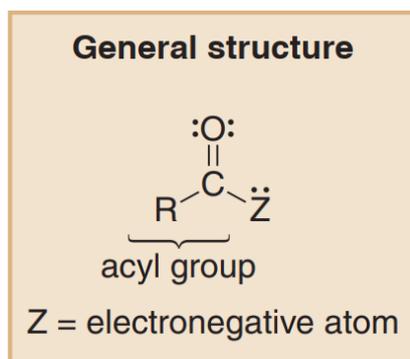


كلية التربية للعلوم الصرفة	الكلية
قسم الكيمياء	القسم
Organic chemistry	المادة باللغة الانجليزية
الكيمياء العضوية	المادة باللغة العربية
المرحلة الثانية	المرحلة الدراسية
د. عمر جمال مهدي العسافي	اسم التدريسي
Amide	عنوان المحاضرة باللغة الانجليزية
الاميد	عنوان المحاضرة باللغة العربية
الثالثة عشر	رقم المحاضرة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

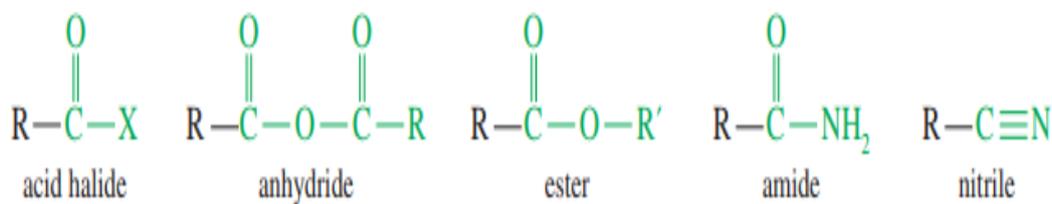


1. Introduction

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



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



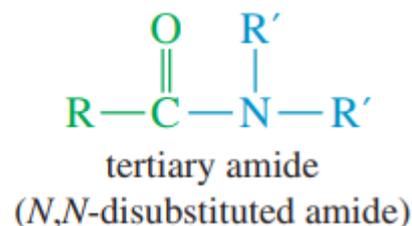
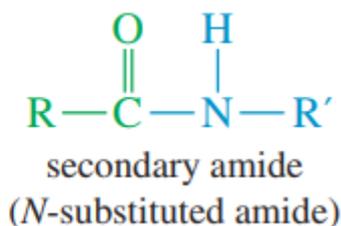
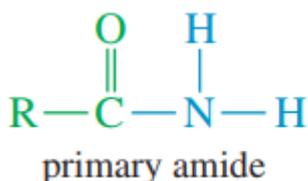
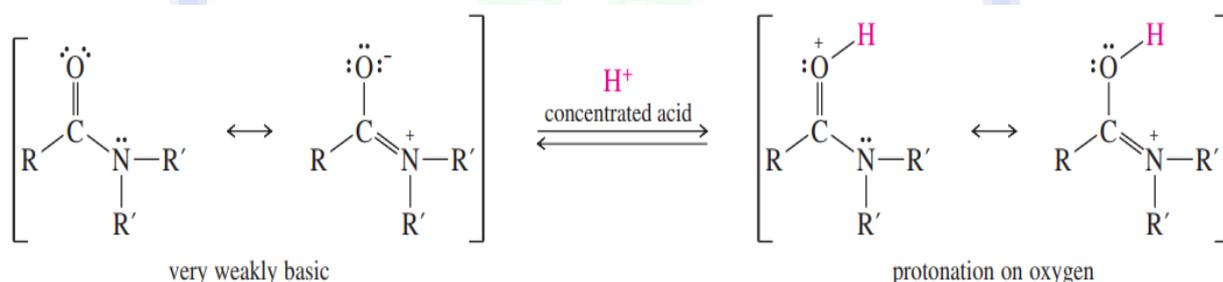
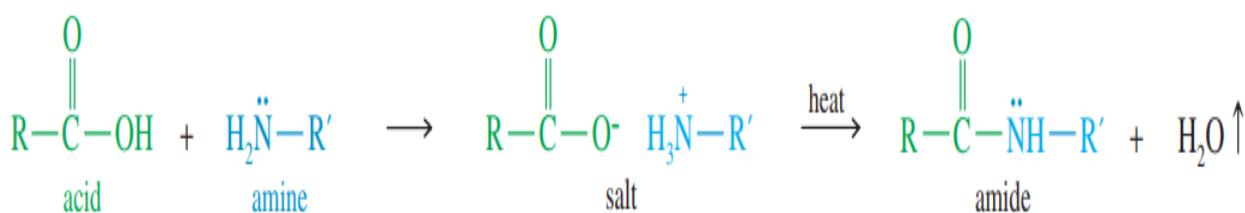
Condensed structure: RCOX $(\text{RCO})_2\text{O}$ $\text{RCO}_2\text{R}'$ RCONH_2 RCN

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.

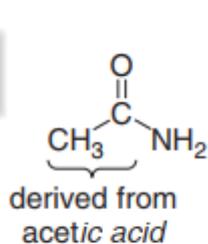
➤ Naming an Amide

An amide is a composite of a carboxylic acid and ammonia or an amine. An acid reacts with an amine to form an ammonium carboxylate salt. When this salt is heated to well above 100 °C, water is driven off and an amide results.

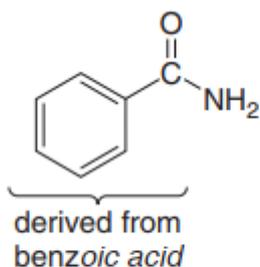


All 1° amides are named by replacing the *-ic acid*, *-oic acid*, or *-ylic acid* ending with the suffix **amide**.

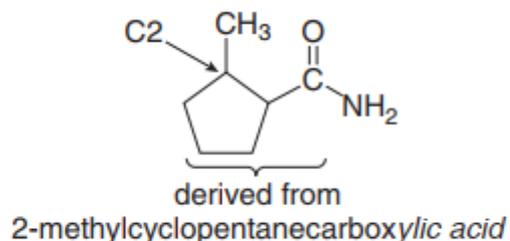
Naming 1° amides



acetamide



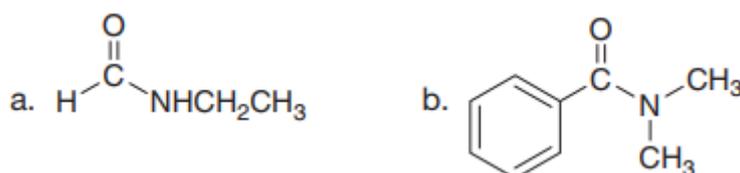
benzamide



2-methylcyclopentanecarboxamide

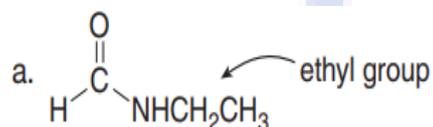
A 2° or 3° amide has two parts to its structure: an **acyl group** that contains the carbonyl group (**RCO-**) and one or two **alkyl groups** bonded to the nitrogen atom.

Example Give a systematic name for each amide:

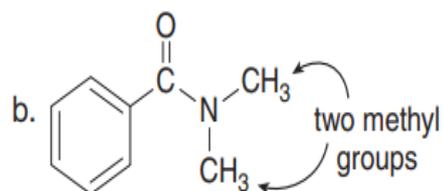


Step [1] Name the alkyl group (or groups) bonded to the N atom of the amide. Use the prefix “N-” preceding the name of each alkyl group.

- The names of the alkyl groups form the first part of each amide name.
- For 3° amides, use the prefix **di-** if the two alkyl groups on N are the same. If the two alkyl groups are different, **alphabetize** their names. One “N-” is needed for each alkyl group, even if both R groups are identical.



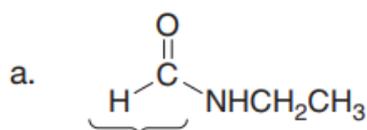
- The compound is a 2° amide with one ethyl group → *N*-ethyl.



- The compound is a 3° amide with two methyl groups.
- Use the prefix di- and two “N-” to begin the name → *N,N*-dimethyl.

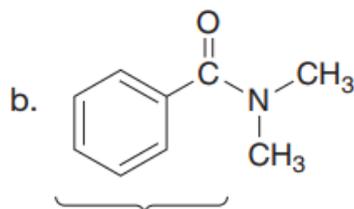
Step [2] Name the acyl group (RCO –) with the suffix –amide

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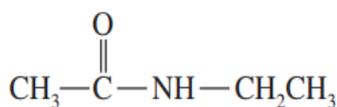
derived from
formic acid -----> formamide

- Change the *-ic acid* or *-oic acid* suffix of the parent carboxylic acid to the suffix *-amide*.
- Put the two parts of the name together.
- **Answer: N-ethylformamide**

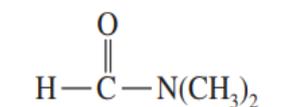


derived from
benzoic acid -----> benzamide

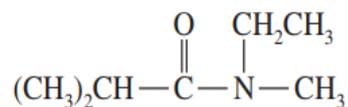
- Change *benzoic acid* to *benzamide*.
- Put the two parts of the name together.
- **Answer: N,N-dimethylbenzamide**



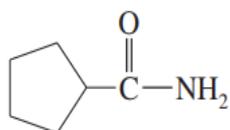
IUPAC name: *N*-ethylethanamide
common name: *N*-ethylacetamide



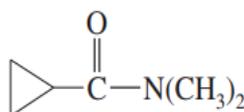
IUPAC name: *N,N*-dimethylmethanamide
common name: *N,N*-dimethylformamide



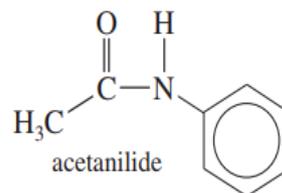
IUPAC name: *N*-ethyl-*N*,2-dimethylpropanamide
common name: *N*-ethyl-*N*-methylisobutyramide



cyclopentanecarboxamide

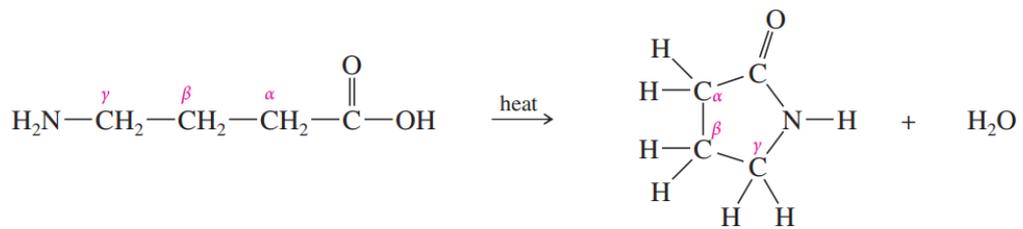


N,N-dimethylcyclopropanecarboxamide



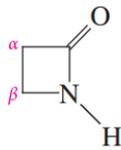
acetanilide

Lactams Cyclic amides are called **lactams**. Lactams are formed from amino acids, where the amino group and the carboxyl group have joined to form an amide. Lactams are named like lactones, by adding the term lactam at the end of the IUPAC name of the parent acid. Common names of lactams are formed by changing the *-ic acid* ending of the amino acid to *-olactam*.

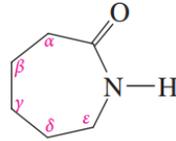


IUPAC name: 4-aminobutanoic acid
 common name: γ -aminobutyric acid

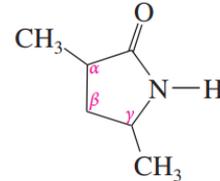
4-aminobutanoic acid lactam
 γ -butyrolactam



IUPAC name: 3-aminopropanoic acid lactam
 common name: β -propiolactam

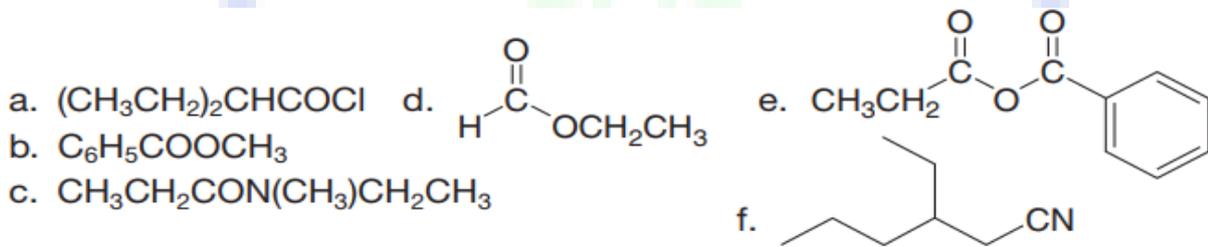


6-aminohexanoic acid lactam
 ϵ -caprolactam

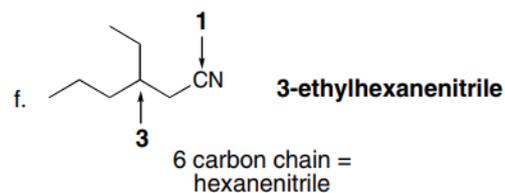
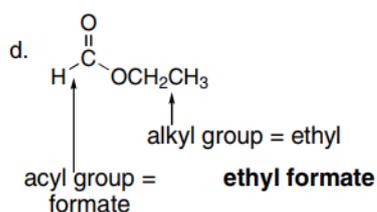
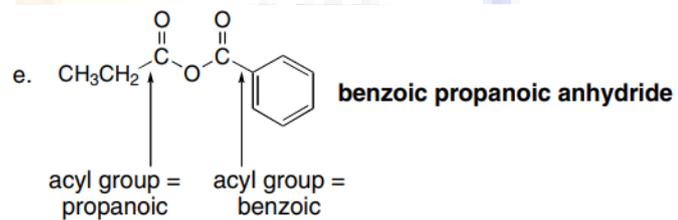
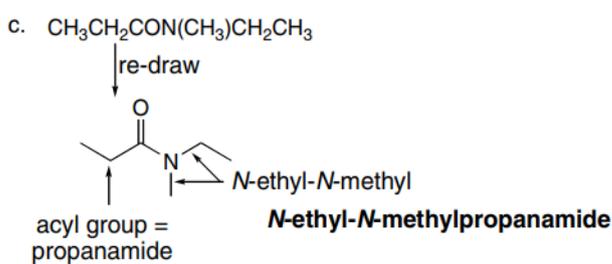
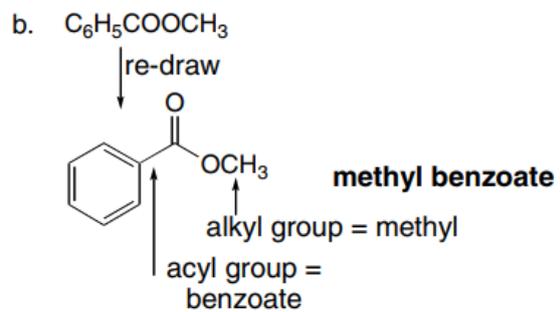
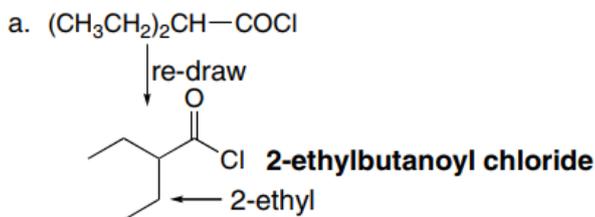


4-amino-2-methylpentanoic acid lactam
 α -methyl- γ -valerolactam

Problem: Give an IUPAC or common name for each compound



Solution



Problem: Draw the structure corresponding to each name.

a. 5-methylheptanoyl chloride

e. 3-methylpentanenitrile

b. isopropyl propanoate

f. o-cyanobenzoic acid

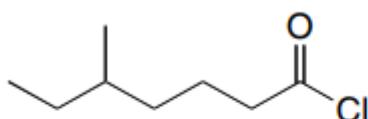
c. acetic formic anhydride

g. sec-butyl 2-methylhexanoate

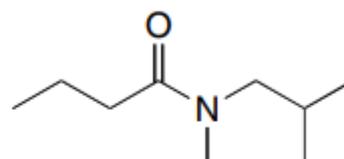
d. N-isobutyl-N-methylbutanamide

h. N-ethylhexanamide

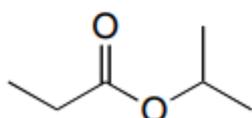
a. 5-methylheptanoyl chloride



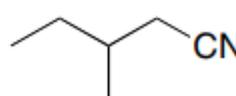
d. N-isobutyl-N-methylbutanamide



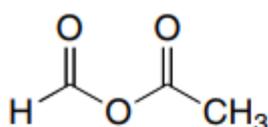
b. isopropyl propanoate



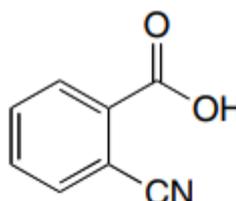
e. 3-methylpentanenitrile



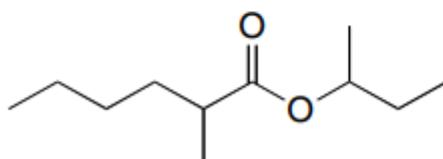
c. acetic formic anhydride



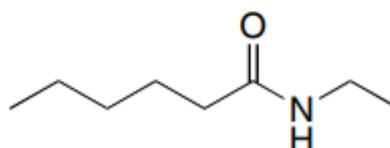
f. o-cyanobenzoic acid



g. sec-butyl 2-methylhexanoate



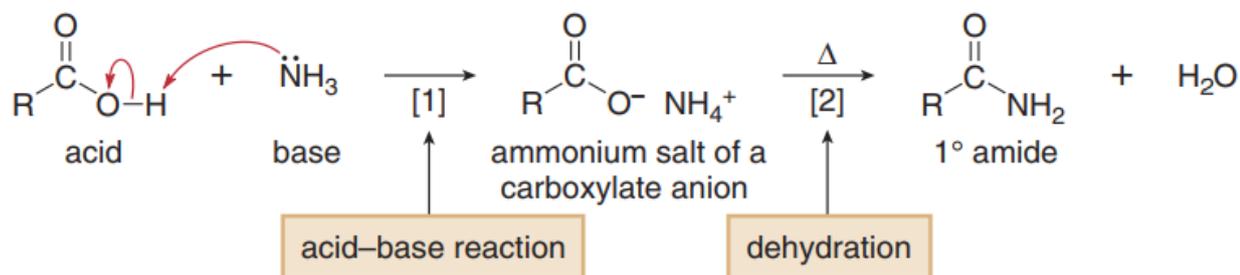
h. N-ethylhexanamide



3. Conversion of RCOOH to RCONR'2

The direct conversion of a carboxylic acid to an amide with NH_3 or an amine is very difficult, even though a more reactive acyl compound is being transformed into a less reactive one. The problem is that carboxylic acids are strong organic acids and NH_3 and amines are bases, so they undergo an acid–

base reaction to form an ammonium salt before any nucleophilic substitution occurs.

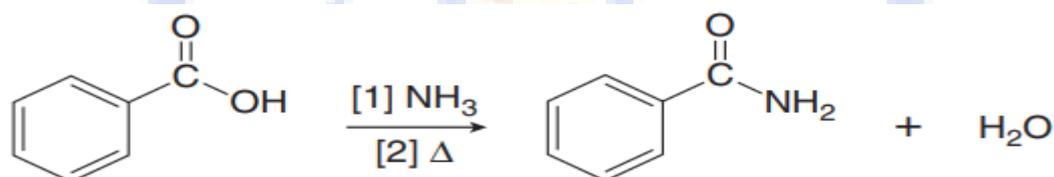


Heating at high temperature (>100 °C) dehydrates the resulting ammonium salt of the carboxylate anion to form an amide, though the yield can be low.

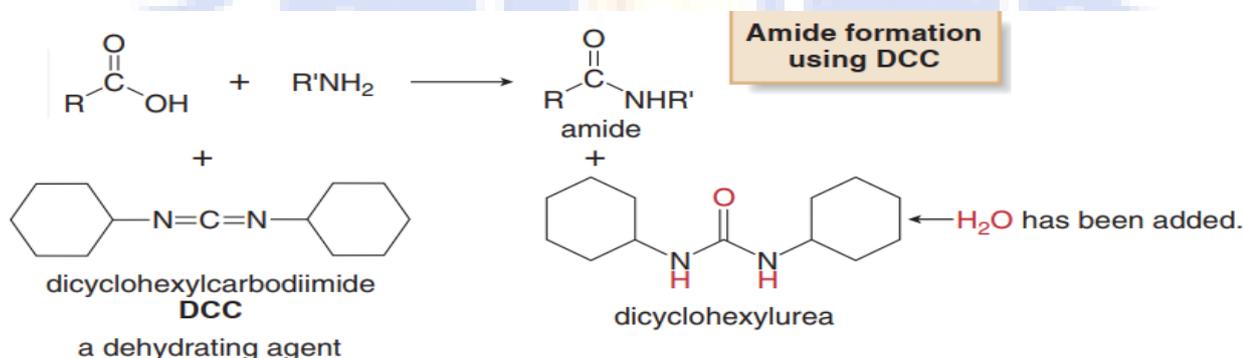
Therefore, the overall conversion of RCOOH to RCONH₂ requires two steps:

[1] Acid–base reaction of RCOOH with NH₃ to form an ammonium salt

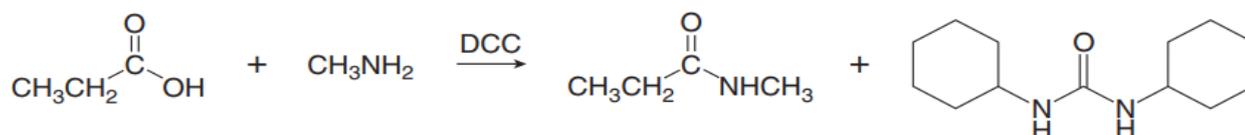
[2] Dehydration at high temperature (>100 °C)



A carboxylic acid and an amine readily react to form an amide in the presence of an additional reagent, dicyclohexylcarbodiimide (DCC), which is converted to the by-product dicyclohexylurea in the course of the reaction



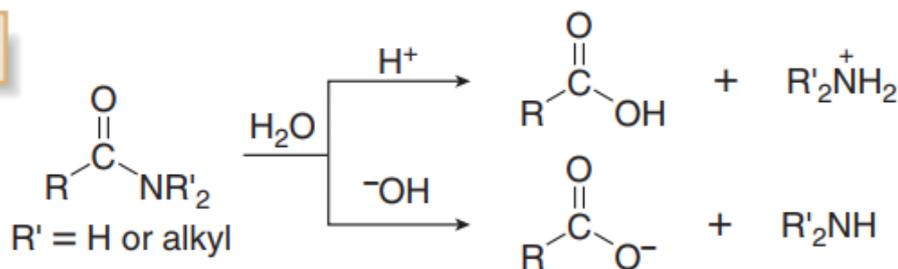
DCC is a dehydrating agent. The dicyclohexylurea by-product is formed by adding the elements of H₂O to DCC. DCC promotes amide formation by converting the carboxy OH group into a better leaving group.



4. Reactions of Amides

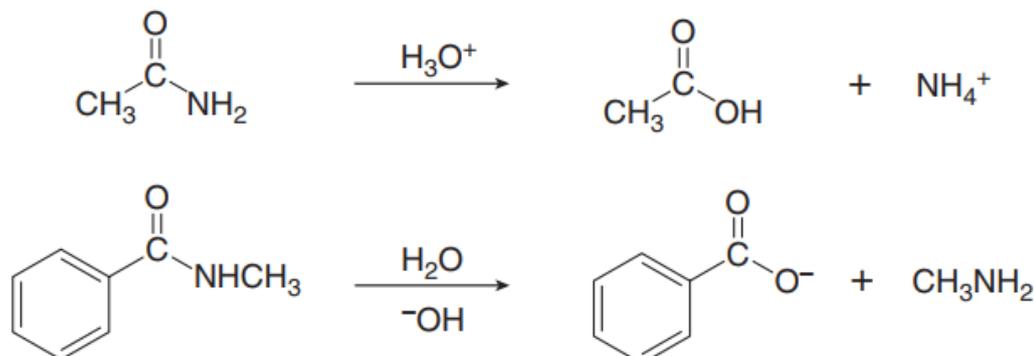
Because amides have the poorest leaving group of all the carboxylic acid derivatives, they are the least reactive. Under strenuous reaction conditions, amides are hydrolyzed in acid or base to form carboxylic acids or carboxylate anions.

Amide hydrolysis



In acid, the amine by-product is protonated as an ammonium ion, whereas in base, a neutral amine is formed.

Examples





Increasing reactivity

Table 4: Summary of the Nucleophilic Substitution Reactions of Carboxylic Acids and Their Derivatives

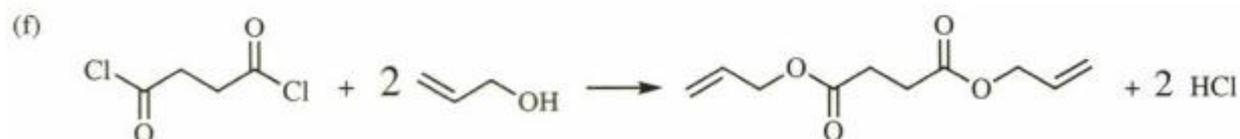
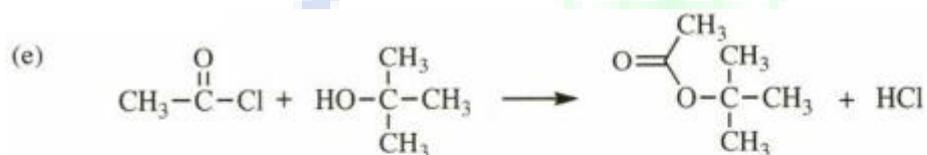
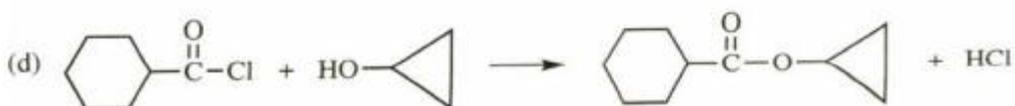
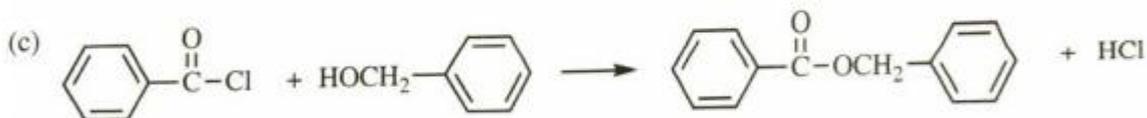
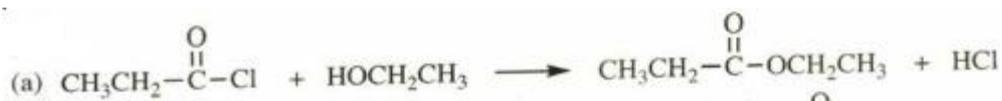
Starting material	Product				
	RCOCl	(RCO) ₂ O	RCOOH	RCOOR'	RCONR' ₂
[1] RCOCl →	-	✓	✓	✓	✓
[2] (RCO) ₂ O →	X	-	✓	✓	✓
[3] RCOOH →	✓	✓	-	✓	✓
[4] RCOOR' →	X	X	✓	-	✓
[5] RCONR' ₂ →	X	X	✓	X	-

Table key: ✓ = A reaction occurs.
X = No reaction occurs.

PROBLEM

Show how you would synthesize the following esters from appropriate acyl chlorides and alcohols.

- (a) ethyl propionate
- (b) phenyl 3-methylhexanoate
- (c) benzyl benzoate
- (d) cyclopropyl cyclohexanecarboxylate
- (e) *tert*-butyl acetate
- (f) diallyl succinate

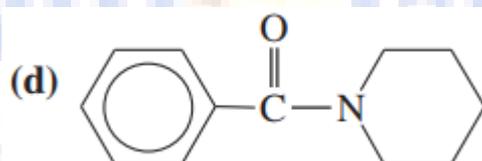


PROBLEM Show how you would use appropriate acyl chlorides and amines to synthesize the following amides.

(a) N,N-dimethylacetamide

(b) acetanilide (PhNHCOCH_3)

(c) cyclohexanecarboxamide



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