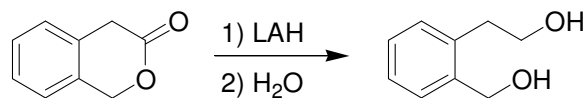


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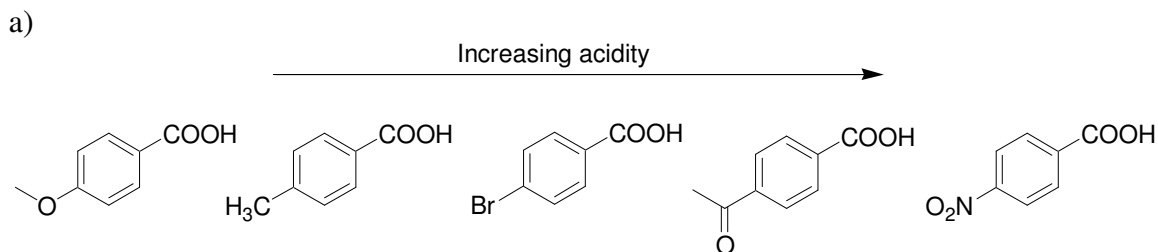




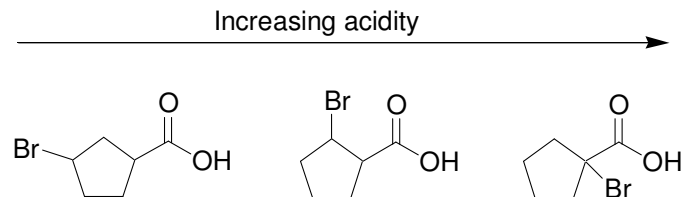
21.38. The signal at 1740 cm^{-1} indicates that the carbonyl group is not conjugated with the aromatic ring (it would be at a lower wavenumber if it was conjugated),



21.39.

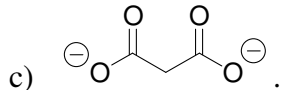


b)



21.40.

- a) The second carboxylic acid moiety is electron withdrawing, and stabilizes the conjugate base that is formed when the first proton is removed.
 b) The carboxylate ion is electron rich and it destabilizes the conjugate base that is formed when the second proton is removed.



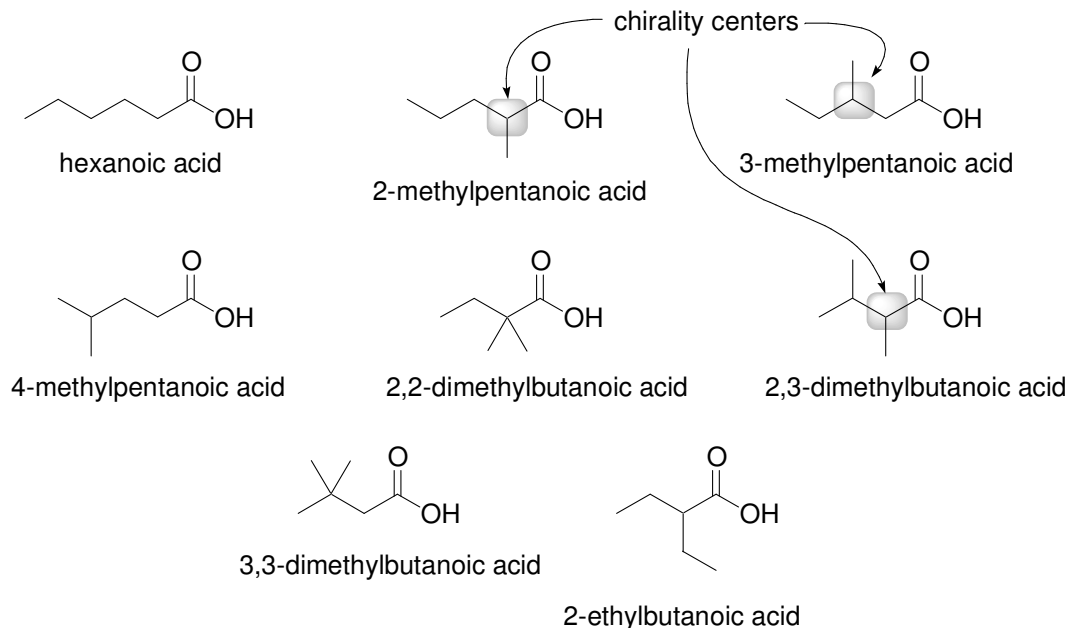
- d) The number of methylene groups (CH₂) separating the carboxylic acid moieties is greater in succinic acid than in malonic acid. Therefore, the inductive effects are not as strong.

21.41.

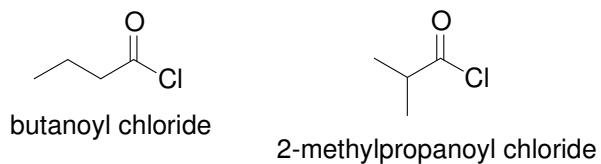
- a) cyclopentanecarboxylic acid
 b) cyclopentanecarboxamide
 c) benzoyl chloride
 d) ethyl acetate
 e) hexanoic acid
 f) pentanoyl chloride
 g) hexanamide

21.42.

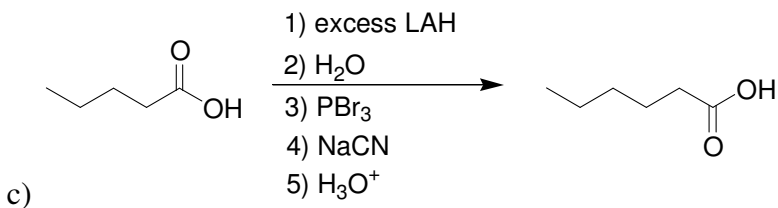
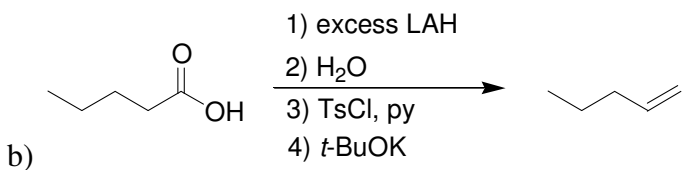
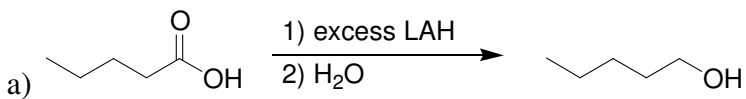
- a) acetic anhydride
 b) benzoic acid
 c) formic acid
 d) oxalic acid

21.43.

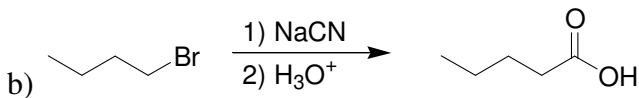
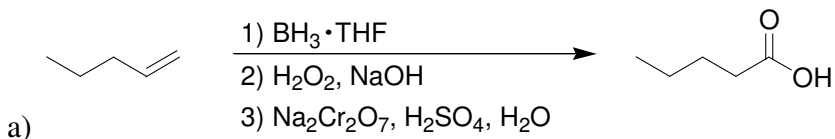
21.44.



21.45.

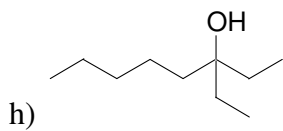
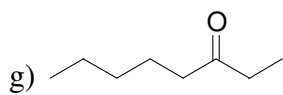
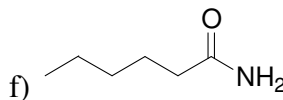
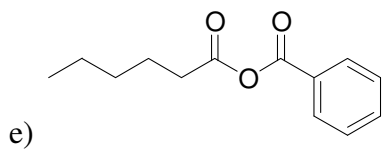
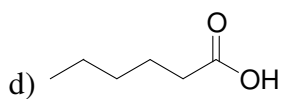
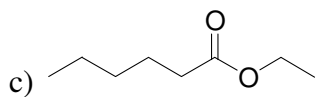
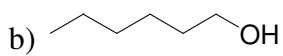
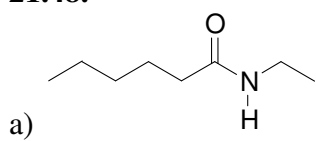


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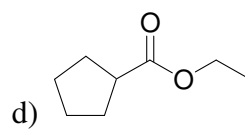
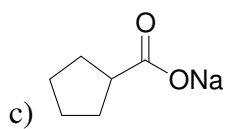
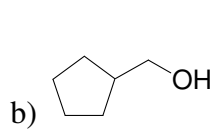
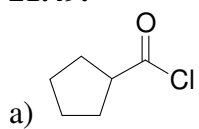


21.47. As discussed in Chapter 19, the methoxy group is electron donating via resonance, but electron withdrawing via induction. The resonance effect is stronger, but only occurs when the methoxy group is in an *ortho* or *para* position.

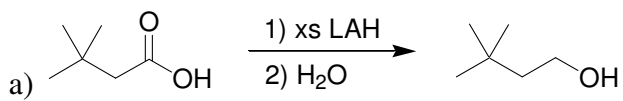
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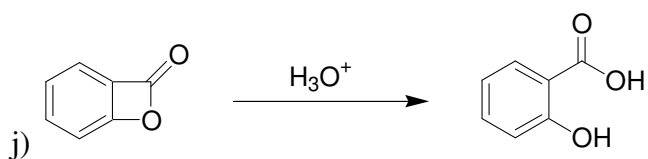
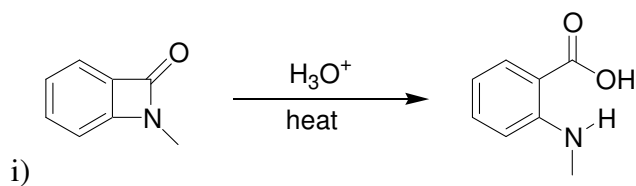
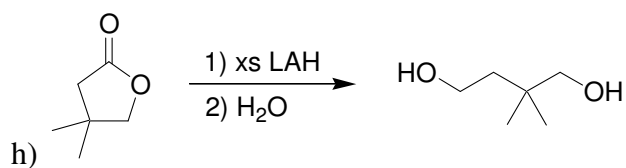
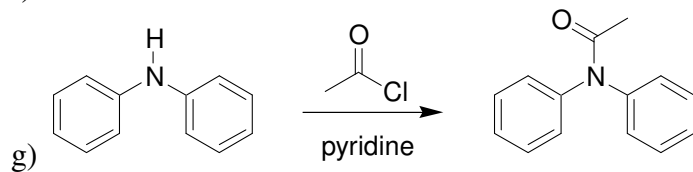
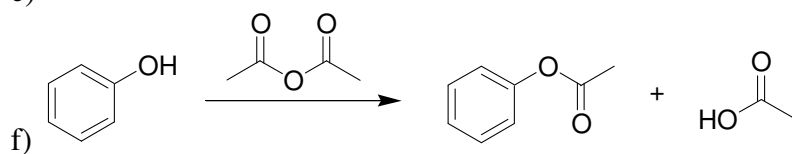
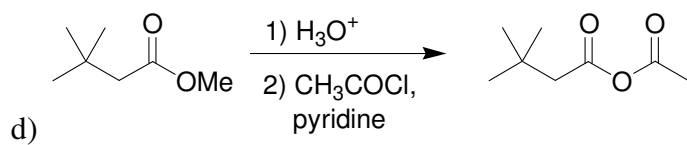
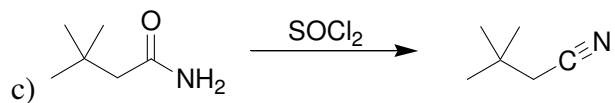
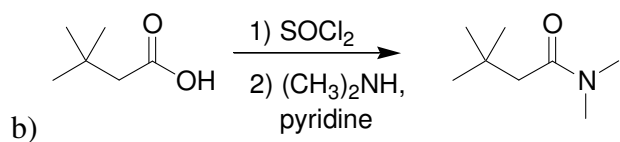


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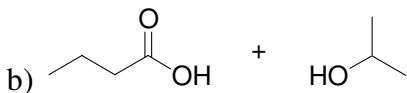
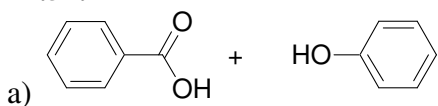


21.50.

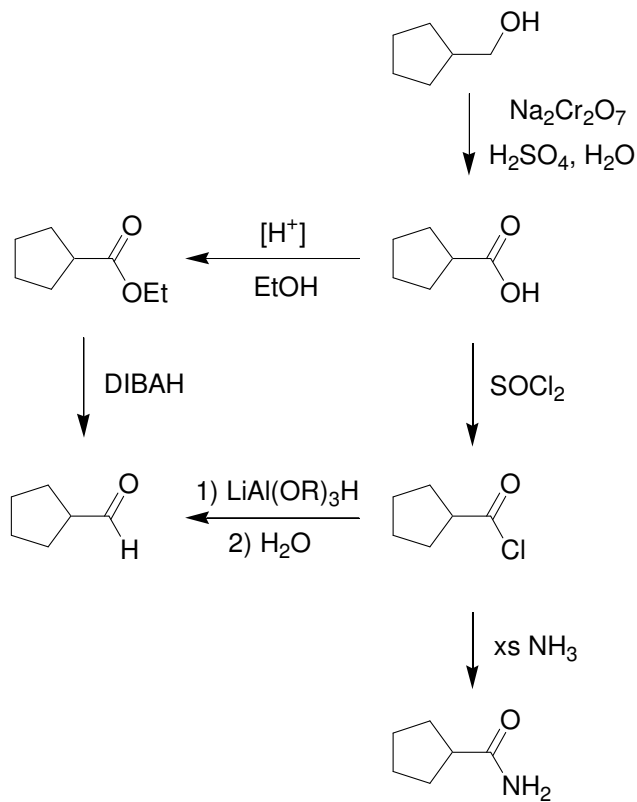




21.51.



21.52.



21.53.

a) NaOH , followed by $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , H_2O

b) NaCN followed by H_3O^+

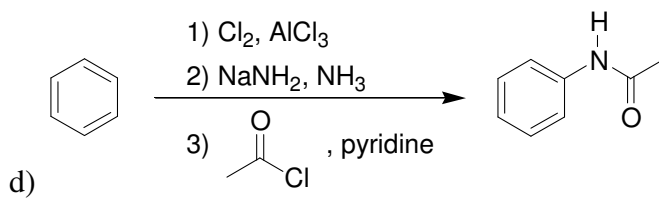
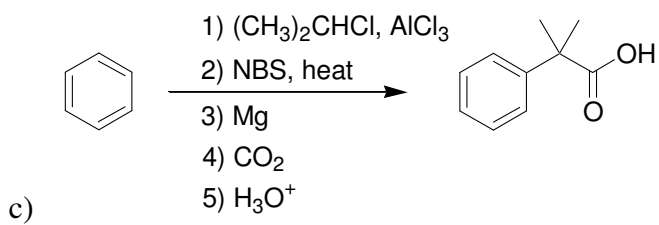
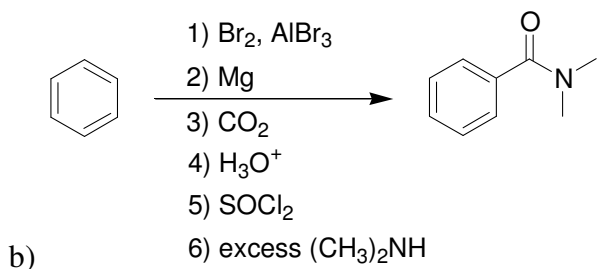
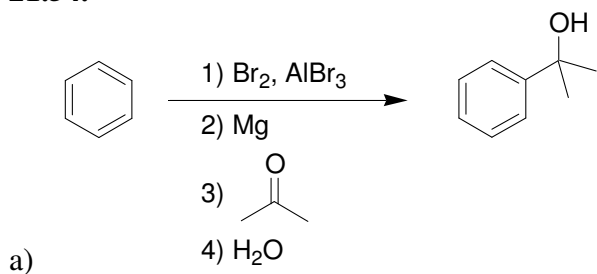
c) NaOH , followed by $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , H_2O , followed by SOCl_2

d) NaCN , followed by H_3O^+ , followed by SOCl_2 , followed by xs NH_3

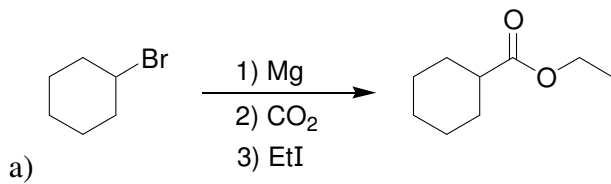
e) NaOH , followed by $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , H_2O , followed by SOCl_2 , followed by xs NH_3

f) NaCN followed by H_3O^+ , followed by $[\text{H}^+]$, EtOH (with removal of water)

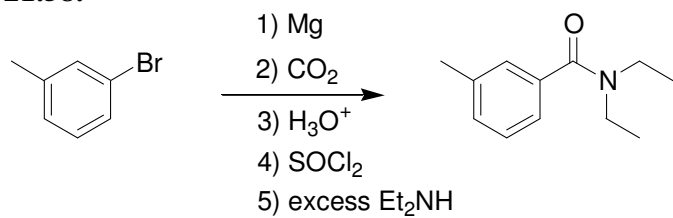
21.54.



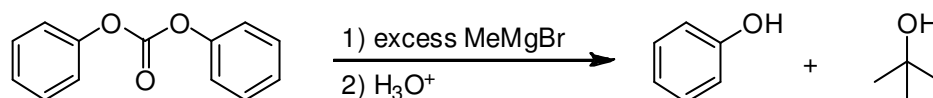
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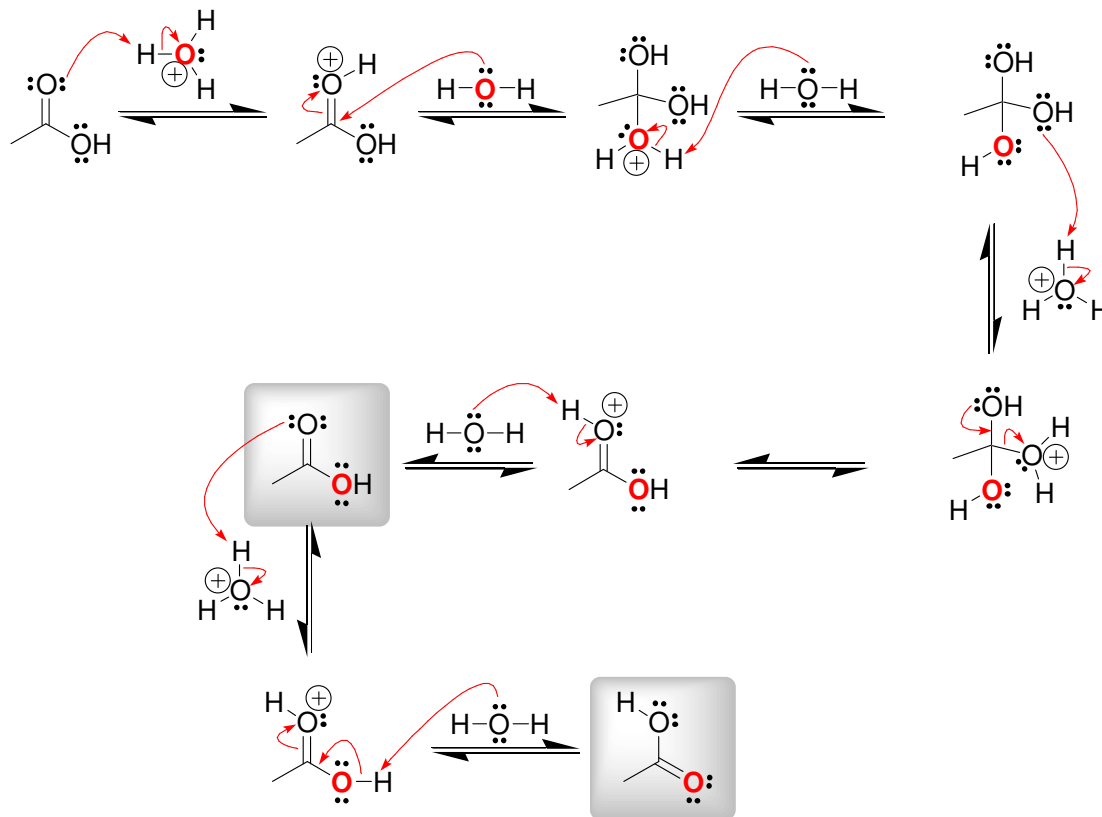
21.58.



21.59.

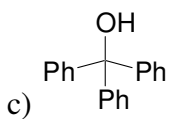
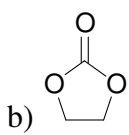
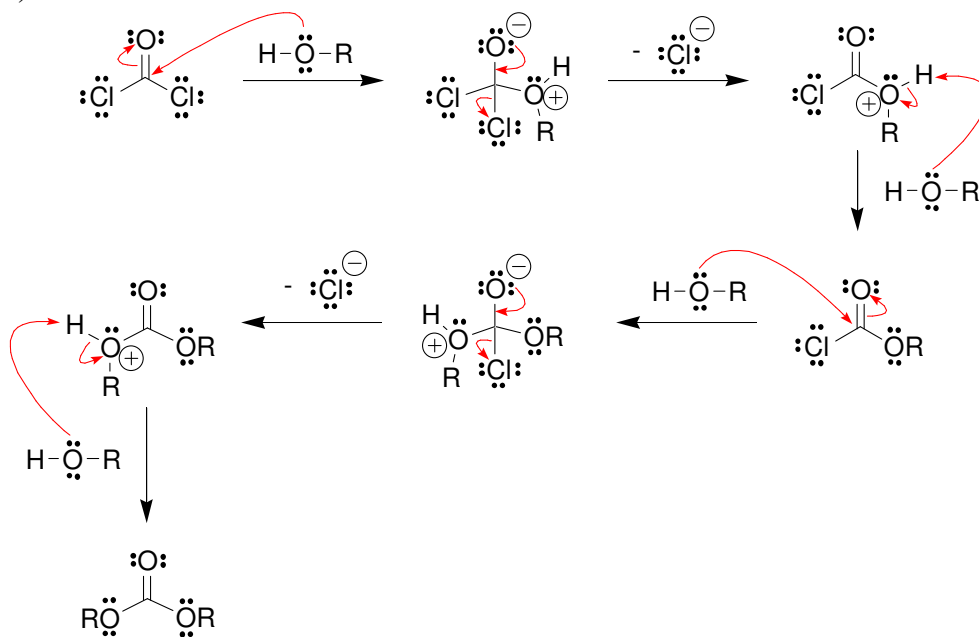


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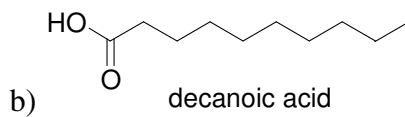
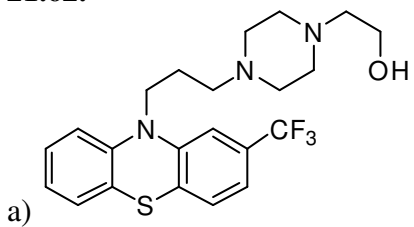


21.61.

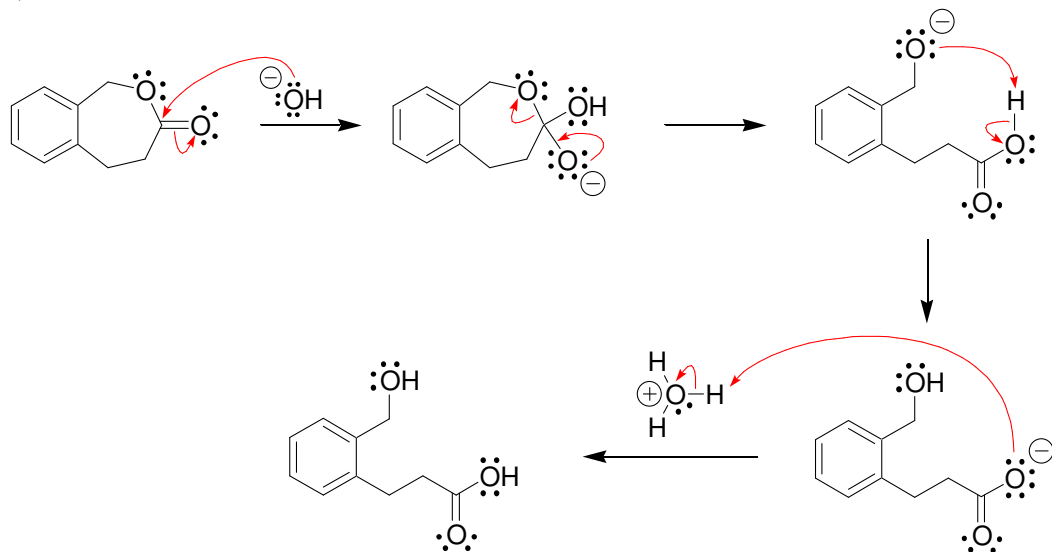
a)



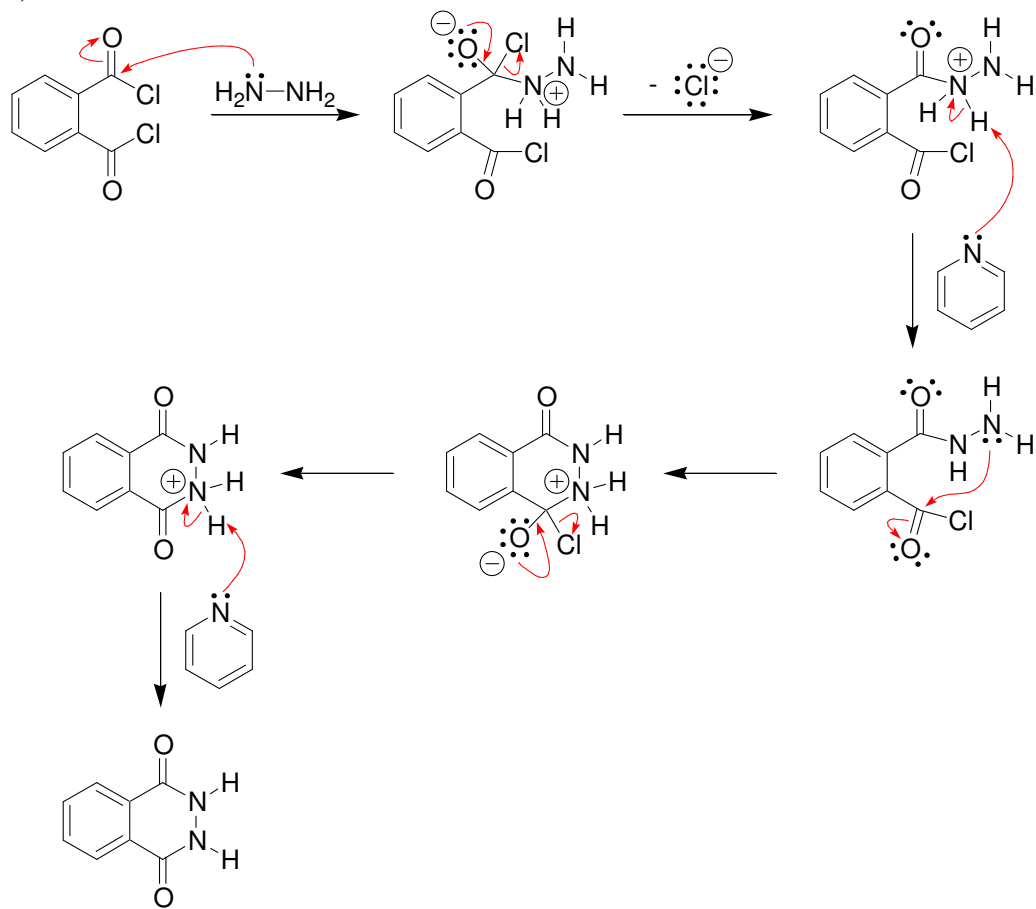
21.62.

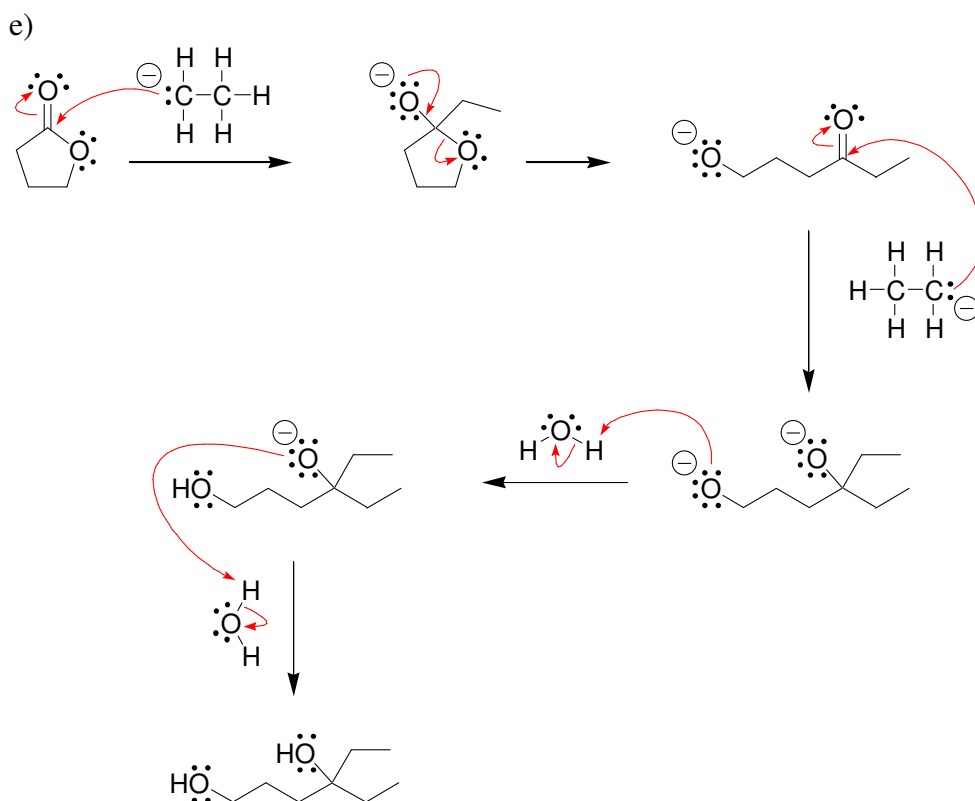


c)



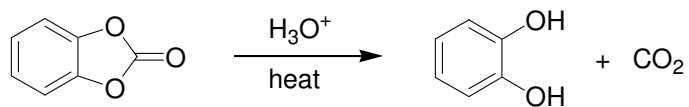
d)



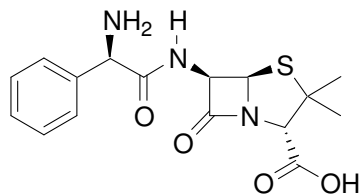


21.66. The three chlorine atoms withdraw electron density via induction. This effect renders the carbonyl group more electrophilic.

21.67.

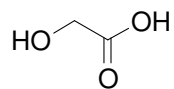


21.68



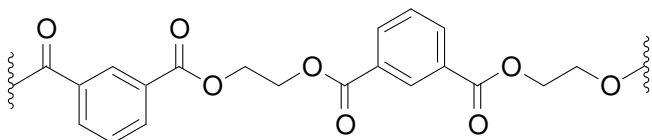
- a)
b) Ampicillin

21.69.

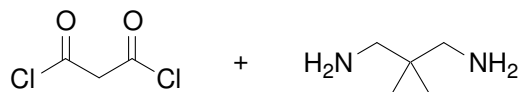


(glycolic acid)
hydroxyacetic acid

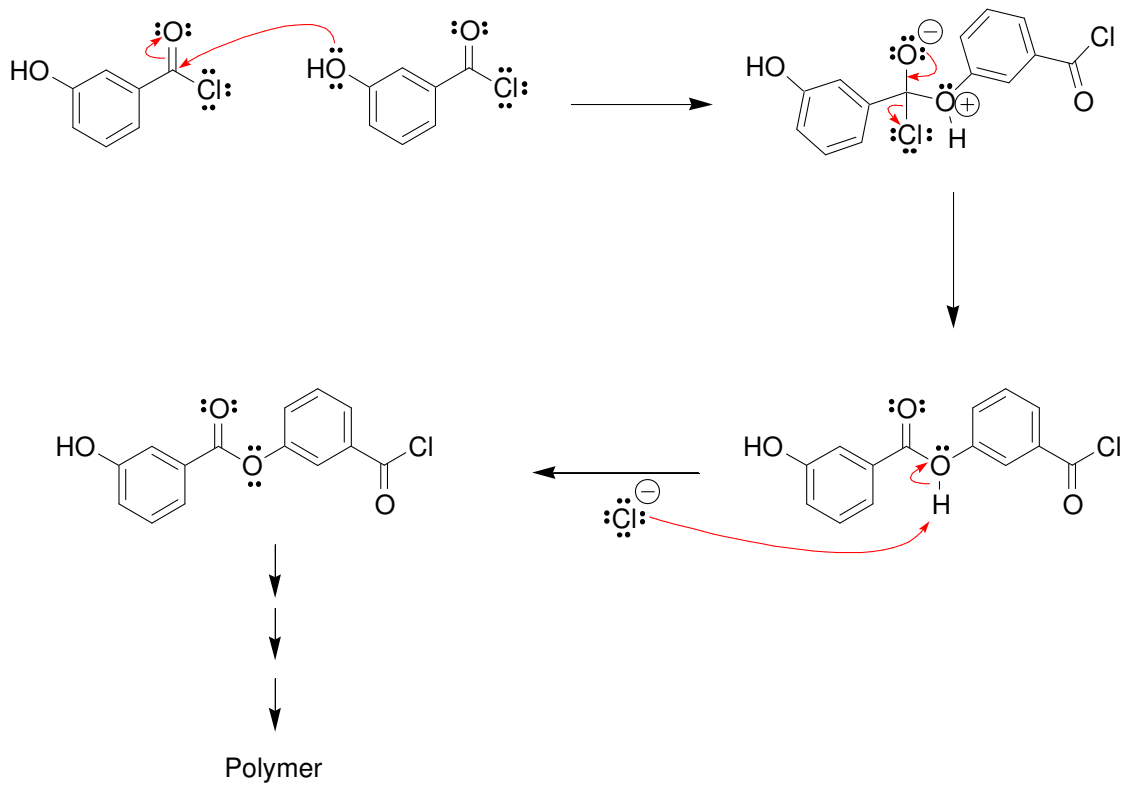
21.70.



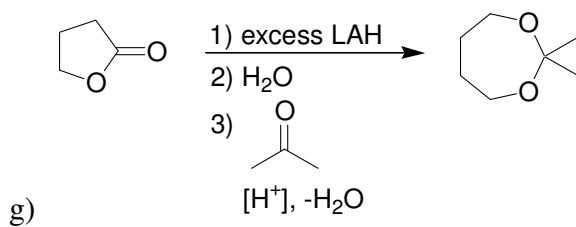
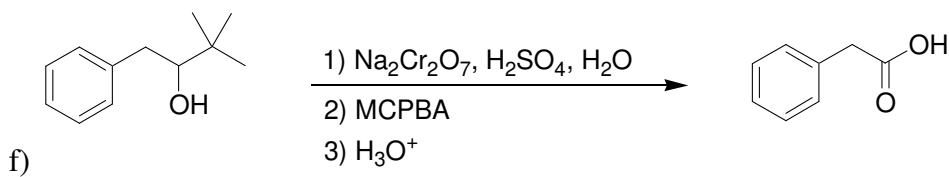
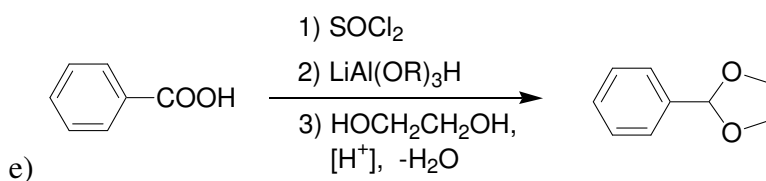
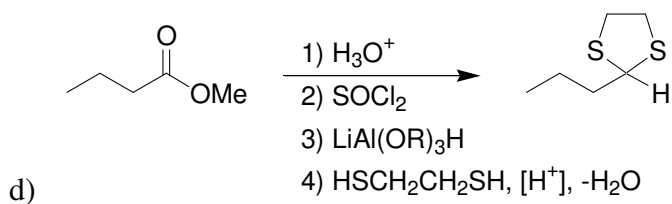
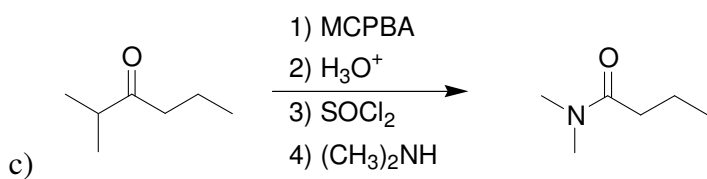
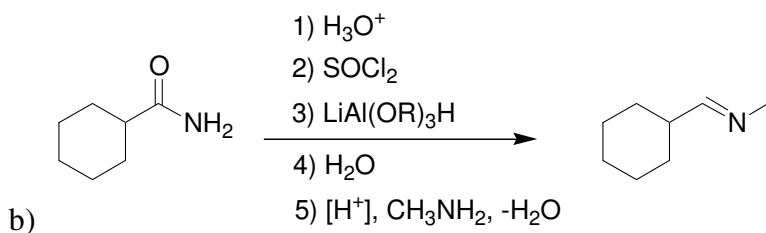
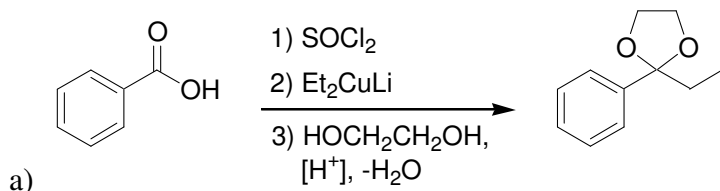
21.71.



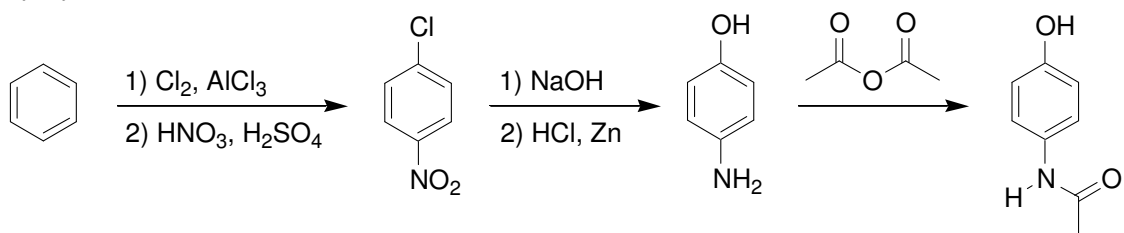
21.72.



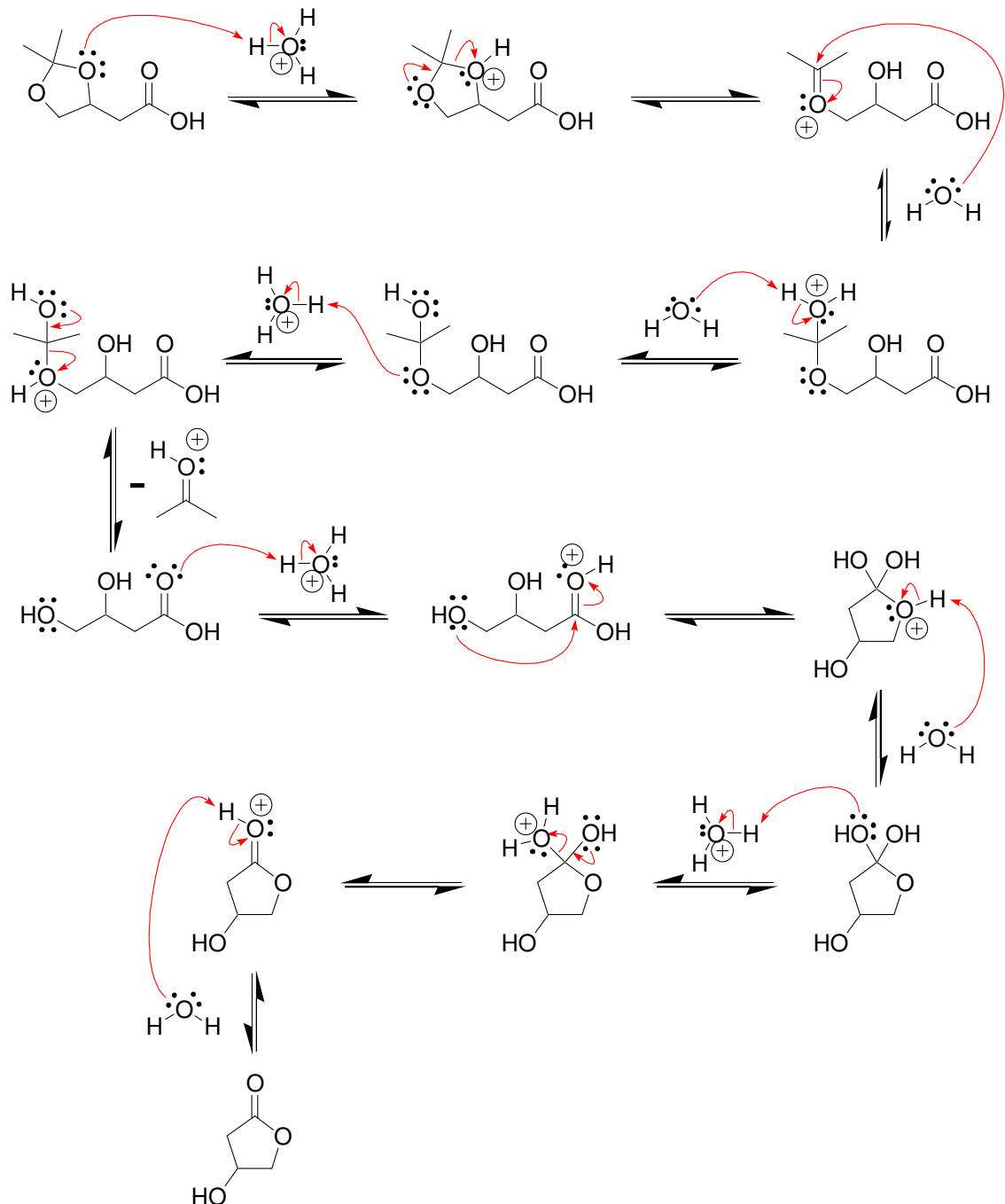
21.73.



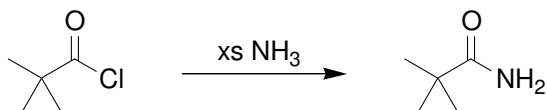
21.74.



21.75.

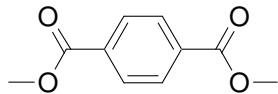


21.76.



Compound A

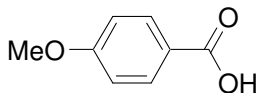
21.77.



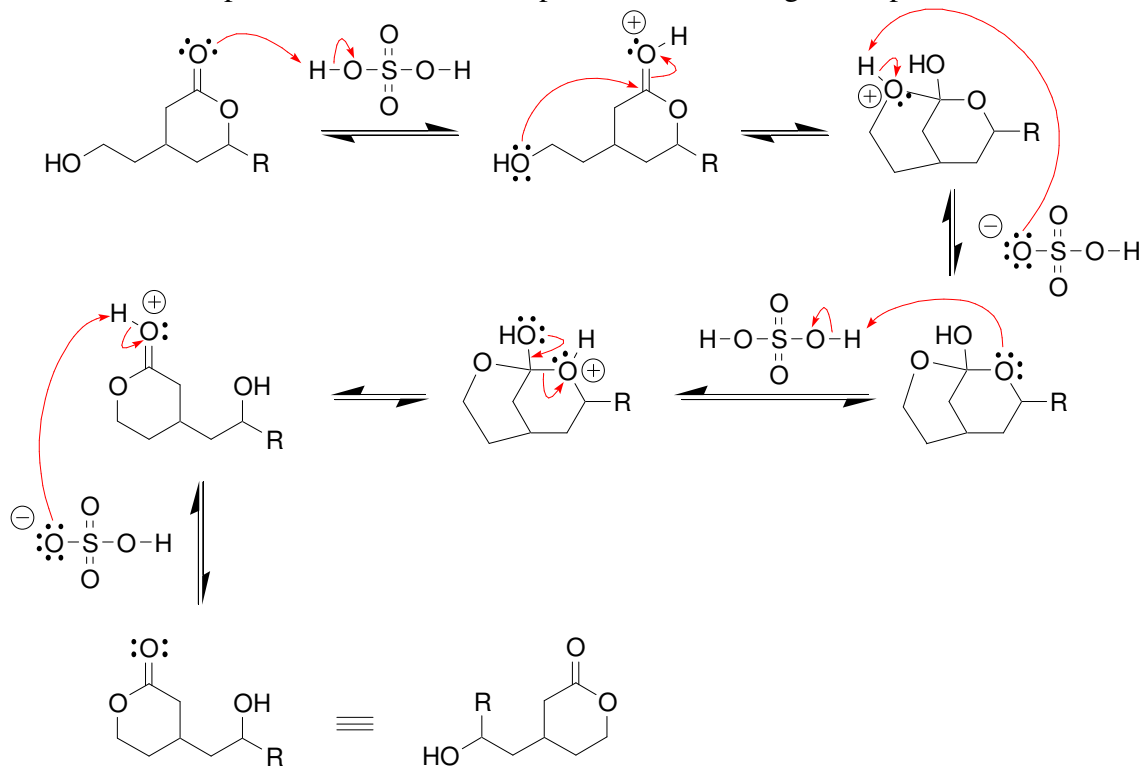
21.78. An IR spectrum of butyric acid should have a broad signal between 2500 cm^{-1} and 3600 cm^{-1} . An IR spectrum of ethyl acetate will not have this signal.

21.79. The ^1H NMR spectrum of *para*-chlorobenzaldehyde should have a signal at approximately 10 ppm corresponding to the aldehydic proton. The ^1H NMR spectrum of benzoyl chloride should not have a signal near 10 ppm.

21.80.



21.81. If the oxygen atom of the OH group in the starting material is an isotopic label, then we would expect the label to be incorporated into the ring of the product:



21.82. The lone pair of the nitrogen atom in this case is participating in resonance and is less available to donate electron density to the carbonyl group. As a result, the carbonyl group is more electrophilic than the carbonyl group of a regular amide (where the lone pair contributes significant electron density to the carbonyl group). Also, when this compound functions as an electrophile in a nucleophilic acyl substitution reaction, the leaving group is particularly stable because it is an aromatic anion. With a good leaving group, this compound more closely resembles the reactivity of an acid halide than an amide.

21.83.

a) DMF, like most amides, exhibits restricted rotation about the bond between the carbonyl group and the nitrogen atom. This restricted rotation causes the methyl groups to be in different electronic environments. They are not chemically equivalent, and will therefore produce two different signals (in addition to the signal from the other proton in the compound). Upon treatment with excess LAH followed by water, DMF is reduced to an amine that does not exhibit restricted rotation. As such, the methyl groups are now chemically equivalent and will together produce only one signal.

b) Restricted rotation causes the methyl groups to be in different electronic environments. As a result, the ^{13}C NMR spectrum of DMF should have three signals.