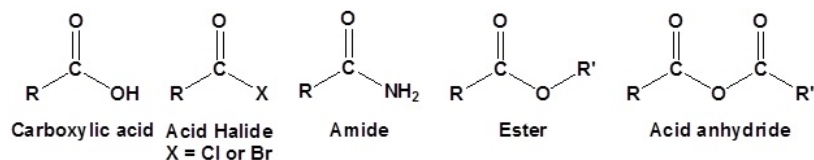


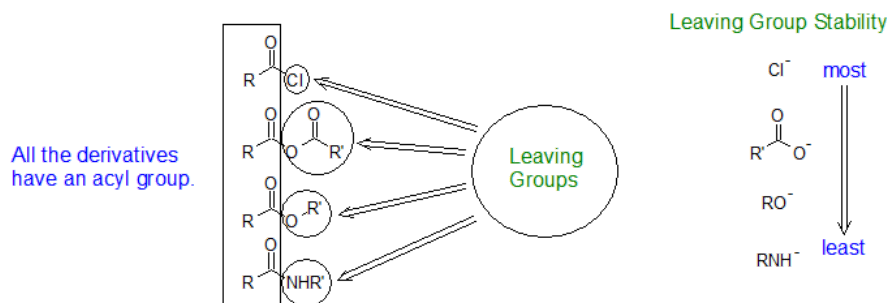
22.1: STRUCTURE AND PHYSICAL PROPERTIES OF ACID DERIVATIVES

THE STRUCTURE OF CARBOXYLIC ACID DERIVATIVES

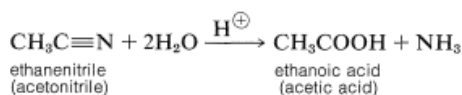
Carboxylic acid and its derivatives are functional groups with closely related chemistry.



The carboxylic acid derivatives all include an acyl group, an R-group bonded to a carbonyl carbon. The "other group" bonded to the carbonyl carbon distinguishes the derivatives from each other and has a strong influence on the relative reactivity between the derivatives. This "other group" takes the role of the "Leaving Group or LG" in Nucleophilic Acyl Substitution (NAS) reactions.




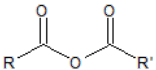
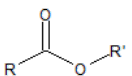

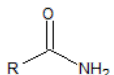
Although there are many types of carboxylic acid derivatives known, this chapter focuses on four: acid halides (acyl halides), acid anhydrides, esters, and amides. Another common feature of carboxylic acid derivatives is that they can be hydrolyzed back to the original carboxylic acid. For this reason, nitriles are sometimes grouped with the carboxylic acid derivatives and will also be discussed in this chapter. The hydrolysis reaction for acetonitrile is shown below as an example.



PHYSICAL PROPERTIES OF CARBOXYLIC ACID DERIVATIVES

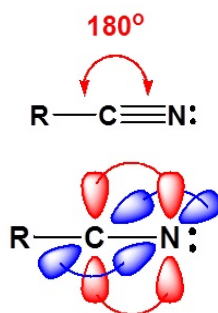
The intermolecular forces of the respective acyl group combine with the size and structure of the R-group to determine the physical properties of the the carboxylic acid derivatives as shown in the summary below.

Carboxylic Acid Derivatives and their Physical Properties

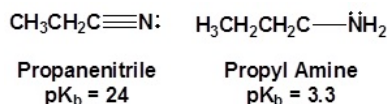
Name	Carboxylic Acid Derivative	Polarity & IMF's	Relative BP	Soluble in H ₂ O	General Comments
acyl chloride		polar no H's to donate	51	no	acid piercing odors
acid anhydride		polar no H's to donate	140	no	acid piercing odors
ester		polar no H's to donate	57	no	volatile fragrant liquids
carboxylic acid		H-bond dimers	118	yes if $\leq C_4$	acid piercing odors
amide		complex H-bonds	221	yes if $\leq C_3$	biologically important (proteins)
nitrile	$R-C\equiv N$	among most polar cpds w/o H-bonds	82	yes if $\leq C_3$	CH ₃ CN is useful, polar aprotic solvent

STRUCTURE AND PROPERTIES OF NITRILES

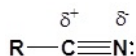
The electronic structure of nitriles is very similar to that of an alkyne with the main difference being the presence of a set of lone pair electrons on the nitrogen. Both the carbon and the nitrogen are *sp* hybridized which leaves them both with two p orbitals which overlap to form the two π bond in the triple bond. The R-C-N bond angle in a nitrile is 180° which gives a nitrile functional group a linear shape.



The lone pair electrons on the nitrogen are contained in a *sp* hybrid orbital which makes them much less basic than an amine. The 50% character of an *sp* hybrid orbital close to the nucleus and therefore less basic compared to other nitrogen containing compounds such as amines.



The presence of an electronegative nitrogen causes nitriles to be very polar molecules. Consequently, nitriles tend to have higher boiling points than molecules with a similar size.

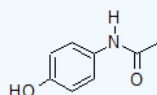


Boiling Point

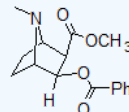
$\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$	96-98 °C
Propanenitrile	
$\text{CH}_3\text{CH}_2\text{C}\equiv\text{C}-\text{H}$	8.1 °C
Butyne	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	-1-1 °C
Butane	

Exercise

1. Design an extraction separation strategy to separate acetaminophen from cocaine using ether, 1 M HCl, and 3 M NaHCO₃. The structures for acetaminophen and cocaine are shown below.



acetaminophen

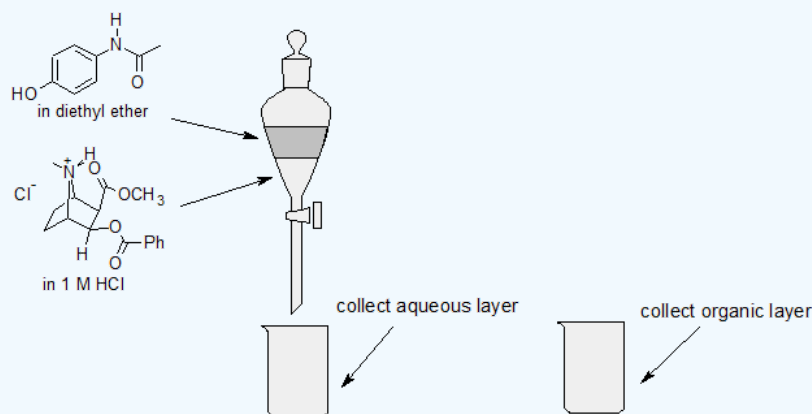


cocaine (free base form)

Answer

1.

Step 1: Dissolve both compounds in ether and add to a separatory funnel.
 Step 2: Add 1 M HCl to the separatory funnel.
 Step 3: Mix well to protonate the cocaine to a water soluble ammonium ion.
 Step 4: Collect the aqueous and organic layers.



Step 5: Neutralize the aqueous layer using 3 M NaHCO₃ to deprotonate cocaine hydrochloride to the free base.
 Step 6: Isolate the free base cocaine by vacuum filtration and allow the sample to dry.
 Step 7: Isolate the acetaminophen by removing the ether from the organic layer with evaporation using a warm water bath & a gentle flow of nitrogen gas.

CONTRIBUTORS AND ATTRIBUTIONS

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