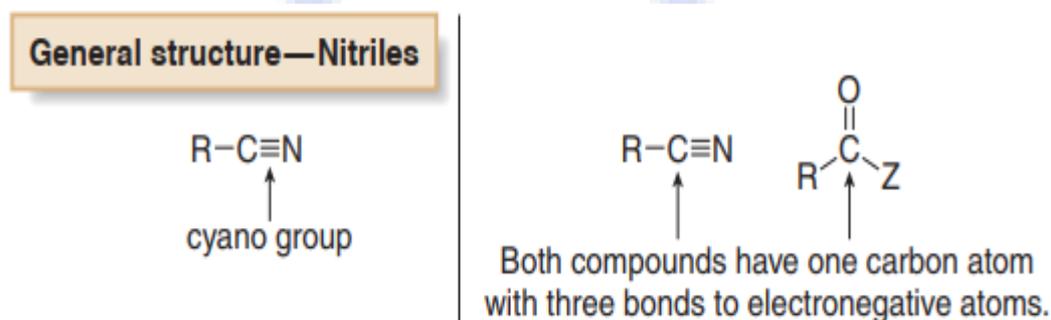


كلية التربية للعلوم الصرفة	الكلية
قسم الكيمياء	القسم
Organic chemistry	المادة باللغة الانجليزية
الكيمياء العضوية	المادة باللغة العربية
المرحلة الثانية	المرحلة الدراسية
د. عمر جمال مهدي العسافي	اسم التدريسي
Nitrile	عنوان المحاضرة باللغة الانجليزية
النتريل	عنوان المحاضرة باللغة العربية
الرابعة عشر	رقم 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	



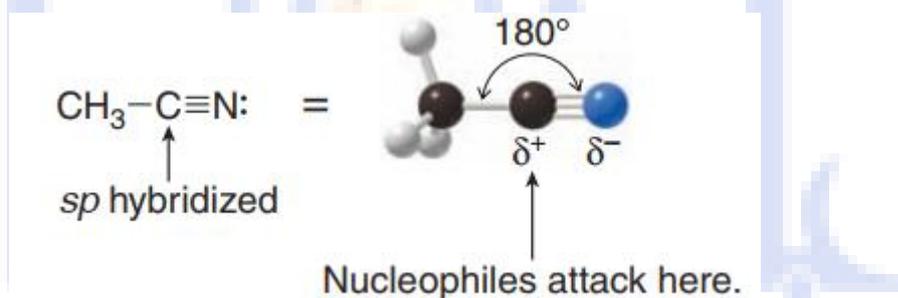
Nitriles are compounds that contain a cyano group, C N, bonded to an alkyl group. Nitriles have no carbonyl group, so they are structurally distinct from carboxylic acids and their derivatives. The carbon atom of the cyano group, however, has the same oxidation state as the carbonyl carbon of carboxylic acid derivatives, so there are certain parallels in their chemistry.



Both compounds have one carbon atom with three bonds to electronegative atoms.

2- Structure and Bonding

The structure and bonding in nitriles is very different from the carboxylic acid derivatives, and resembles the carbon–carbon triple bond of alkynes.



- The carbon atom of the CN group is *sp* hybridized, making it linear with a bond angle of 180°.

- The triple bond consists of one σ and two π bonds.

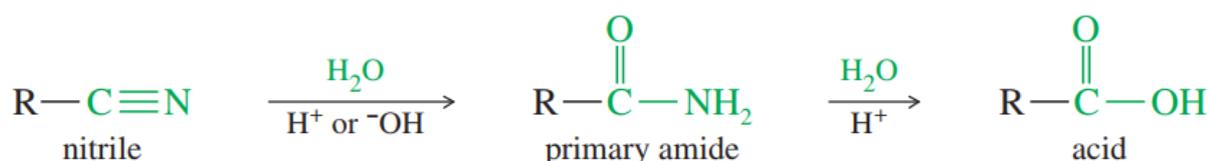
Like the carboxylic acid derivatives, nitriles contain an electrophilic carbon atom, making them susceptible to nucleophilic attack.

3-Nomenclature

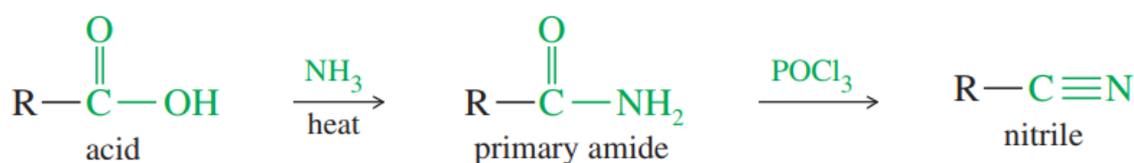
➤ Naming a Nitrile

Nitriles contain the **cyano group**, -CN . Although nitriles lack the carbonyl group of carboxylic acids, they are classified as acid derivatives because they hydrolyze to give carboxylic acids and can be synthesized by dehydration of amides.

Hydrolysis to an acid



Synthesis from an acid



In contrast to the carboxylic acid derivatives, **nitriles are named as alkane derivatives**. To name a nitrile using IUPAC rules:

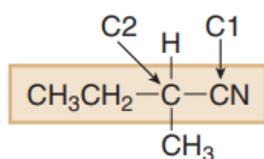
- **Find the longest chain that contains the CN and add the word nitrile to the name of the parent alkane. Number the chain to put CN at C1, but omit this number from the name.**

Common names for nitriles are derived from the names of the carboxylic acid having the same number of carbon atoms by replacing the **-ic acid** ending of the carboxylic acid by the suffix **-onitrile**.

When CN is named as a substituent, it is called a **cyano** group.

In naming a nitrile, the CN carbon is one carbon atom of the longest chain. $\text{CH}_3\text{CH}_2\text{CN}$ is propanenitrile, not ethanenitrile.

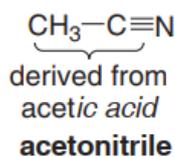
a. IUPAC name for a nitrile



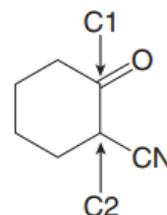
butane + nitrile
(4 C's)

2-methylbutanenitrile

b. Common name for a nitrile

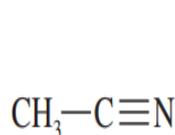


c. CN as a substituent

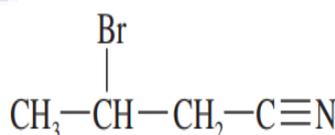


2-cyanocyclohexanone

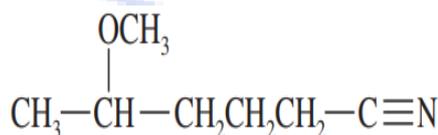
IUPAC name:
common name:



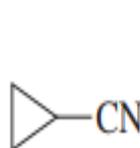
ethanenitrile
acetonitrile



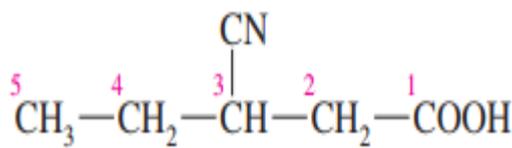
3-bromobutanenitrile
 β -bromobutyronitrile



5-methoxyhexanenitrile
 δ -methoxycapronitrile



cyclopropanecarbonitrile



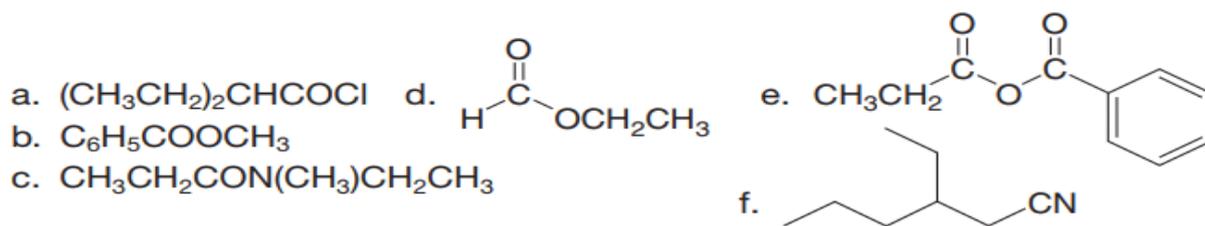
3-cyanopentanoic acid

Table 2 summarizes the most important points about the nomenclature of carboxylic acid derivatives.

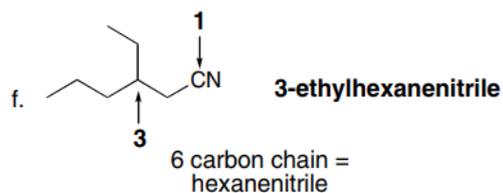
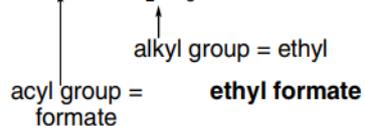
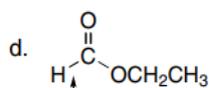
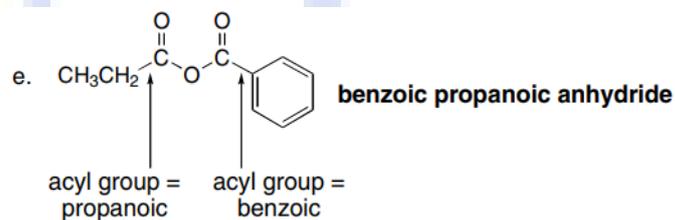
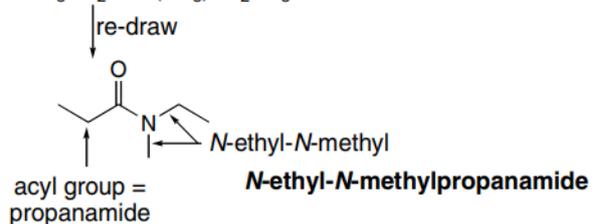
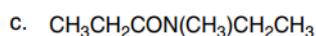
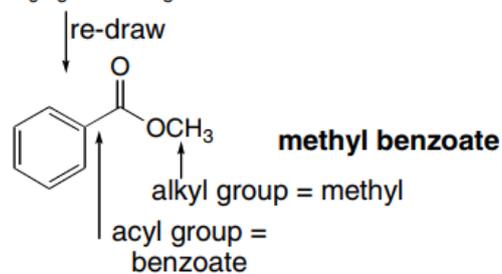
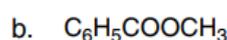
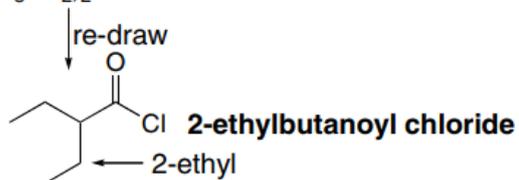
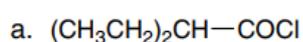
Table 2 Summary: Nomenclature of Carboxylic Acid Derivatives and Nitriles

Compound	Name ending	Example	Name
acid chloride	-yl chloride or -carbonyl chloride		benzoyl chloride
anhydride	anhydride		benzoic anhydride
ester	-ate		ethyl benzoate
amide	-amide		<i>N</i> -methylbenzamide
nitrile	-nitrile or -onitrile	$C_6H_5-C\equiv N$	benzonitrile

Problem: Give an IUPAC or common name for each compound



Solution



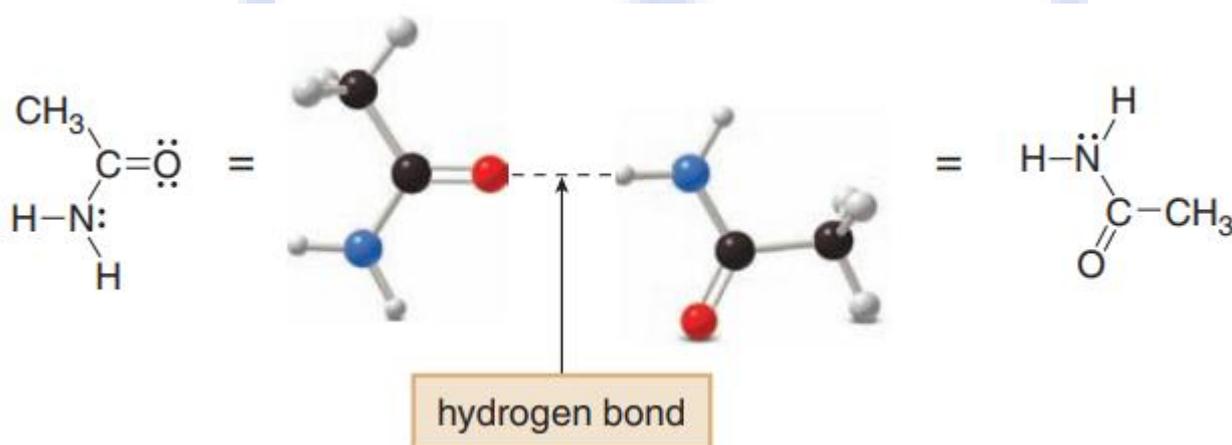
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4- Physical Properties

Because all carbonyl compounds have a polar carbonyl group, they exhibit dipole–dipole interactions. Nitriles also have dipole–dipole interactions because they have a polar CN group.

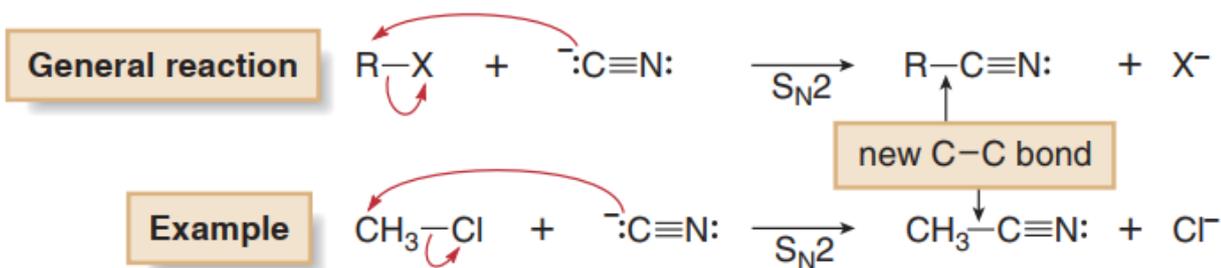
Because they contain one or two N-H bonds, 1° and 2° amides are capable of intermolecular hydrogen bonding. The N – H bond of one amide intermolecularly hydrogen bonds to the CO of another amide, as shown using two acetamide molecules (CH₃CONH₂).

How these factors affect the physical properties of carboxylic acid derivatives is summarized in Table 3.

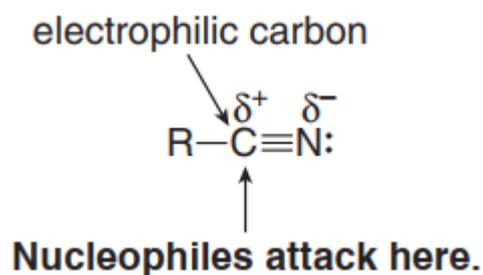


5. Reaction of Nitriles

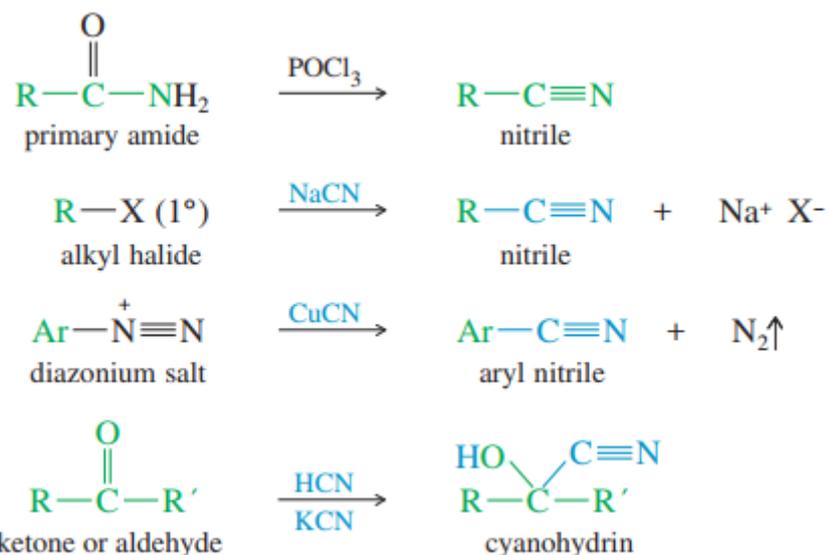
Nitriles are readily prepared by S_N2 substitution reactions of unhindered methyl and 1° alkyl halides with –CN. This reaction adds one carbon to the alkyl halide and forms a new carbon–carbon bond.



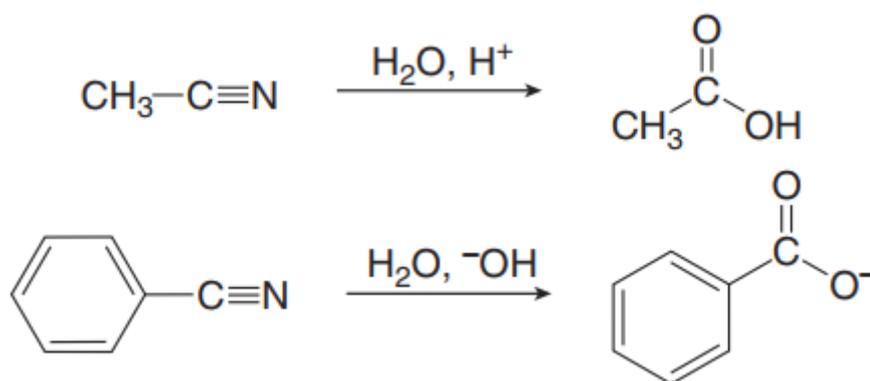
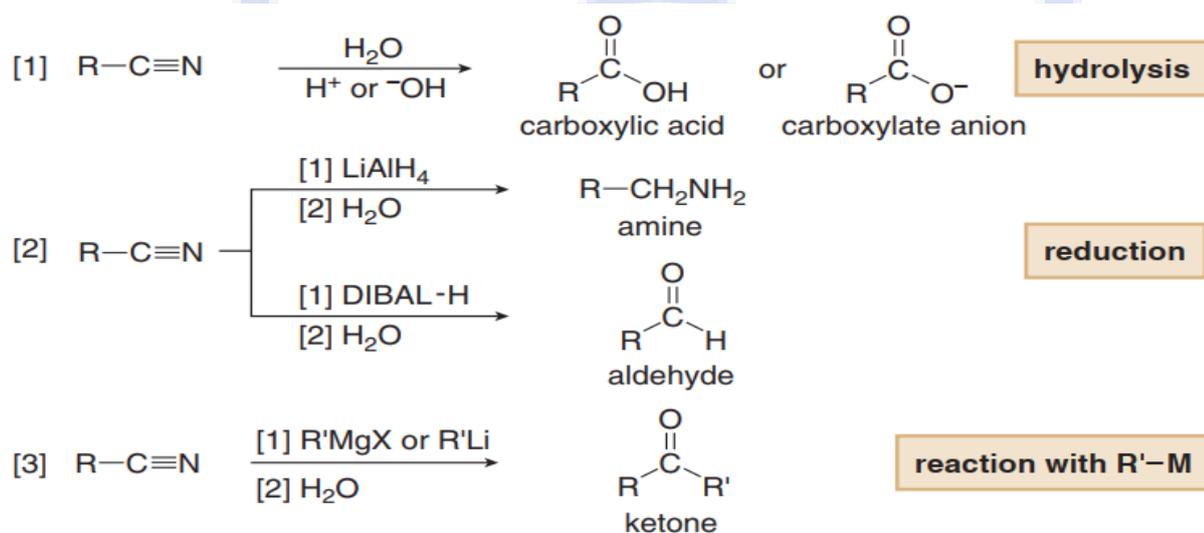
Because nitriles have no leaving group, they do not undergo nucleophilic substitution reactions like carboxylic acid derivatives. Because the cyano group contains an electrophilic carbon atom that is part of a multiple bond, a nitrile reacts with nucleophiles by a nucleophilic addition reaction. The nature of the nucleophile determines the structure of the product.



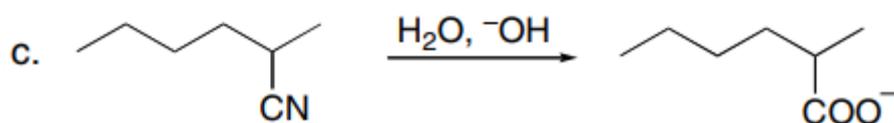
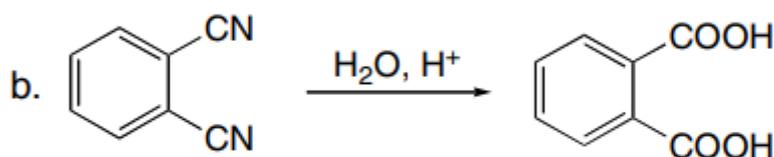
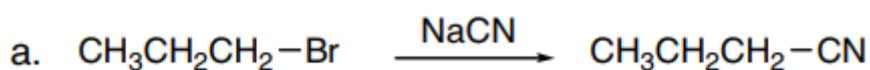
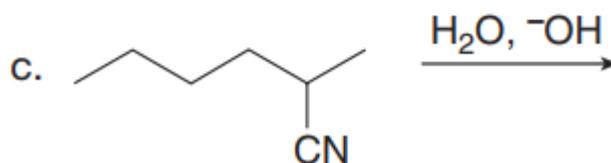
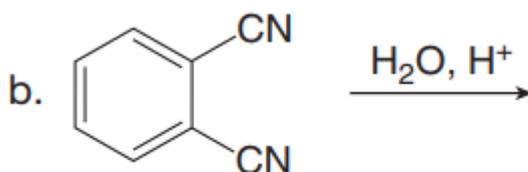
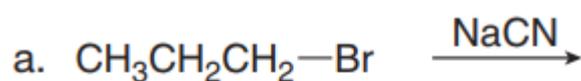
Although nitriles lack an acyl group, they are considered acid derivatives because they hydrolyze to carboxylic acids. Nitriles are frequently made from carboxylic acids (with the same number of carbons) by conversion to primary amides followed by dehydration. They are also made from primary alkyl halides and tosylates (adding one carbon) by nucleophilic substitution with cyanide ion. Aryl cyanides can be made by the Sandmeyer reaction of an aryldiazonium salt with cuprous cyanide. α -Hydroxynitriles (cyanohydrins) are made by the reaction of ketones and aldehydes with HCN.



The reactions of nitriles with water, hydride, and organometallic reagents as nucleophiles are as follows:



Problem: Draw the products of each reaction.

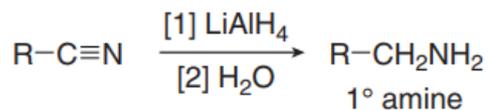


Reduction of Nitriles

Nitriles are reduced with metal hydride reagents to form either 1° amines or aldehydes, depending on the reducing agent.

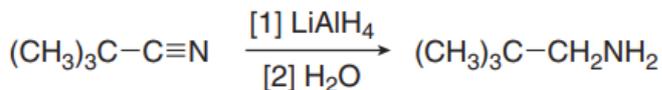
- Treatment of a nitrile with LiAlH_4 followed by H_2O adds two equivalents of H_2 across the triple bond, forming a 1° amine.

General reaction



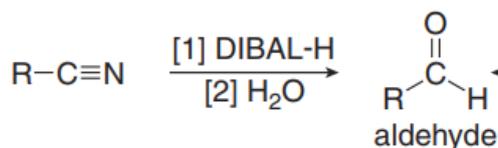
addition of two equivalents of H₂

Example



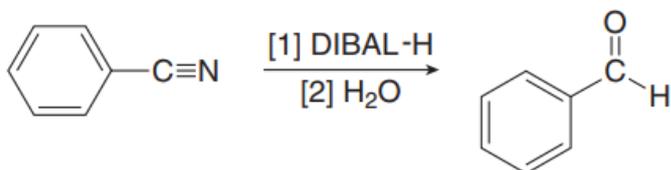
- Treatment of a nitrile with a milder reducing agent such as DIBAL-H followed by H₂O forms an aldehyde.

General reaction



addition of one equivalent of H₂

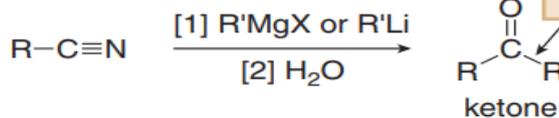
Example



Addition of Grignard and Organolithium Reagents to Nitriles

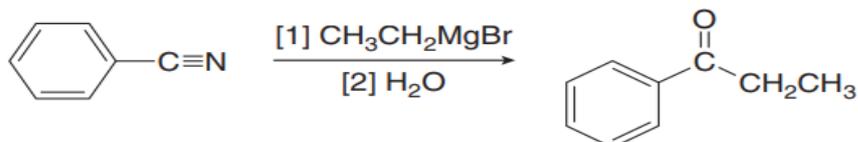
Both Grignard and organolithium reagents react with nitriles to form ketones with a new carbon-carbon bond.

General reaction



new C-C bond

Example



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