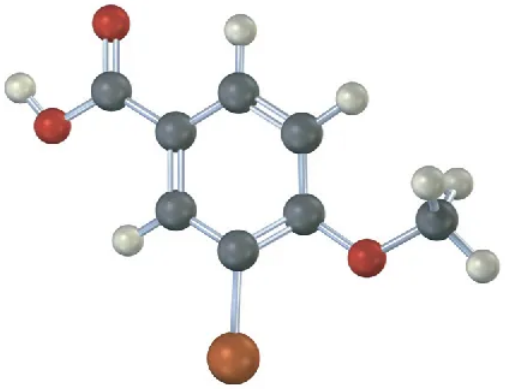
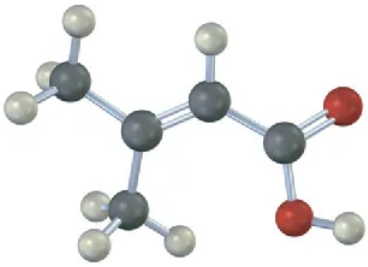
6.10: Additional Problems

Visualizing Chemistry

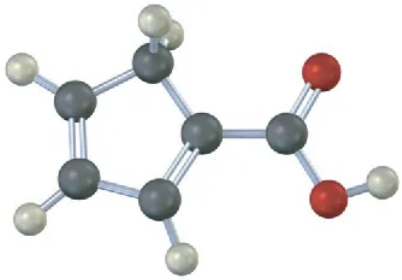
Give IUPAC names for the following carboxylic acids (reddish brown = Br): (a)



(b)



(c)



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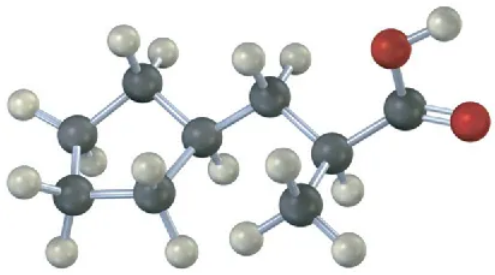
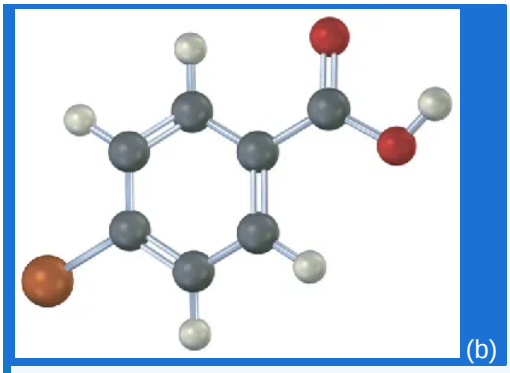
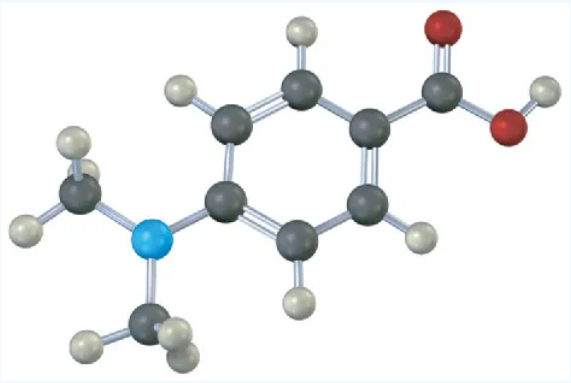
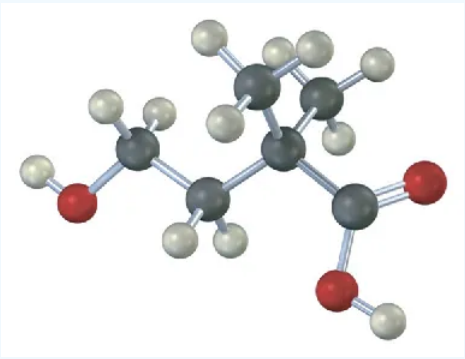



(b)

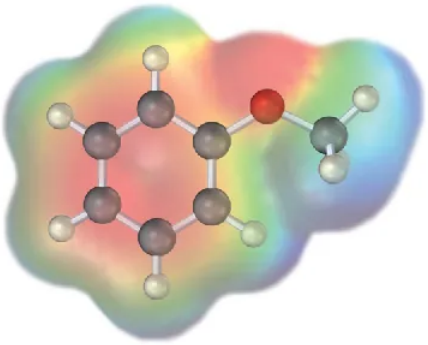


Problem 20-19

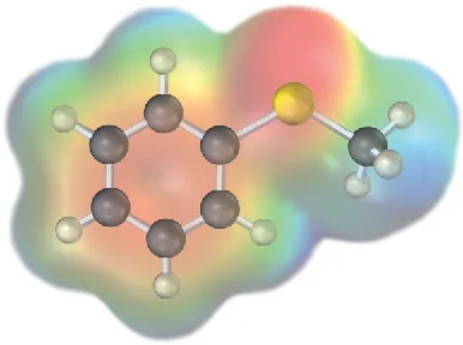
The following carboxylic acid can't be prepared from an alkyl halide by either the nitrile hydrolysis route or the Grignard carboxylation route. Explain.



Electrostatic potential maps of anisole and thioanisole are shown. Which do you think is the stronger acid, *p*-methoxybenzoic acid or *p*-(methylthio)benzoic acid? Explain.

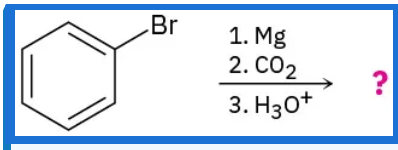


Anisole ($C_6H_5OCH_3$)



Thioanisole ($C_6H_5SCH_3$)

Mechanism Problems



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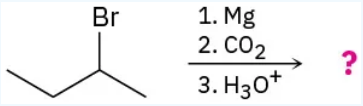
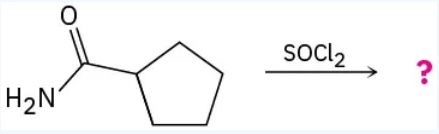
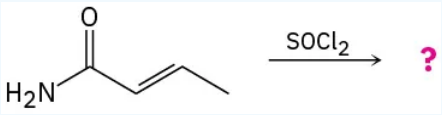


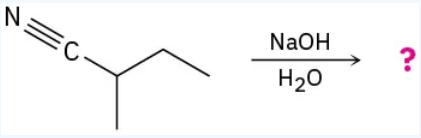
Problem 20-22
Predict the product(s) and write the mechanism of each of the following reactions: (a)



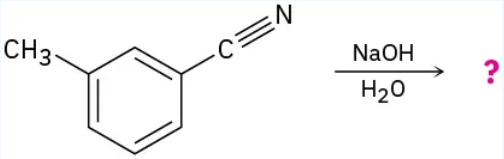
(b)



Problem 20-23
Predict the product(s) and write the mechanism of each of the following reactions: (a)

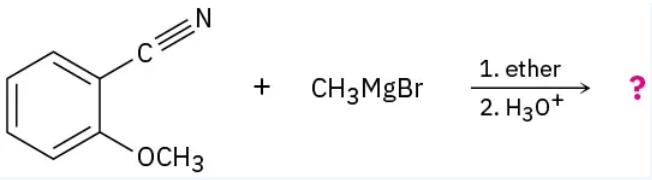


(b)

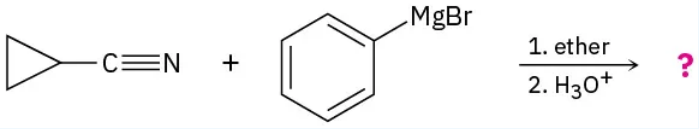


Problem 20-24
Predict the product(s) and write the complete mechanism of each of the following reactions: (a)

https://chem.libretexts.org/@go/page/507241

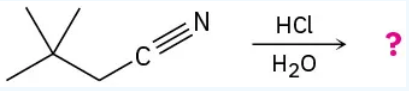


(b)

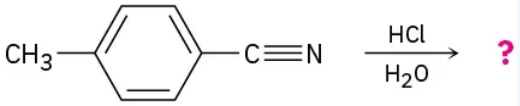


Problem 20-25

Acid-catalyzed hydrolysis of a nitrile to give a carboxylic acid occurs by initial protonation of the nitrogen atom, followed by nucleophilic addition of water. Review the mechanism of base-catalyzed nitrile hydrolysis in Section 20.7 and then predict the products for the following reactions. Write the steps involved in the acid-catalyzed reaction, using curved arrows. (a)

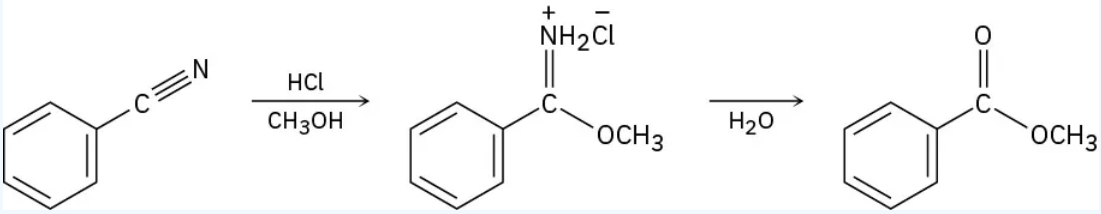


(b)



Problem 20-26

Nitriles can be converted directly to esters by the Pinner reaction, which first produces an iminoester salt that is isolated and then treated with water to give the final product. Propose a mechanism for the Pinner reaction using curved arrows to show the flow of electrons at each step.

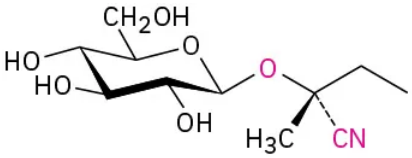


cyanogenic glycosides, such as lotaustralin, release hydrogen cyanide, HCN, when treated with aqueous acid. The reaction occurs by hydrolysis of the acetal linkage to form a cyanohydrin, which then expels HCN and gives a carbonyl compound. (a)

Show the mechanism of the acetal hydrolysis and the structure of the cyanohydrin that results.

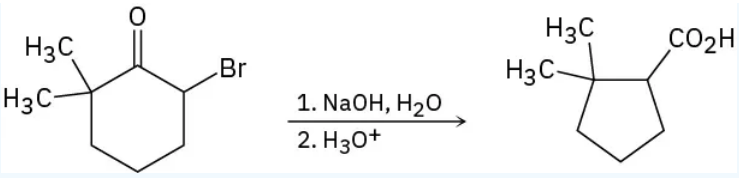
(b)

Propose a mechanism for the loss of HCN, and show the structure of the carbonyl compound that forms.

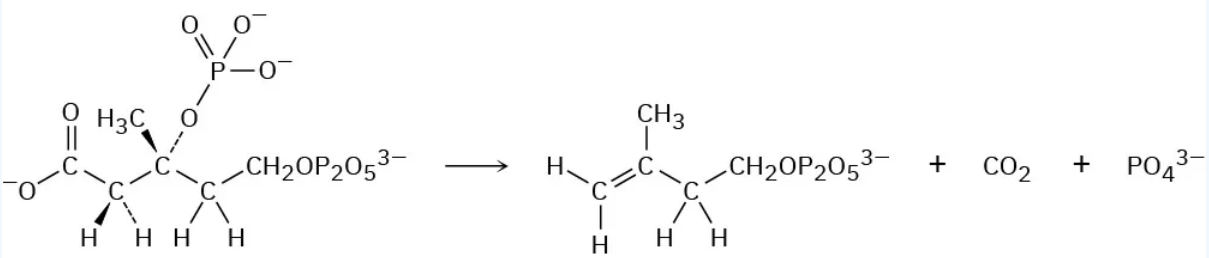


Lotaustralin

2-Bromo-6,6-dimethylcyclohexanone gives 2,2-dimethylcyclopentanecarboxylic acid on treatment with aqueous NaOH followed by acidification, a process called the Favorskii reaction. Propose a mechanism.

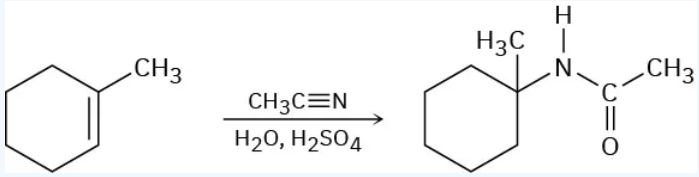


Naturally occurring compounds called *terpenoids*, which we'll discuss in **Section 27.5**, are biosynthesized by a pathway that involves loss of CO_2 from 3-phosphomevalonate 5-diphosphate to yield isopentenyl diphosphate. Use curved arrows to show the mechanism of this reaction.

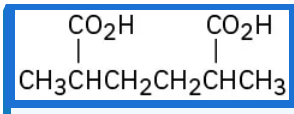


3-Phosphomevalonate 5-diphosphate **Isopentenyl diphosphate**

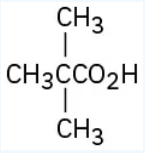
In the Ritter reaction, an alkene reacts with a nitrile in the presence of strong aqueous sulfuric acid to yield an amide. Propose a mechanism.



Naming Carboxylic Acids and Nitriles



(b)



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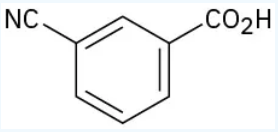
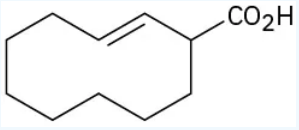
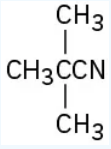


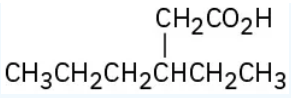
(d)

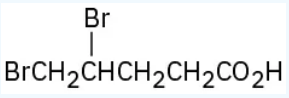


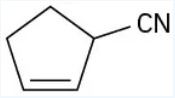
(e)



(f)

 (g)

 (h)



cis-1,2-Cyclohexanedicarboxylic acid

(b) Heptanedioic acid

(c) 2-Hexen-4-ynoic acid (d) 4-Ethyl-2-propyloctanoic acid (e) 3-Chlorophthalic acid (f) Triphenylacetic acid (g) 2-Cyclobutenecarbonitrile (h) *m*-Benzoylbenzonitrile

The eight carboxylic acids with the formula $C_6H_{12}O_2$

(b) Three nitriles with the formula C_5H_7N

Pregabalin, marketed as Lyrica, is an anticonvulsant drug that is also effective in treating chronic pain. The IUPAC name of pregabalin is (*S*)-3-(aminomethyl)-5-methylhexanoic acid. (An aminomethyl group is $–CH_2NH_2$.) Draw the structure of pregabalin.

Isocitric acid, an intermediate in the citric acid cycle of food metabolism, has the systematic name (2*R*,3*S*)-3-carboxy-2-hydroxypentanedioic acid. Draw the structure.

Acidity of Carboxylic Acids

Acetic acid, oxalic acid, formic acid

(b) *p*-Bromobenzoic acid, *p*-nitrobenzoic acid, 2,4-dinitrobenzoic acid (c) Fluoroacetic acid, 3-fluoropropanoic acid, iodoacetic acid

Magnesium acetate, magnesium hydroxide, methylmagnesium bromide

(b) Sodium benzoate, sodium *p*-nitrobenzoate, sodium acetylide (c) Lithium hydroxide, lithium ethoxide, lithium formate

K_a's of the following acids: (a)
Lactic acid, $K_a = 8.4 \times 10^{-4}$

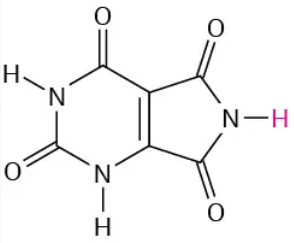
(b) Acrylic acid, $K_a = 5.6 \times 10^{-6}$

K_a's of the following acids: (a)
Citric acid, $pK_a = 3.14$

(b) Tartaric acid, $pK_a = 2.98$

Thioglycolic acid, $HSCH_2CO_2H$, a substance used in depilatory agents (hair removers) has $pK_a = 3.42$. What is the percent dissociation of thioglycolic acid in a buffer solution at pH = 3.0?

In humans, the final product of purine degradation from DNA is uric acid, $pK_a = 5.61$, which is excreted in the urine. What is the percent dissociation of uric acid in urine at a typical pH = 6.0? Why do you think uric acid is acidic even though it does not have a CO_2H group?



Uric acid

Some pK_a data for simple dibasic acids is shown. How can you account for the fact that the difference between the first and second ionization constants decreases with increasing distance between the carboxyl groups?

NameStructurepK_1pK_2 Oxalic HO_2CCO_2H 1.2 4.2 Succinic $HO_2CCH_2CH_2CO_2H$ 4.2 5.6 Adipic $HO_2C(CH_2)_4CO_2H$ 4.4 5.4

Reactions of Carboxylic Acids and Nitriles

1-Butanol

(b) 1-Bromobutane (c) Pentanoic acid (d) 1-Butene (e) Octane

1-Butanol

(b) 1-Bromobutane (c) 1-Butene (d) 1-Bromopropane (e) 4-Octene

1-Butanol

(b) Butylamine (c) 2-Methyl-3-hexanone

***m*-Chlorobenzoic acid**

(b) *p*-Bromobenzoic acid (c) Phenylacetic acid, $C_6H_5CH_2CO_2H$

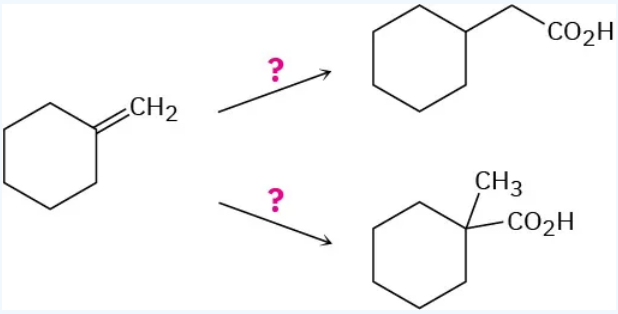
p-methylbenzoic acid with each of the following: (a)
$LiAlH_4$, then H_3O^+

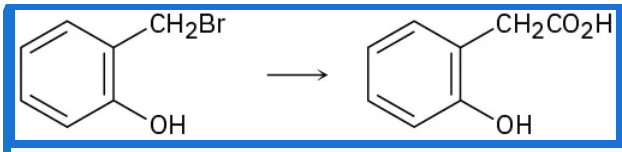
(b) *N*-Bromosuccinimide in CCl_4 (c) CH_3MgBr in ether, then H_3O^+ (d) $KMnO_4$, H_3O^+

$13CO_2$ as your only source of labeled carbon, along with any other compounds needed, how would you synthesize the following compounds? (a)
$CH_3CH_2{}^{13}CO_2H$

(b) PRODCH$_3{}^{13}$CH$_2$CO$_2$H

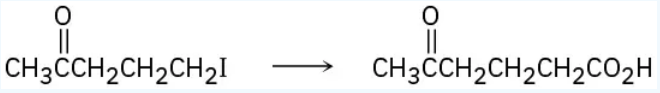
How would you carry out the following transformations?





(b)


(c)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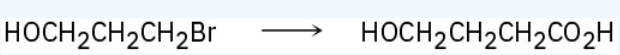
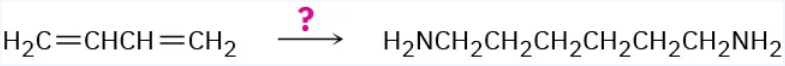


1,6-Hexanediamine, a starting material needed for making nylon, can be made from 1,3-butadiene. How would you accomplish the synthesis?

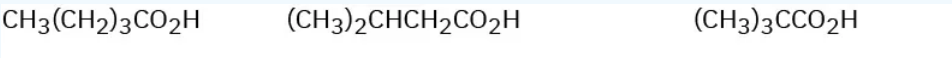


3-Methyl-2-hexenoic acid (mixture of *E* and *Z* isomers) has been identified as the substance responsible for the odor of human sweat. Synthesize the compound from starting materials having five or fewer carbons.

Spectroscopy

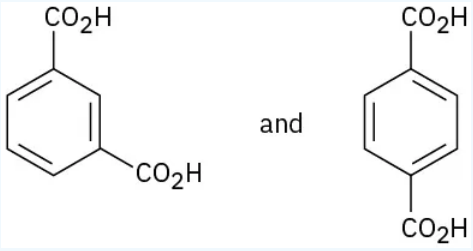
Propose a structure for a compound $C_6H_{12}O_2$ that dissolves in dilute NaOH and shows the following ^1H NMR spectrum: 1.08 δ (9 H, singlet), 2.2 δ (2 H, singlet), and 11.2 δ (1 H, singlet).

What spectroscopic method could you use to distinguish among the following three isomeric acids? Tell what characteristic features you would expect for each acid.



Pentanoic acid **3-Methylbutanoic acid** **2,2-Dimethylpropanoic acid**

13C or ^1H) to distinguish between the following pairs of isomers? (a)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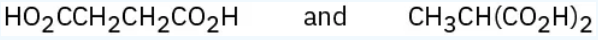
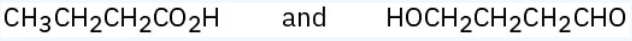
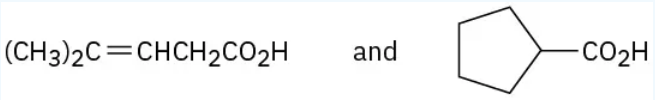
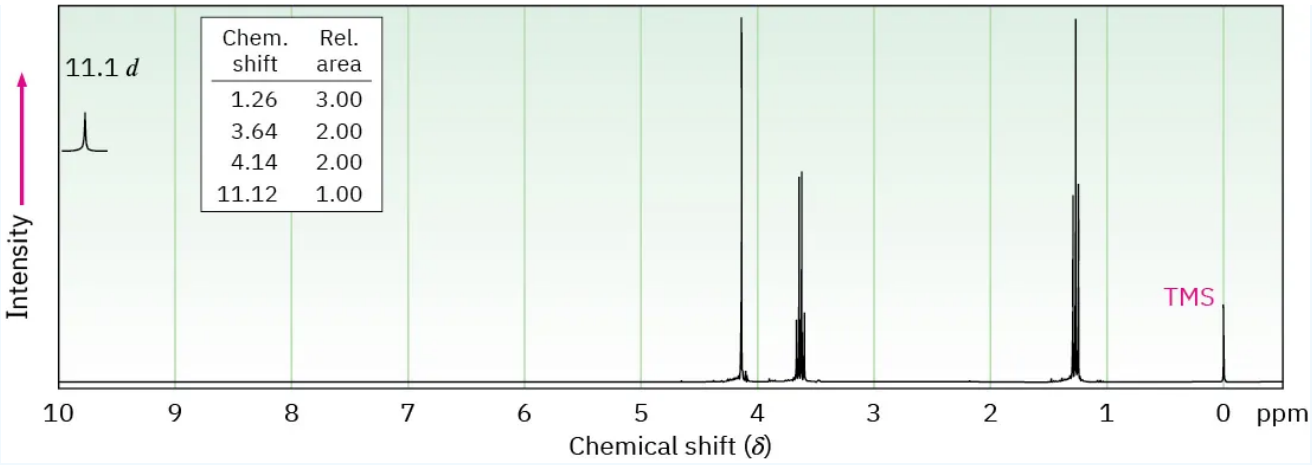

(c)


(d)



Problem 20-56

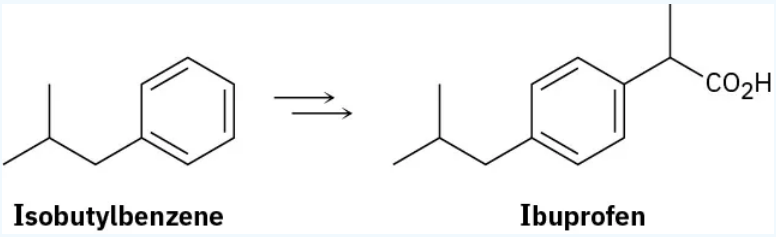
Compound A, $C_4H_8O_3$, has infrared absorptions at 1710 and 2500 to 3100 cm^{-1} and has the ^1H NMR spectrum shown. Propose a structure for A.

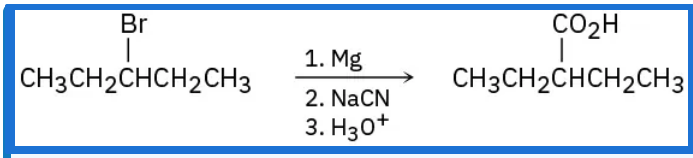


General Problems

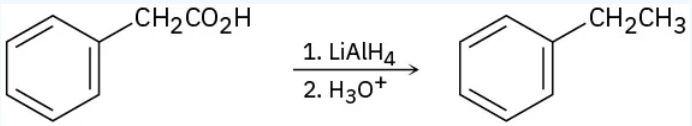
A chemist in need of 2,2-dimethylpentanoic acid decided to synthesize some by reaction of 2-chloro-2-methylpentane with NaCN, followed by hydrolysis of the product. After the reaction sequence was carried out, however, none of the desired product could be found. What do you suppose went wrong?

Show how you might prepare the anti-inflammatory agent ibuprofen starting from isobutylbenzene. More than one step is needed.

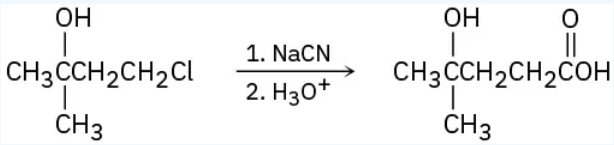




(b)

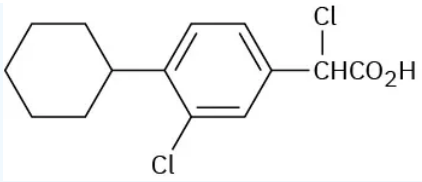


(c)



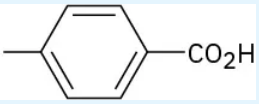
Problem 20-60
***p*-Aminobenzoic acid (PABA) was once widely used as a sunscreen agent. Propose a synthesis of PABA starting from toluene.**

Propose a synthesis of the anti-inflammatory drug fenclorac from phenylcyclohexane.

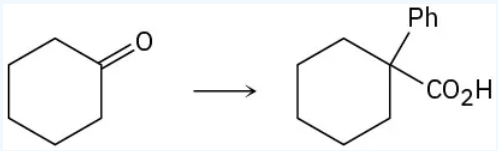


Fenclorac

The pK_a's of five *p*-substituted benzoic acids ($YC_6H_4CO_2H$) are listed below. Rank the corresponding substituted benzenes (YC_6H_5) in order of their increasing reactivity toward electrophilic aromatic substitution. If benzoic acid has pK_a = 4.19, which of the substituents are activators and which are deactivators?

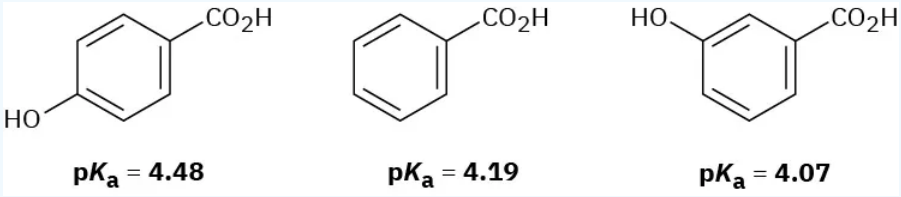
Substituent Y	pK_a of 
–Si(CH$_3$)$_3$	4.27
–CH=CHC≡N	4.03
–HgCH$_3$	4.10
–OSO$_2$CH$_3$	3.84
–PCl$_2$	3.59

(b)



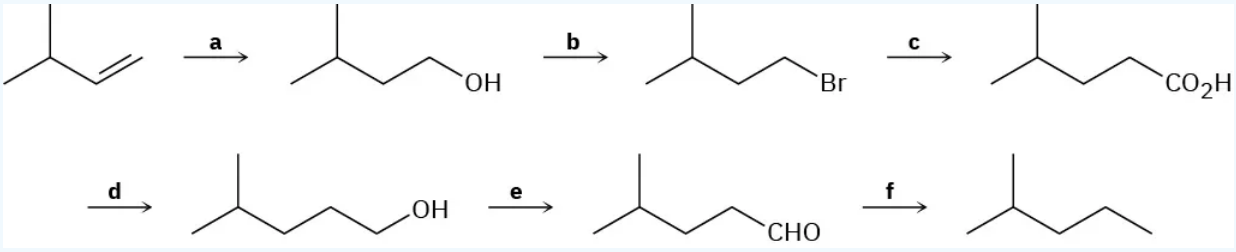
Problem 20-64

The following pK_a values have been measured. Explain why a hydroxyl group in the para position decreases the acidity while a hydroxyl group in the meta position increases the acidity.

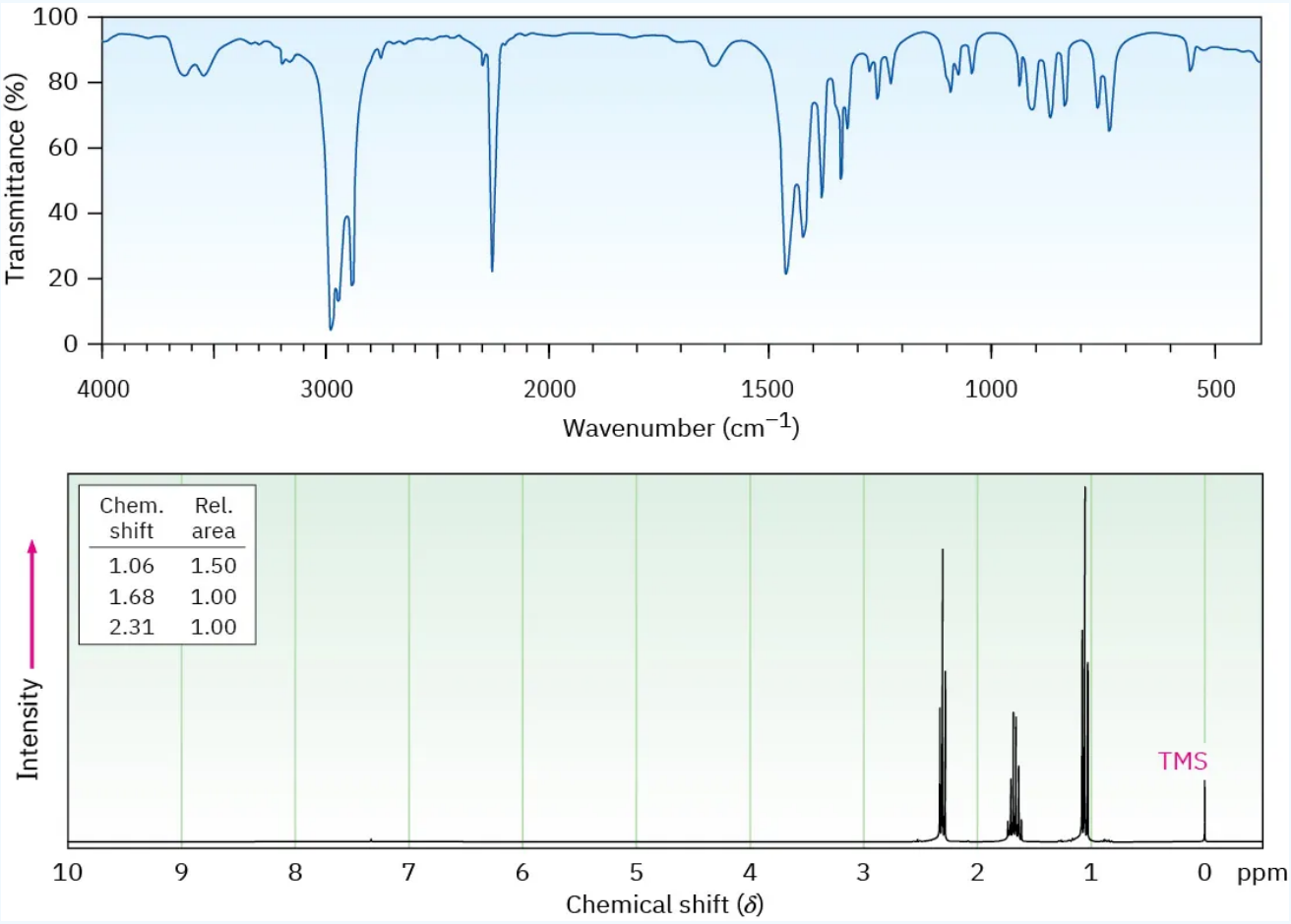


pK_a = 4.48 pK_a = 4.19 pK_a = 4.07

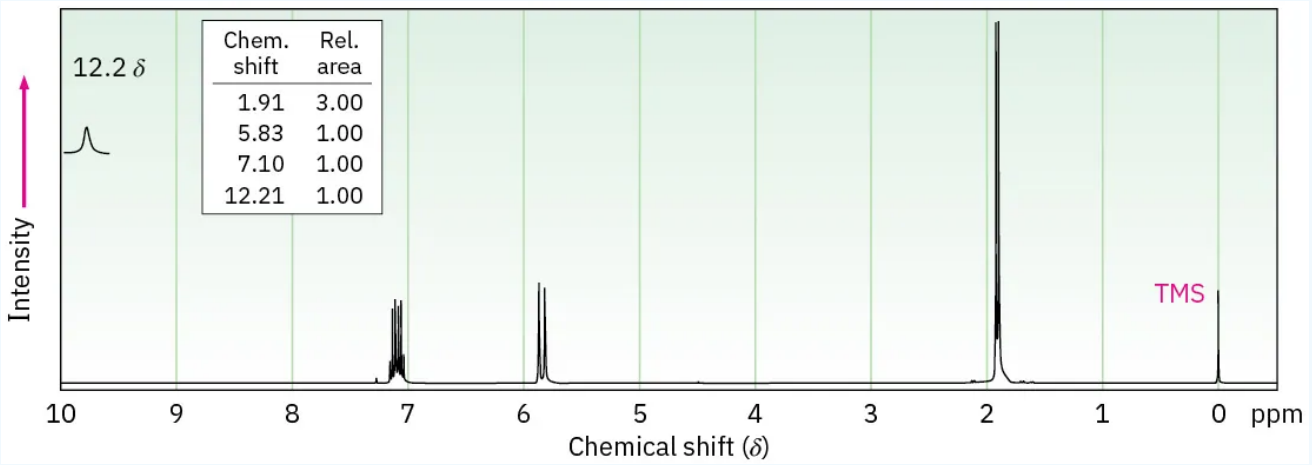
Identify the missing reagents a–f in the following scheme:



Propose a structure for a compound, C_4H_7N, that has the following IR and ^1H NMR spectra:



1H NMR spectra shown here belong to crotonic acid (*trans*-CH_3CH Unexpected text node: ' CHCO' $_2H$) and methacrylic acid [$H_2C{=}C(CH_3)CO_2H$]. Which spectrum corresponds to which acid? Explain. (a)



(b)

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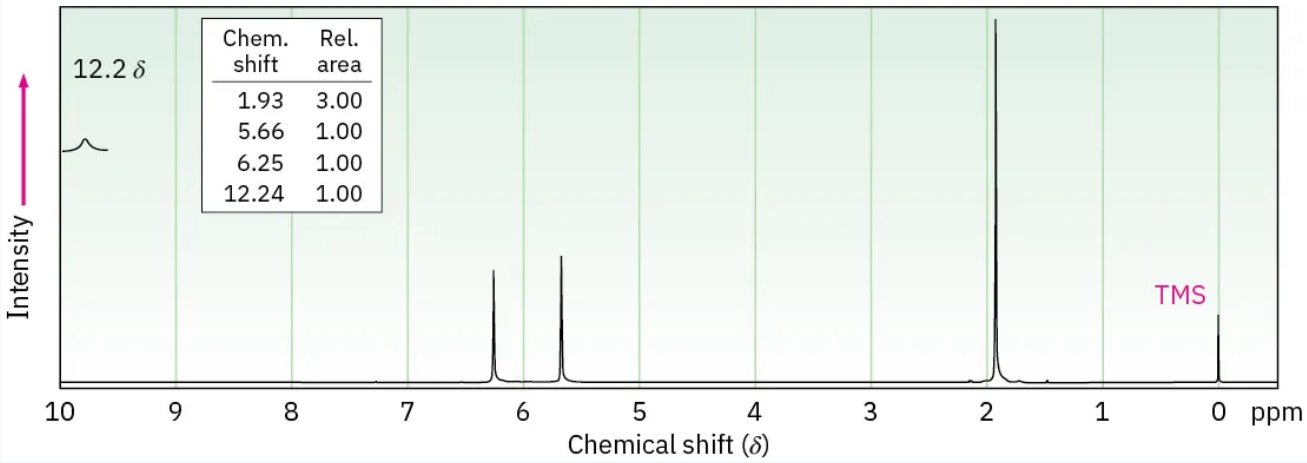
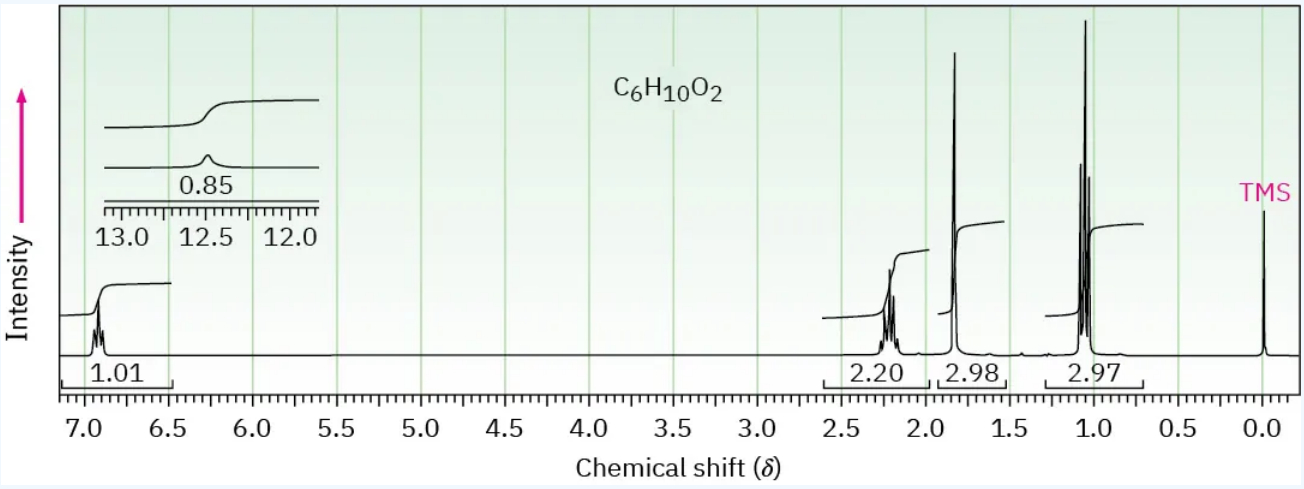
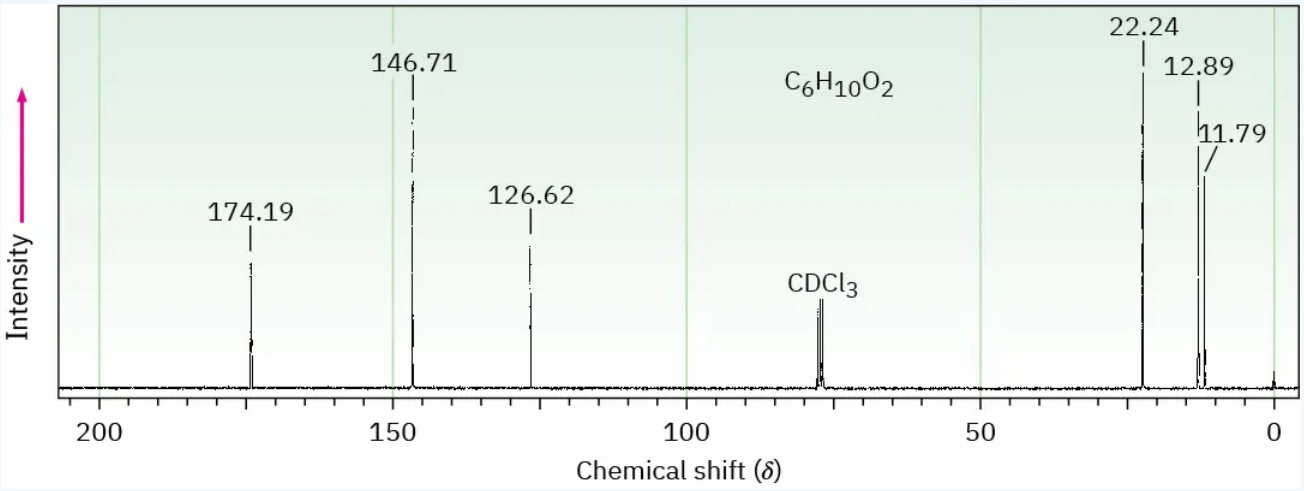


Problem 20-68

The ^{1}H and ^{13}C NMR spectra below belong to a compound with formula $C_6H_{10}O_2$. Propose a structure for this compound. (a)



(b)

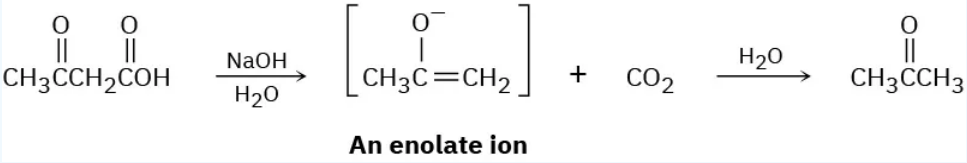


Problem 20-69

Propose structures for carboxylic acids that show the following peaks in their ^{13}C NMR spectra. Assume that the kinds of carbons (1°, 2°, 3°, or 4°) have been assigned by DEPT-NMR. (a) $C_7H_{12}O_2$: 25.5 δ (2°), 25.9 δ (2°), 29.0 δ (2°), 43.1 δ (3°), 183.0 δ (4°)

(b) $C_8H_8O_2$: 21.4 δ (1°), 128.3 δ (4°), 129.0 δ (3°), 129.7 δ (3°), 143.1 δ (4°), 168.2 δ (4°)

Carboxylic acids having a second carbonyl group two atoms away lose CO_2 *(decarboxylate)* through an intermediate enolate ion when treated with base. Write the mechanism of this decarboxylation reaction using curved arrows to show the electron flow in each step.



An enolate ion

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