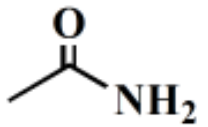
10.20

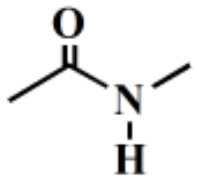
Amides

The amides considered here need to be distinguished from the metal amide bases like $NaNH_2$ and $LiN(i\text{-}Pr)_2$ studied earlier. The present ones are of general structure $RC(=O)NR'R''$ where the different R's may be H's, alkyl groups, or aryl groups. They are named by dropping "-ic acid" from the name of the parent acid and adding "amide."

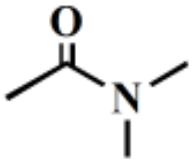
Examples:



Acetamide



***N*-Methyl-acetamide**

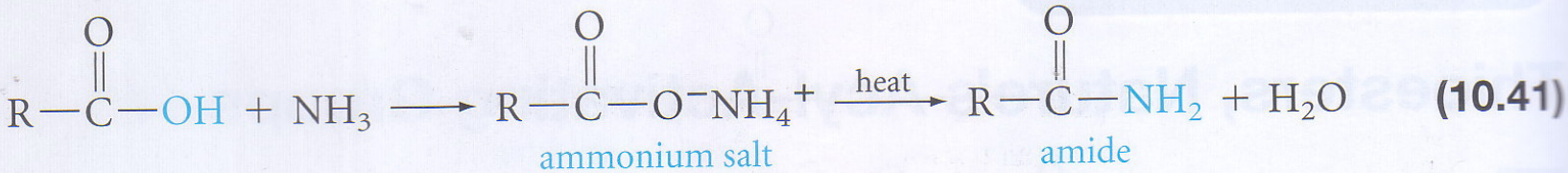


***N,N*-Dimethyl-acetamide**

MP (°C)	82	28	-20
BP (°C)	221	205	166

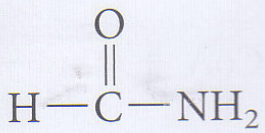
Note how both MP and BP decrease with decreasing opportunity for intramolecular hydrogen bonding.

Amides can be prepared by heating the ammonium salts of acids.

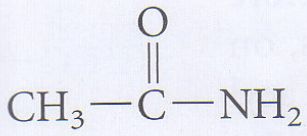


(10.41)

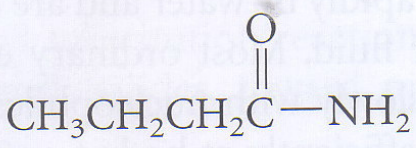
Amides are named by replacing the *-ic* or *-oic* ending of the acid name, either the common or the IUPAC name, with the *-amide* ending.



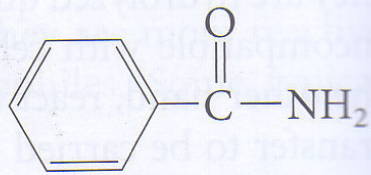
formamide
(methanamide)



acetamide
(ethanamide)



butanamide

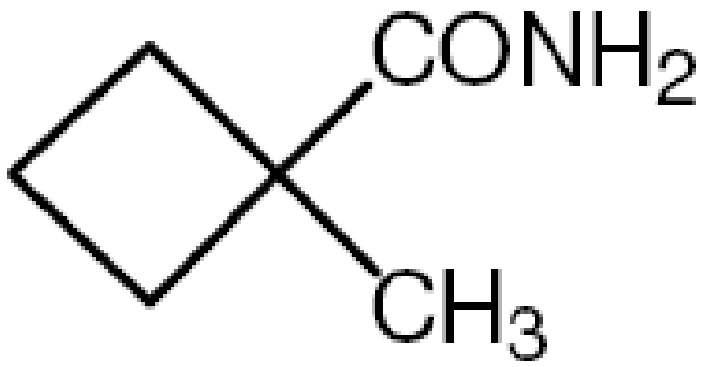


benzamide
(benzenecarboxamide)

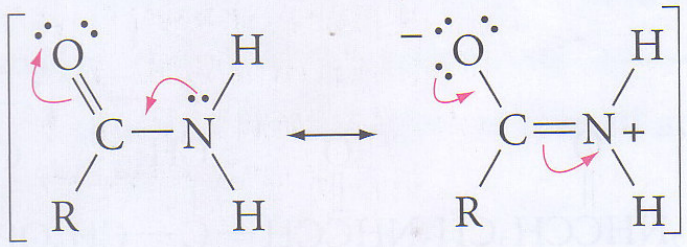
PROBLEM 10.31

a. Name $(CH_3)_2CHCONH_2$.
b. Write the structure of 1-methylcyclobutanecarboxamide.

10.31 a. 2-methylpropanamide

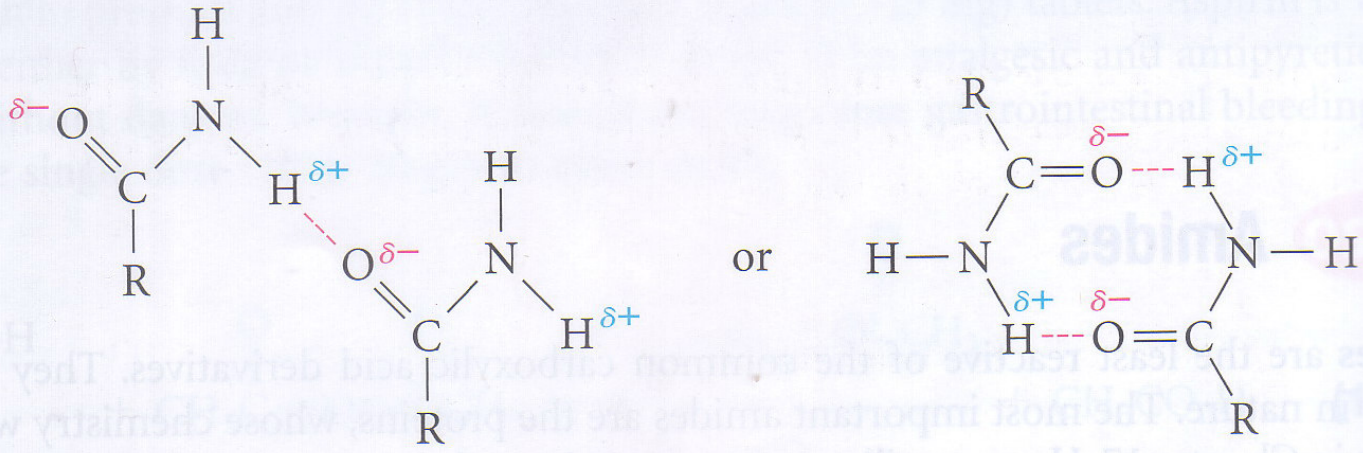
b. 

Amides have a planar geometry. Even though the carbon–nitrogen bond is normally written as a single bond, rotation around that bond is restricted, because of resonance.

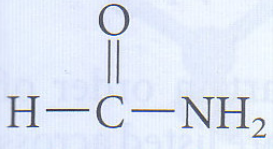


amide resonance

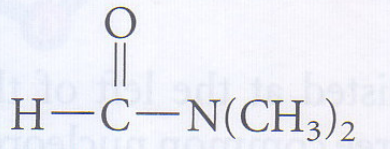
As the dipolar resonance contributor suggests, amides are highly polar and form strong hydrogen bonds.



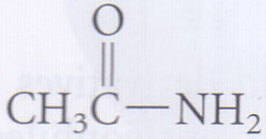
Amides have exceptionally high boiling points for their molecular weights, although alkyl substitution on the nitrogen lowers the boiling and melting points by decreasing the hydrogen-bonding possibilities, as shown in the following two pairs of compounds:



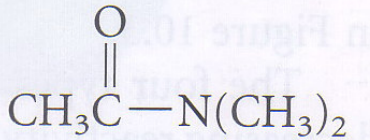
formamide
bp 210°C
mp 2.5°C



N,*N*-dimethylformamide
153°C
−60.5°C

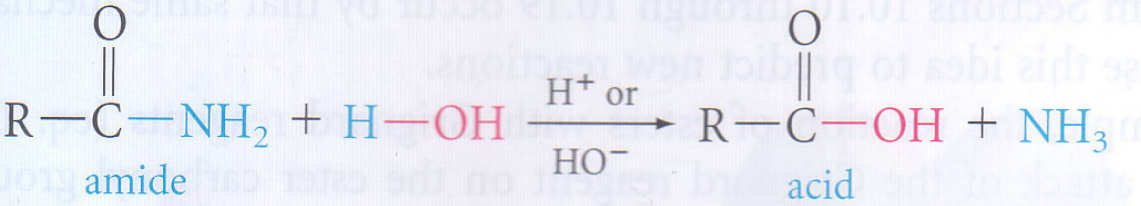


acetamide
222°C
81°C



N,*N*-dimethylacetamide
165°C
−20°C

Like other acid derivatives, amides react with nucleophiles. For example, they can be hydrolyzed by water.

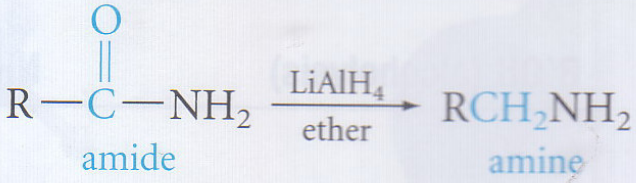


amide — acid

(10.42)

The reactions are slow, and prolonged heating or acid or base catalysis is usually necessary.

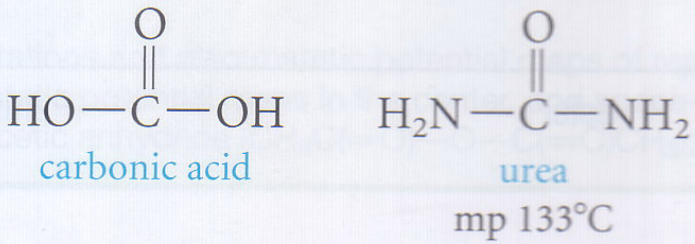
Amides can be reduced by lithium aluminum hydride to give amines.



(10.43)

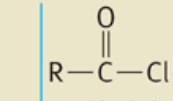
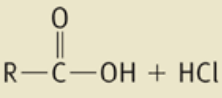
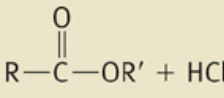
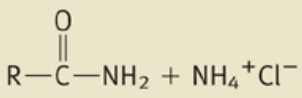
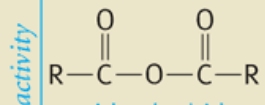
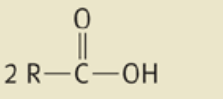
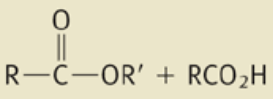
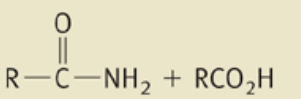
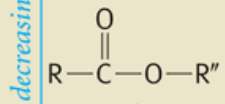
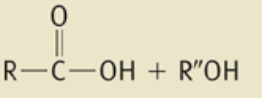
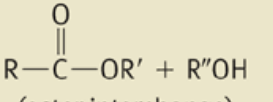
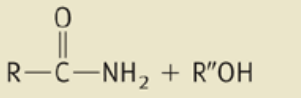
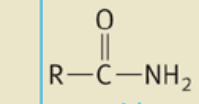
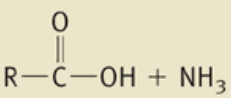
This is an excellent way to make primary amines, whose chemistry is discussed in the next chapter.

Urea is a special amide, a diamide of carbonic acid. A colorless, water-soluble, crystalline solid, urea is the normal end product of protein metabolism. An average adult excretes approximately 30 g of urea in their urine daily. Urea is produced commercially from carbon dioxide and ammonia, mainly for use as a fertilizer.



10.21 A Summary of Carboxylic Acid Derivatives

Table 10.5 Reactions of acid derivatives with certain nucleophiles

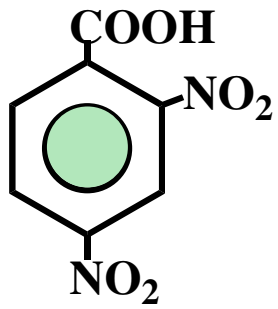
Acid derivative	Nucleophile: HOH (hydrolysis)	Nucleophile: R′OH (alcoholysis)	Nucleophile: NH_3 (ammonolysis)
 acyl halide			
 acid anhydride			
 ester		 (ester interchange)	
 amide		———	———
Main organic product	acid	ester	amide

decreasing reactivity ↓

Quiz 18.01

Provide IUPAC (systematic) names for the following carboxylic acids.

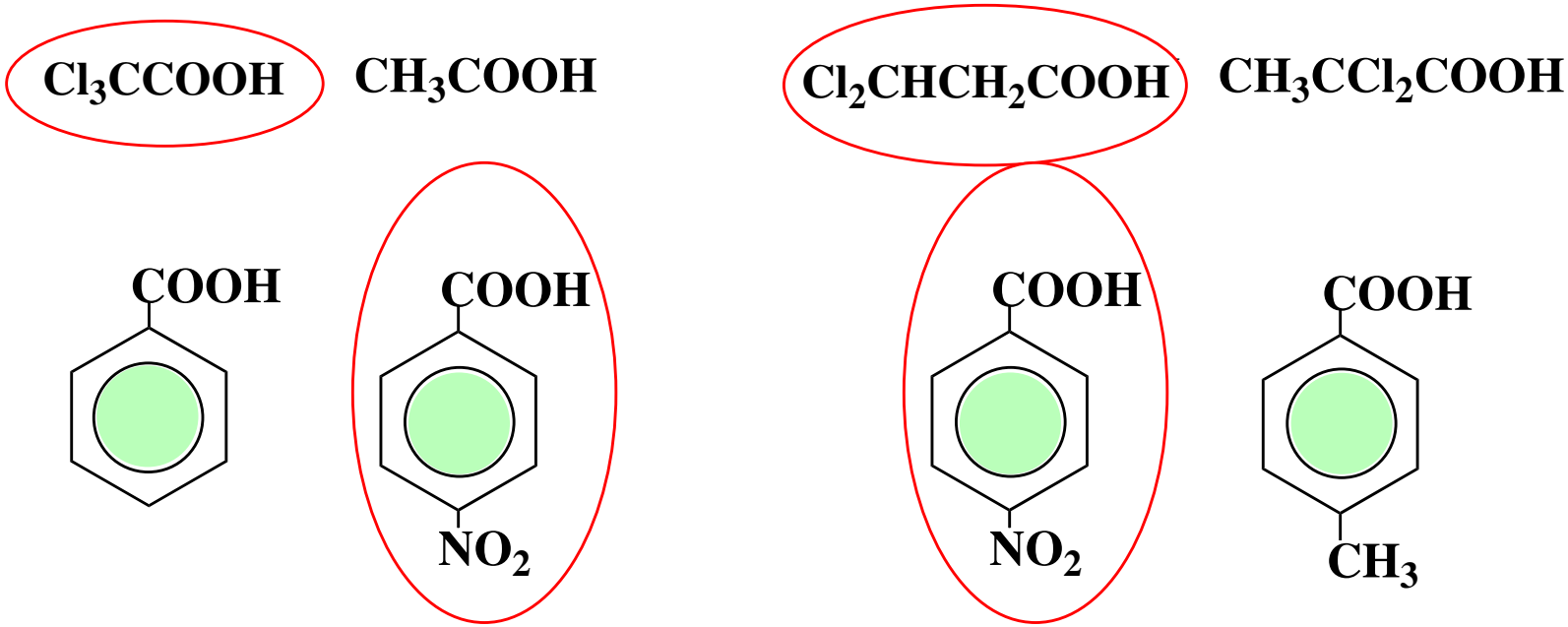
2-Chloro-4-methylpentanoic acid



2,4-Dinitrobenzoic acid

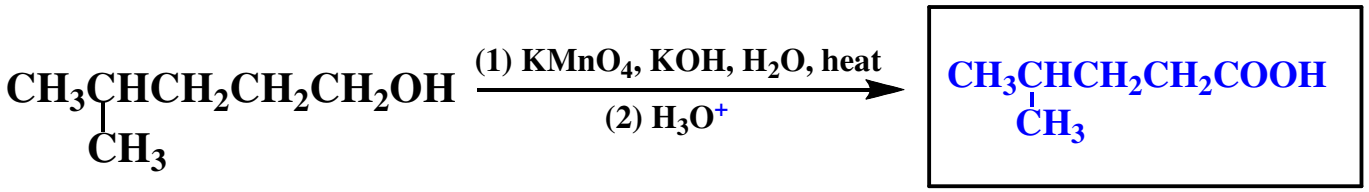
Quiz 18.02

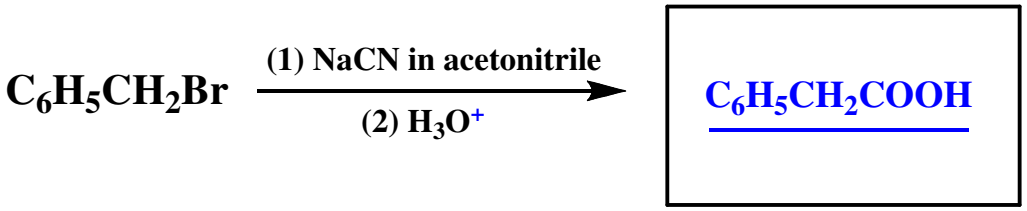
In each pair of compounds below, circle the stronger carboxylic acid.

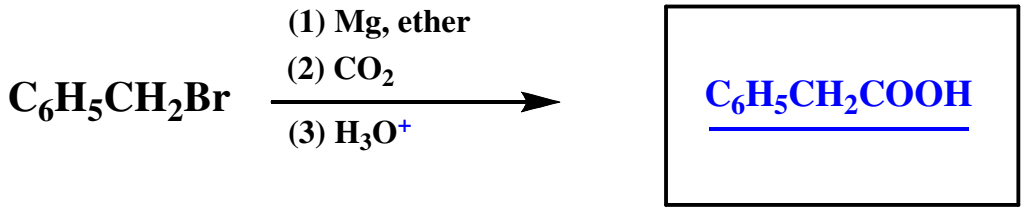


Quiz 18.03

Draw the structures of the products of the following synthetic procedures.

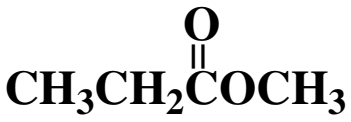




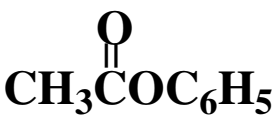


Quiz 18.04

Provide IUPAC names for the following acid derivatives.

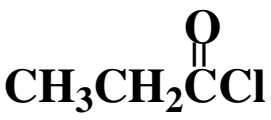


Methyl propanoate

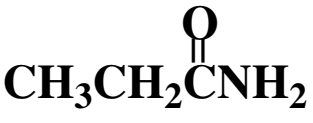


Phenyl ethanoate (phenyl acetate)

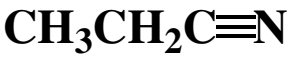
Ethanoic anhydride (acetic anhydride)



Propanoyl chloride



Propanamide



Propanenitrile

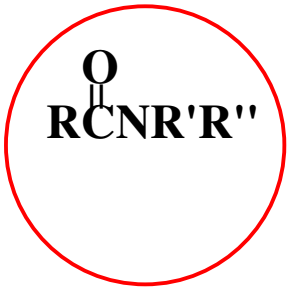
Quiz 18.06

Circle the least reactive acid derivative among those below.

ester

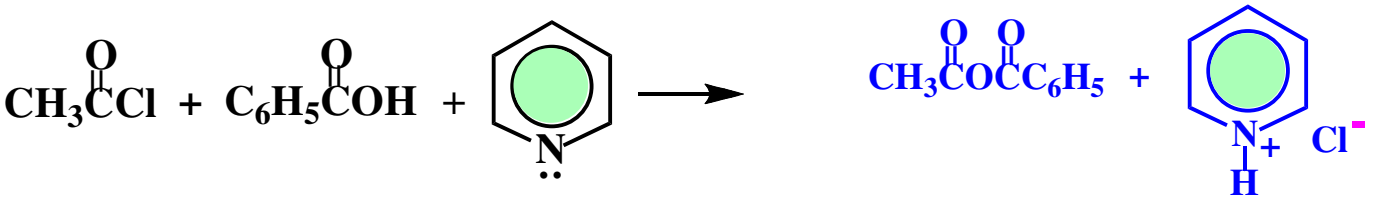
acid anhydride

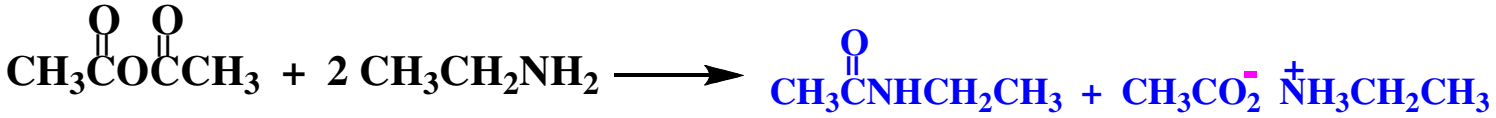
acyl chloride



Quiz 18.07

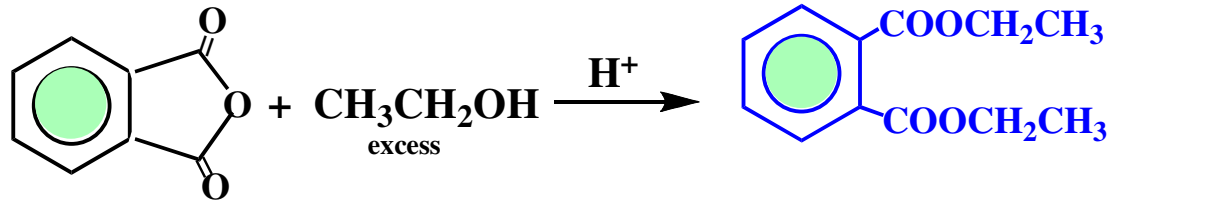
Draw the structures of the products of the following reactions.

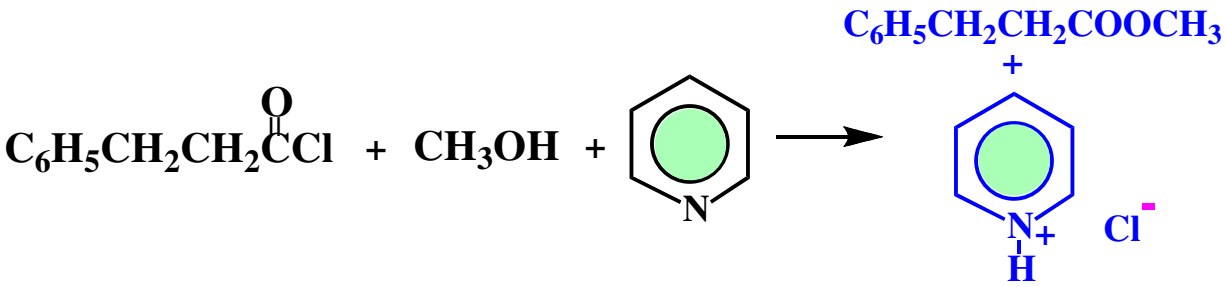




Quiz 18.08

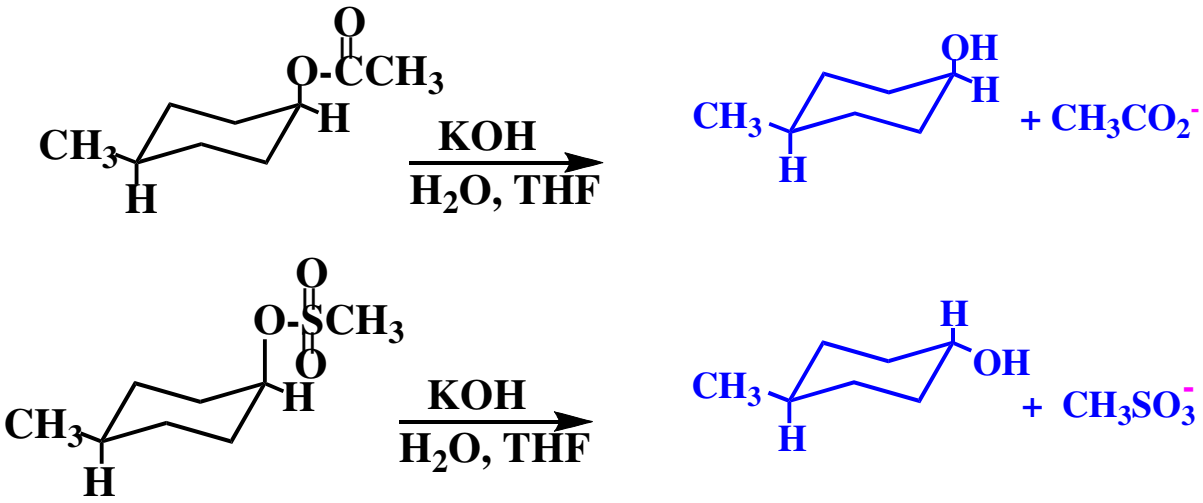
Draw the structures of the products of the following reactions.





Quiz 18.09

Draw the structures of the products of the following alkaline hydrolysis reactions.



End of Chapter 10

Dr. Abdullah I. Saleh