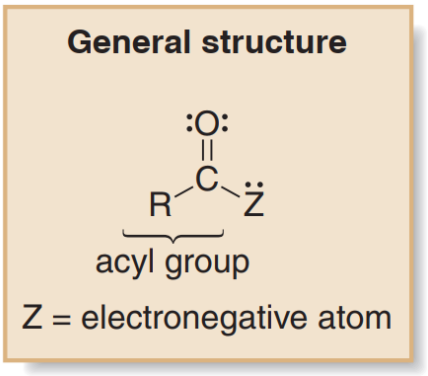
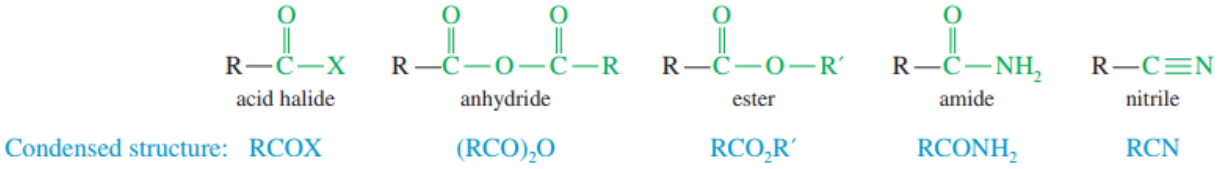
الكلية	كلية التربية للعلوم الصرفة
القسم	قسم الكيمياء
المادة باللغة الانجليزية	Organic chemistry
المادة باللغة العربية	الكيمياء العضوية
المرحلة الدراسية	المرحلة الثانية
اسم التدريسي	د. عمر جمال مهدي العسافي
عنوان المحاضرة باللغة الانجليزية	Anhydride
عنوان المحاضرة باللغة العربية	الانهدريد
رقم المحاضرة	الحادية عشر
المصادر والمراجع	***Organic Chemistry*** 6ed , William H. Brown, Christopher S. Foote, Brent L. Iverson, Eric V. Anslyn, Bruce M. Novak, 2012
	Organic Chemistry 3ed , Janice Gorzynski Smith, 2011
	Organic Chemistry" by Jonathan Clayden, Nick Greeves, and Stuart Warren

1. Introduction

Carbonyl compounds bonded to an electronegative atom called an acyl group. These include carboxylic acids and their derivatives such as acid anhydrides.

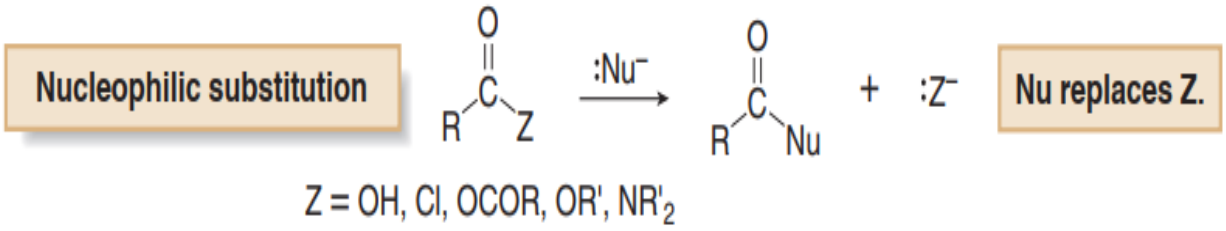


Carboxylic acid derivatives are defined as compounds with functional groups that can be converted to carboxylic acids by a simple acidic or basic hydrolysis.



All of these compounds contain an acyl group bonded to an electronegative atom Z that can serve as a leaving group. As a result, these compounds undergo nucleophilic acyl substitution.

Recall that aldehydes and ketones do not undergo nucleophilic substitution because they have no leaving group on the carbonyl carbon.

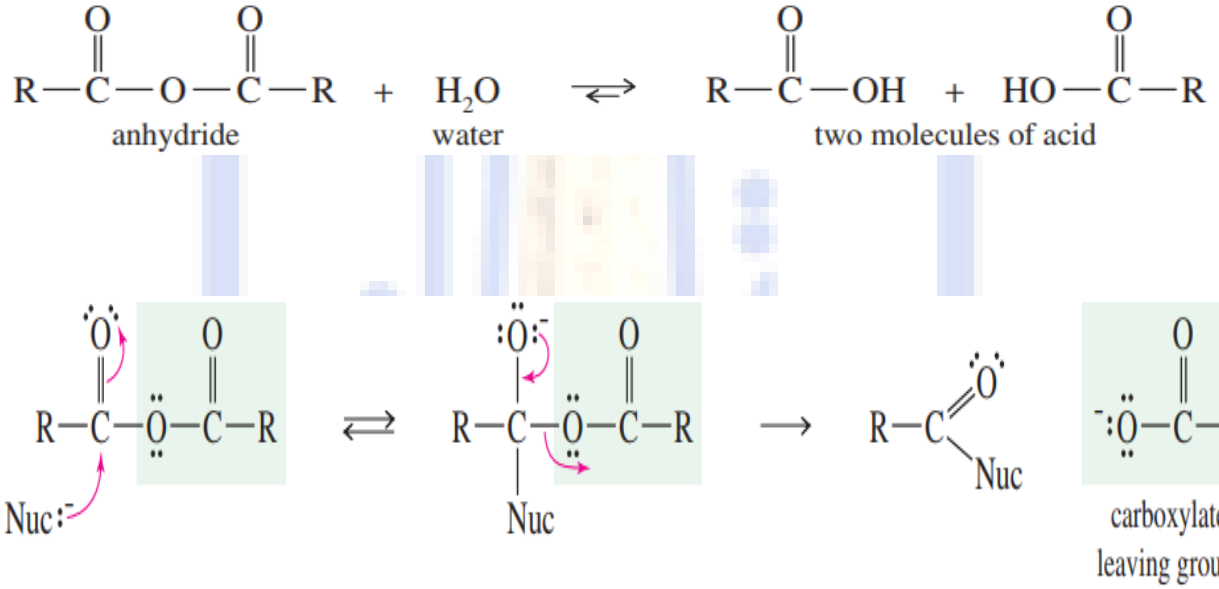


2-Nomenclature

The names of carboxylic acid derivatives are formed from the names of the parent carboxylic acids discussed in section previous. Keep in mind that the common names formic acid, acetic acid, and benzoic acid are virtually always used for the parent acid, so these common parent names are used for their derivatives as well.

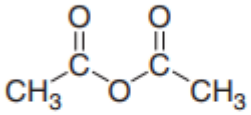
➢ Naming an Anhydride

The word anhydride means "without water." Removing one molecule of water from two molecules of carboxylic acid forms an anhydride.



Symmetrical anhydrides are named by changing the ***acid*** ending of the parent carboxylic acid to the word ***anhydride*.** **Mixed anhydrides**, which are derived from two different carboxylic acids, are named by alphabetizing the names for both acids and replacing the word ***acid*** by the word ***anhydride***.

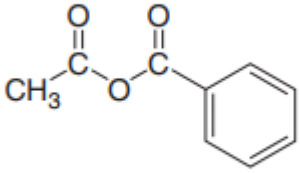
Symmetrical anhydride



derived from acetic acid

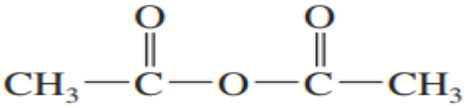
acetic anhydride

Mixed anhydride

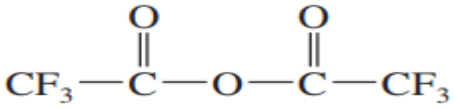


derived from acetic acid and benzoic acid

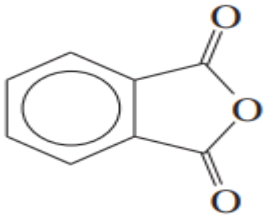
acetic benzoic anhydride



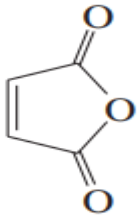
(abbreviated Ac_2O)
ethanoic anhydride
acetic anhydride



(abbreviated TFAA)
trifluoroethanoic anhydride
trifluoroacetic anhydride



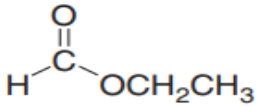
benzene-1,2-dicarboxylic anhydride
phthalic anhydride

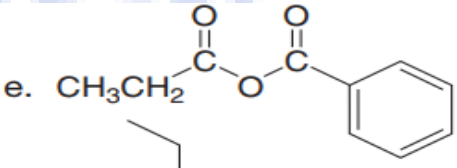


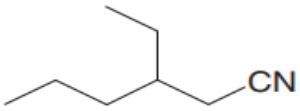
but-2-enedioic anhydride
maleic anhydride

Problem: Give an IUPAC or common name for each compound

a. $(CH_3CH_2)_2CHCOCl$
b. $C_6H_5COOCH_3$
c. $CH_3CH_2CON(CH_3)CH_2CH_3$

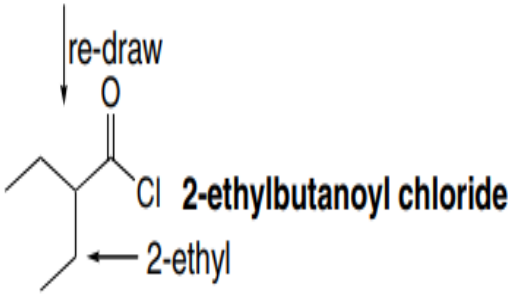
d. 

e. 

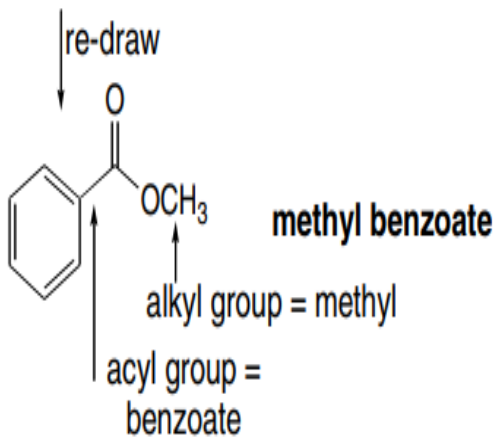
f. 

Solution

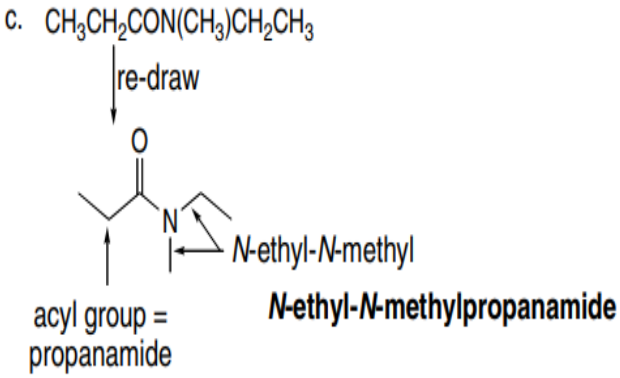
a. $(CH_3CH_2)_2CH-COCl$



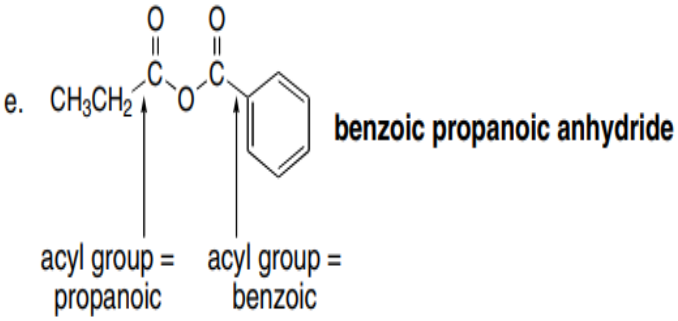
b. $C_6H_5COOCH_3$



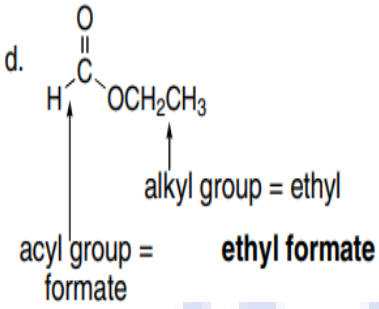
c. $CH_3CH_2CON(CH_3)CH_2CH_3$



e.



d.



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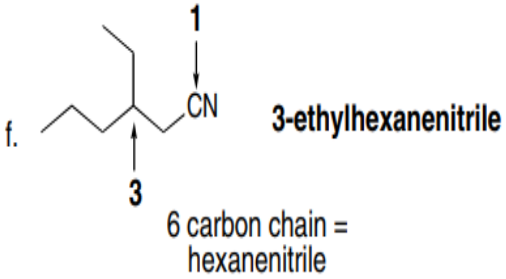
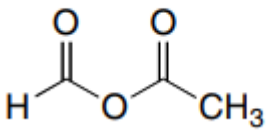


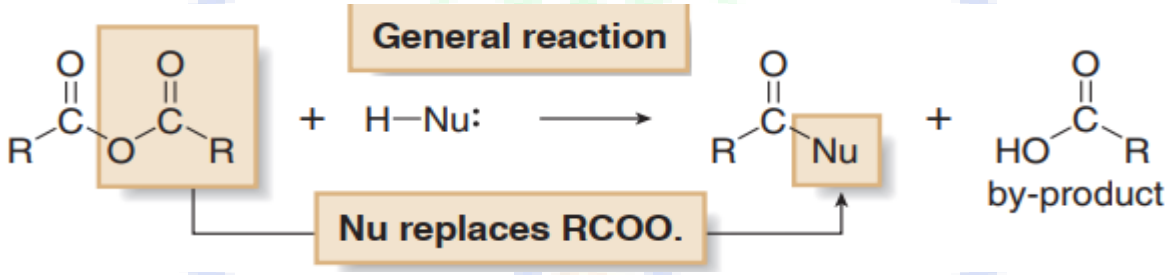
Problem: Draw the structure corresponding to name (acetic formic anhydride).

acetic formic anhydride

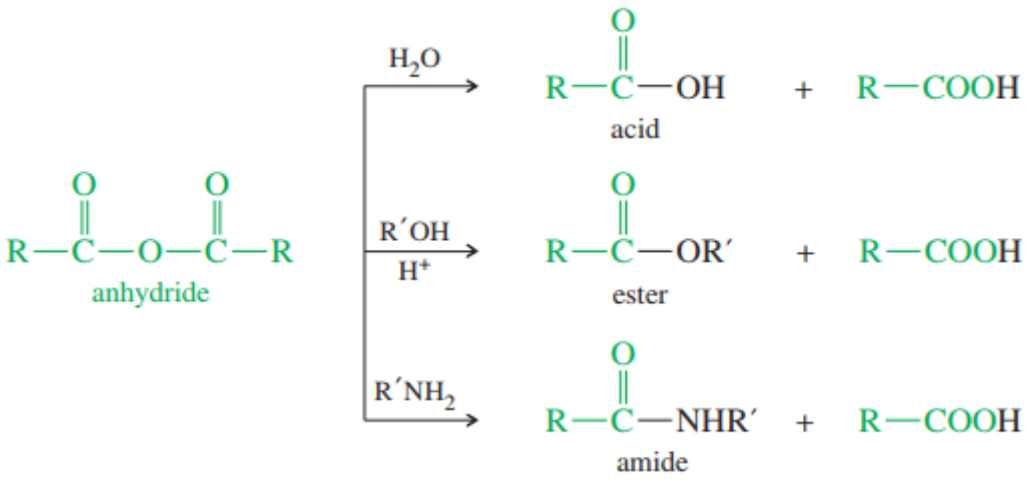


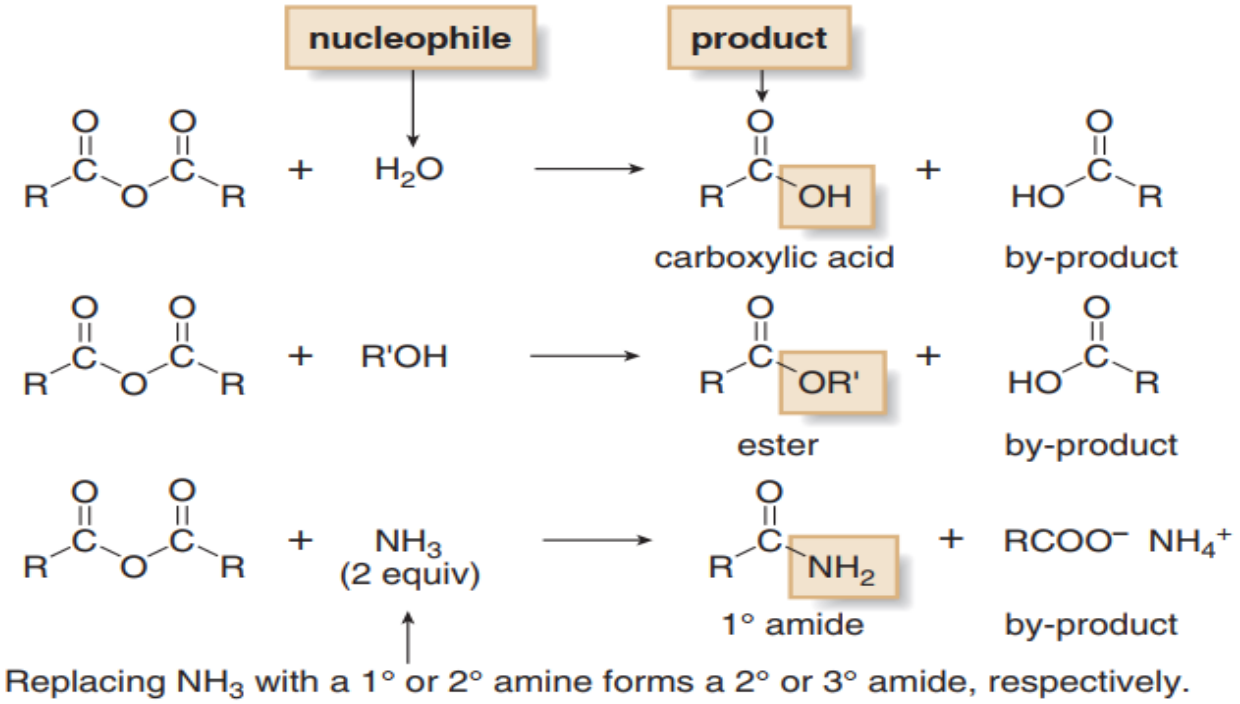
3. Reactions of Anhydrides

Although somewhat less reactive than acid chlorides, anhydrides nonetheless readily react with most nucleophiles to form substitution products. Nucleophilic substitution reactions of anhydrides are no different than the reactions of other carboxylic acid derivatives, even though anhydrides contain two carbonyl groups. Nucleophilic attack occurs at one carbonyl group, while the second carbonyl becomes part of the leaving group.



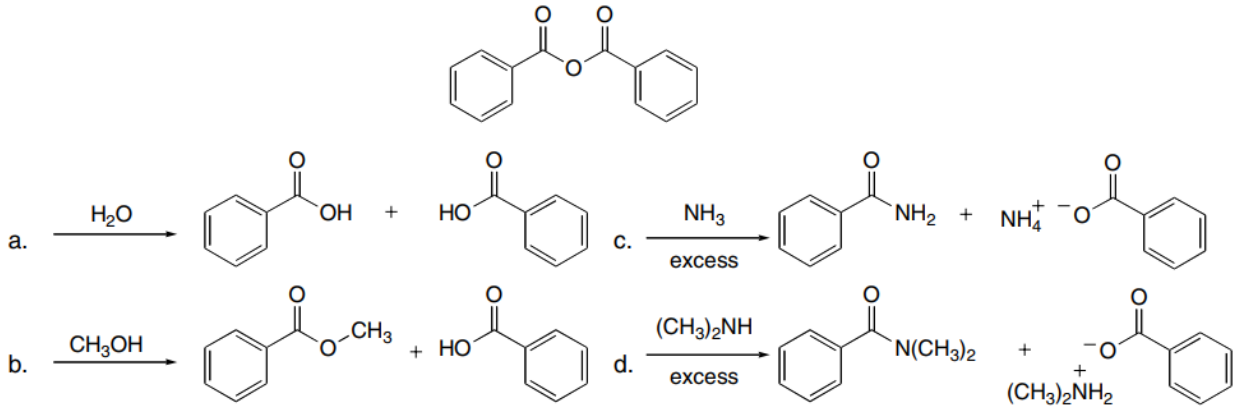
Anhydrides can't be used to make acid chlorides, because RCOO– is a stronger base and therefore a poorer leaving group than Cl–. Anhydrides can be used to make all other acyl derivatives, however. Reaction with water and alcohols yields carboxylic acids and esters, respectively. Reaction with two equivalents of NH3 or amines forms 1°, 2°, and 3° amides. A molecule of carboxylic acid (or a carboxylate salt) is always formed as a by-product.





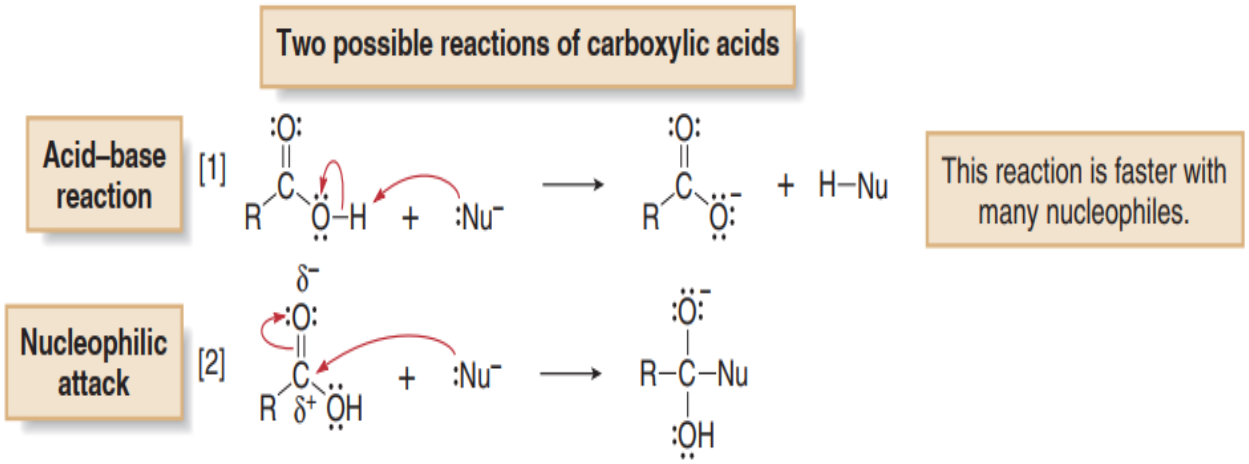
Problem: Draw the products formed when benzoic anhydride [(C6H5CO)2O] is treated with each nucleophile: (a) H2O; (b) CH3OH; (c) NH3 (excess); (d) (CH3)2NH (excess).

Solution:



4. Reactions of Carboxylic Acids

Carboxylic acids are strong organic acids. Because acid–base reactions proceed rapidly, any nucleophile that is also a strong base will react with a carboxylic acid by removing a proton first, before any nucleophilic substitution reaction can take place.



An acid–base reaction (Reaction [1]) occurs with –OH, NH3, and amines, all common nucleophiles used in nucleophilic acyl substitution reactions. Nonetheless, carboxylic acids can be converted to a variety of other acyl derivatives using special reagents, with acid catalysis, or sometimes, by using rather forcing reaction conditions.

Conversion of RCOOH to (RCO)2O

Carboxylic acids cannot be readily converted to anhydrides, but dicarboxylic acids can be converted to cyclic anhydrides by heating to high temperatures. This is a dehydration reaction because a water molecule is lost from the diacid.