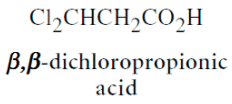
Chapter 20
The Chemistry of Carboxylic Acids

Solutions to In-Text Problems

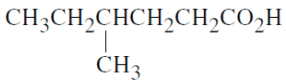
20.1 (b)



$Cl_2CHCH_2CO_2H$

***β,β*-dichloropropionic acid**

(d)



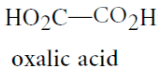
$CH_3CH_2CHCH_2CH_2CO_2H$ (CH_3 branch)

4-methylhexanoic acid

(f)

_p_-methoxybenzoic acid

(h)



$HO_2C—CO_2H$

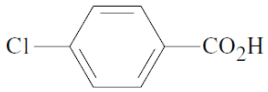
oxalic acid

20.2 (b) 9-Methyldecanoic acid (common: ω-methylcapric acid). Note that the term ω (*omega*, the last letter of the Greek alphabet) is used in common nomenclature for a branch at the end of a carbon chain.

(d) 2,4-Dichlorobenzoic acid

(f) Cyclopropanecarboxylic acid

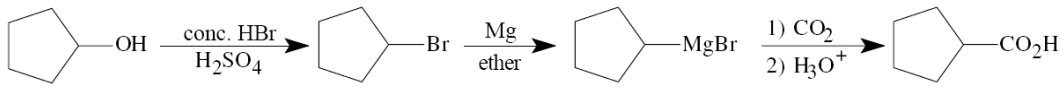
20.5 The NMR data indicate a *para*-substituted benzoic acid derivative; given this deduction, the para substituent must be a chlorine.



_p_-chlorobenzoic acid
(4-chlorobenzoic acid)

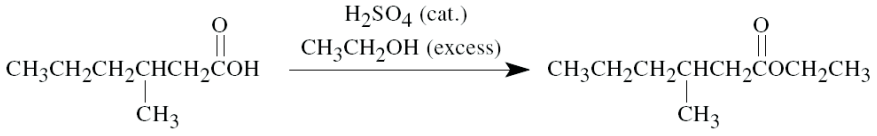
20.8 Extract an ether solution of the two compounds with an aqueous solution of $NaHCO_3$, Na_2CO_3, or NaOH. The acid will ionize and its conjugate-base anion will dissolve in the aqueous layer as the sodium salt; *p*-bromotoluene will remain in the ether layer. After isolating the aqueous layer, acidify it with concentrated HCl; neutral *p*-bromobenzoic acid will precipitate.

20.9 (a)



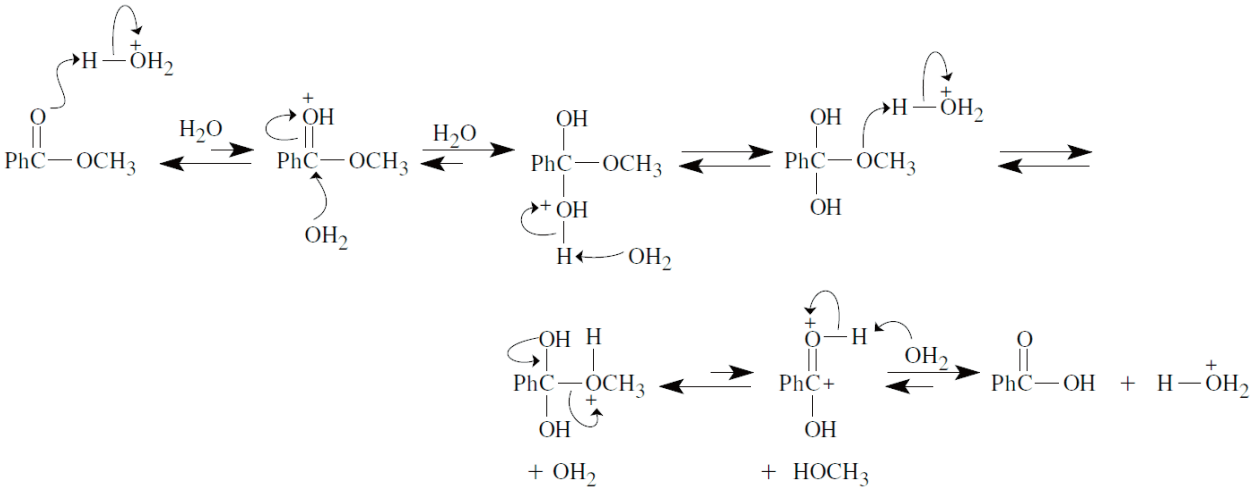
cyclopentanol **cyclopentanecarboxylic acid**

20.10 (a)



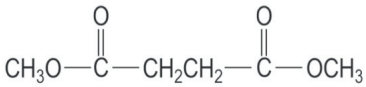
3-methylhexanoic acid **ethyl 3-methylhexanoate**

20.11 (a) Follow the reverse of the steps shown in Eqs. 20.18a–c, text pp. 966–967, with R— = Ph—.



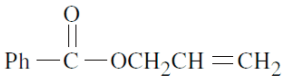
(b) To favor ester hydrolysis rather than ester formation, use a large excess of water as solvent rather than an alcohol. By Le Châtelier's principle, this drives the carboxylic acid–ester equilibrium toward the carboxylic acid.

20.13 (b)



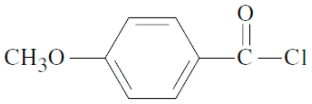
dimethyl succinate

(d)



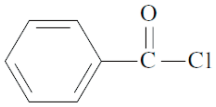
allyl benzoate

20.15 (b)



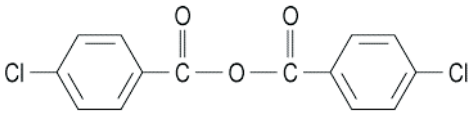
p-methoxybenzoyl chloride
(anisoyl chloride)

20.16 (b)



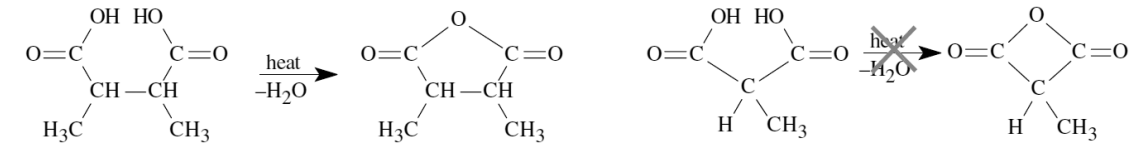
benzoyl chloride

20.18 (b)



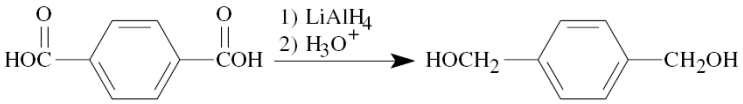
***p*-chlorobenzoic anhydride**

20.19 (b) On heating, 2,3-dimethylbutanedioic acid forms a cyclic anhydride containing a five-membered ring. Because a cyclic anhydride of α-methylmalonic acid would contain a very strained four-membered ring, it is not formed on heating.



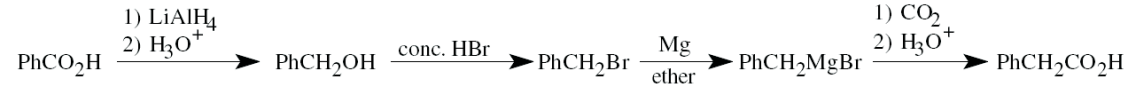
2,3-dimethylbutanedioic acid — 2,3-dimethylbutanedioic anhydride — α-methylmalonic acid — α-methylmalonic anhydride

20.20 (b) 1,4-Benzenedicarboxylic acid (terephthalic acid) is a compound with the formula $C_8H_6O_4$ that gives the indicated diol on treatment with $LiAlH_4$ followed by protonolysis.



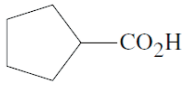
1,4-benzenedicarboxylic acid (terephthalic acid)

20.21 (a) This synthesis requires the addition of one carbon. Follow the general scheme in Study Problem 20.2, text p. 975.

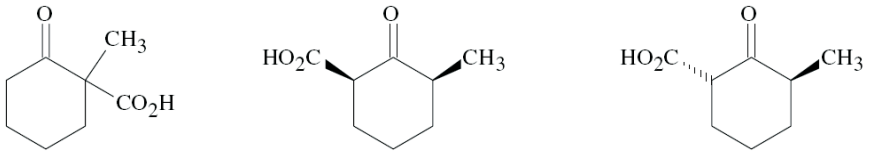


benzoic acid — phenylacetic acid

20.22 (b) The compound decarboxylates; it is a disubstituted malonic acid in which the two α substituents are joined within a ring. The net effect is the replacement of the carboxy group by a hydrogen.



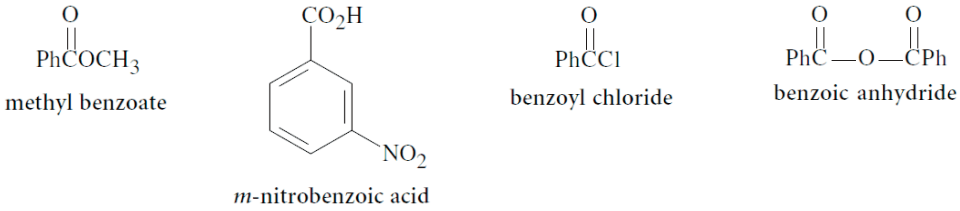
20.23 The following β-keto acids (and their enantiomers) will decarboxylate to give 2-methylcyclohexanone:



1-methyl-2-oxocyclohexanecarboxylic acid — *cis*-3-methyl-2-oxocyclohexanecarboxylic acid — *trans*-3-methyl-2-oxocyclohexanecarboxylic acid

Solutions to Additional Problems

20.26 (a) (b) (c) (d)



20.28 (b) First, calculate the number of millimoles of succinic acid (see Table 20.1, text p. 950) in 100 mg of succinic acid:

$$\text{mmol succinic acid} = \frac{100 \text{ mg succinic acid}}{118.10 \text{ mg succinic acid (mmol succinic acid)}^{-1}} = 0.847$$

Using the facts that sodium hydroxide reacts with the carboxylic acid groups and that succinic acid has two dicarboxylic acid groups per molecule, calculate the millimoles of carboxylic acid groups present in the sample:

$$\text{mmol carboxylic acid} = \frac{2 \text{ mmol carboxylic acid}}{\text{mmol succinic acid}} \times 0.847 \text{ mmol succinic acid} = 1.69$$

Finally, calculate the volume 0.1 *M* NaOH required for the neutralization:

$$\text{mL of NaOH} = \frac{1 \text{ mL of NaOH}}{0.1 \text{ mmol of NaOH}} \times \frac{1 \text{ mmol of NaOH}}{1 \text{ mmol of carboxylic acid}} \times 1.69 \text{ mmol of carboxylic acid} = 16.9$$

20.29 (b)

(d)

(f)

20.31 As the chain length becomes larger the distance between the two carboxy groups becomes greater. Because polar effects decrease with distance, the polar effect is negligible when the chain length is great, and the two pK_a values are nearly equal. (However, they are not *exactly* equal; for an explanation, see the icon comment following the solution to Problem 3.43 on p. 43 of Study Guide and Solutions Manual.)

20.34 Use Eq. 20.7c, text p. 959. (This equation is sometimes called the Henderson–Hasselbalch equation.) Let the ratio $[RCO_2H]/[RCO_2^-]$ given in the problem be r. Rearranging Eq. 20.7c, and noting that $\log (1/r) = -\log r$,

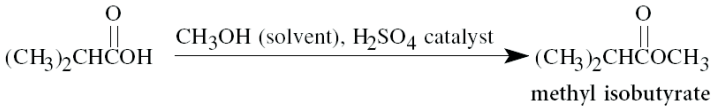
$$\text{pH} = \text{p}K_a - \log r$$

(a) When $r = \frac{1}{3}$, pH = 4.76 – log (⅓) = 5.24.
(b) When $r = 3$, pH = 4.76 – log 3 = 4.28.
(c) When $r = 1$, pH 4.76 – log 1 = 4.76.

Many students confuse pK_a, which is a property of a compound, with pH, which is a property of the solution in which the compound is dissolved. The pK_a is a constant property of an acid that does not vary with concentration; the pH, as text Eq. 20.7c shows, depends on the relative concentrations of the acid and its conjugate base. (See Study Guide Link 3.4, on p. 31 of the Study Guide and Solutions Manual.) As the calculation in this problem is designed to illustrate, the pH equals the pK_a when the concentrations of an acid and its conjugate base are identical. When the concentration of the conjugate acid is greater, the pH is less than the pK_a; when the concentration of the acid is less, the pH is greater than the pK_a.

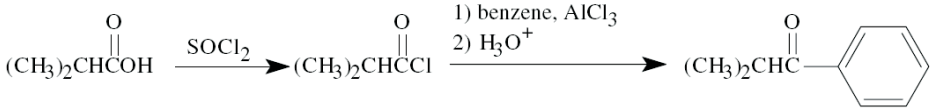
20.35 (b) Use the result in part (a). When acetic acid is the solvent, the most acidic species that can exist is the *conjugate acid* of acetic acid (that is, protonated acetic acid; see structure in Eq. 20.8, text p. 960, with R— = H_3C—), which has a pK_a of about –6 (text p. 960). Table 3.1 on text p. 103 gives the pK_a of HBr as –8 to –9.5. Consequently, the HBr–acetic acid system has an effective pK_a of about –6. In aqueous solution, HBr is dissociated to give H_3O^+, the conjugate acid of water, which has a pK_a of –1.7; therefore the effective pK_a of aqueous HBr is –1.7. Hence, HBr in acetic acid is far more acidic than HBr in water because of the greater acidity of the conjugate acid of acetic acid, the solvent.

20.37 (b)



methyl isobutyrate

(d)



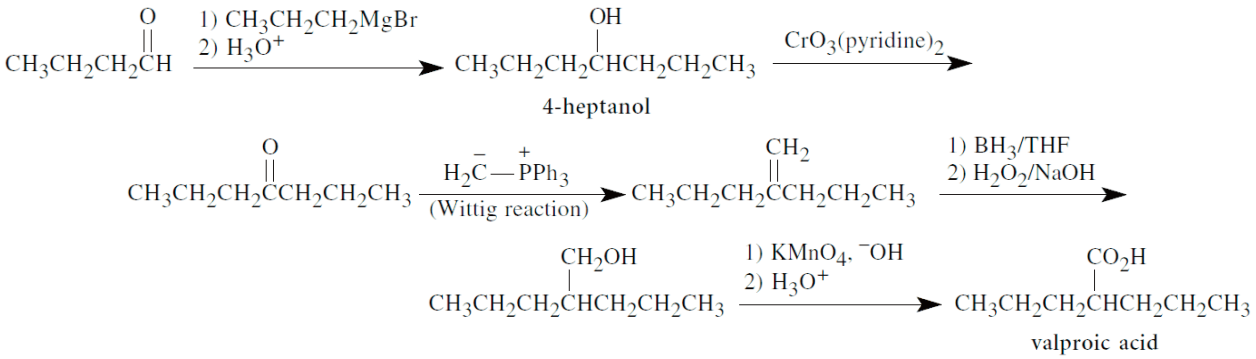
isobutyrophenone
(2-methyl-1-phenyl-1-propanone)

20.39 (a) The substitutive name of valproic acid is 2-propylpentanoic acid.

(b) The common name of valproic acid is α-propylvaleric acid.

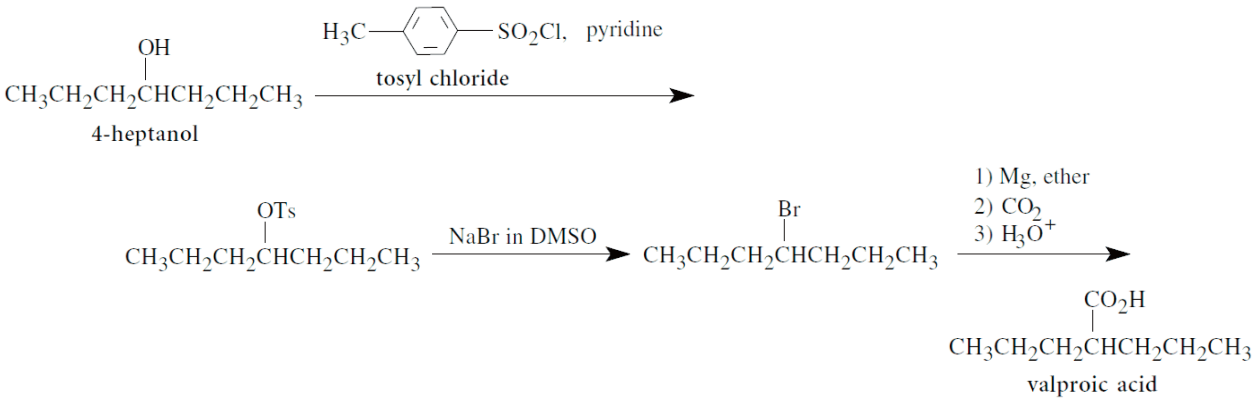
(c) A number of syntheses are possible. Here are two:

Synthesis #1:

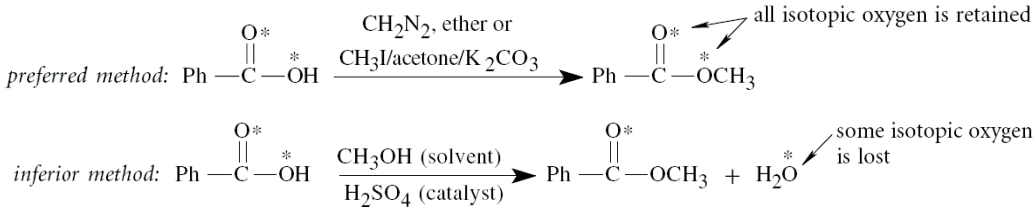


valproic acid

Synthesis #2:

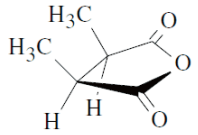


20.41 Use a method that does not involve loss of oxygen from benzoic acid. Thus, acid-catalyzed esterification should not be used, because, as Eq. 20.18c on text p. 967 shows, this method results in cleavage of the bond between the carbonyl carbon and the carboxylate oxygen. Esterification with either diazomethane or methyl iodide and K_2CO_3 would be the preferred method because, as the discussion in Sec. 20.8B, text p. 968, shows, these methods do not involve loss of oxygen. (O* = ^{18}O.)



20.43 The essence of this solution is to determine the ionization state of penicillin-G at the different pH values. The principles involved are discussed in the solution to Problem 20.34. Because penicillin G is a carboxylic acid, its pK_a should be in the 3–5 range. Because the pH of blood, 7.4, is considerably higher than the pK_a of the drug, penicillin-G is ionized in blood. Because the pH of stomach acid is lower than the pK_a of penicillin-G, the penicillin is largely un-ionized in stomach acid. Because carboxylate ions are generally more soluble in aqueous solution than un-ionized carboxylic acids, penicillin-G is more soluble in blood than it is in stomach acid.

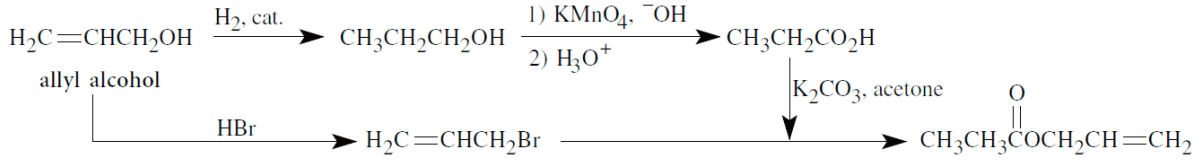
20.45 (b)



meso-**α,β**-dimethylsuccinic anhydride

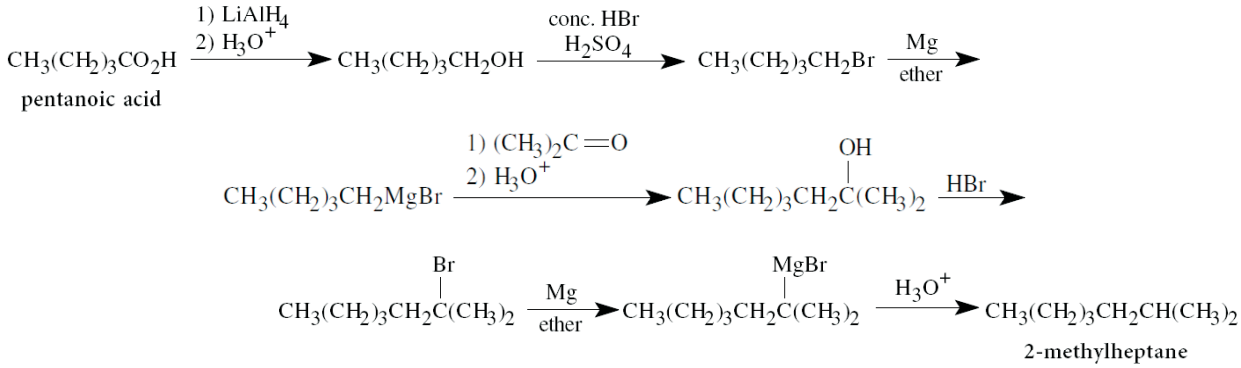
Notice the cis relationship of the methyl groups. (The anhydride with trans methyl substituents would be formed from *racemic* α,β-dimethylsuccinic acid).

20.46 (b)

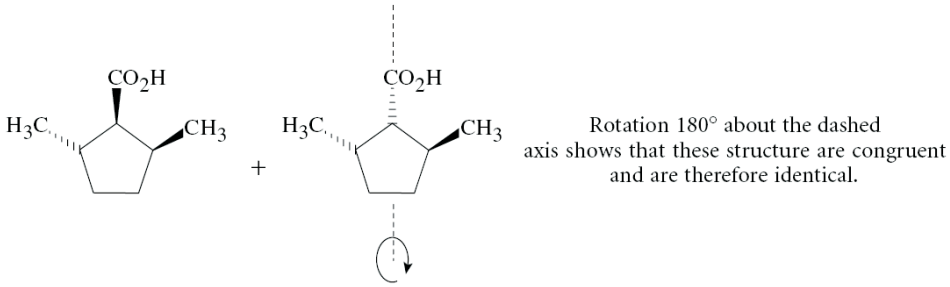


Acid-catalyzed esterification of propionic acid (prepared as shown above) with allyl alcohol could also be used, but this reaction would require an excess of allyl alcohol.

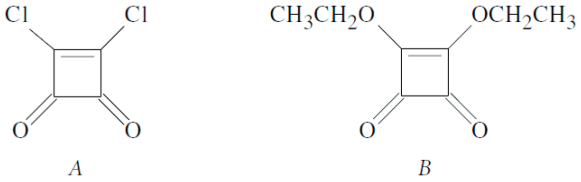
(c)



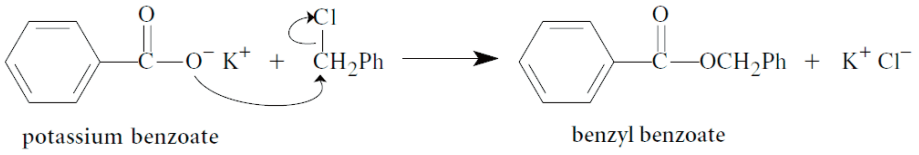
20.47 (b) The question is whether loss of the different carboxy groups gives rise to the same compound or to different compounds. Draw the two possible structures and determine whether they are different or identical. In fact, the two are identical; therefore, only one product is formed when compound *B* decarboxylates.



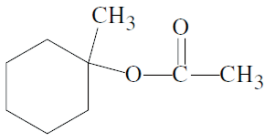
20.48 (c) The reactions of squaric acid with a number of reagents are analogous to the corresponding reactions of carboxylic acids. Thus, reaction with $SOCl_2$ results in the formation of the "di-acid chloride" *A*; and reaction with ethanol and an acid catalyst results in formation of the "di-ester" *B*.



20.49 (b) The KOH converts benzoic acid into its conjugate-base benzoate anion, which is alkylated by benzyl chloride to give benzyl benzoate.

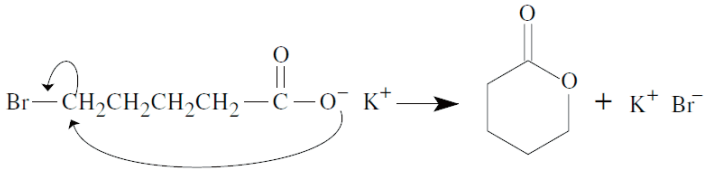


(d) This is an oxymercuration-reduction reaction in which acetic acid rather than water serves as the nucleophile that opens the mercurinium ion. (See the solution to Problem 5.35(c) on pp. 92–93 of Study Guide and Solutions Manual.)

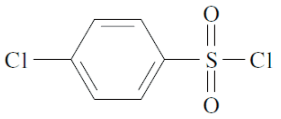


1-methylcyclohexyl acetate

(f) This is an intramolecular variation of the esterification shown in Eq. 20.22, text p. 969. In this case, potassium carbonate converts the carboxylic acid into its conjugate-base potassium carboxylate, which is then intramolecularly alkylated to form the cyclic ester (lactone).

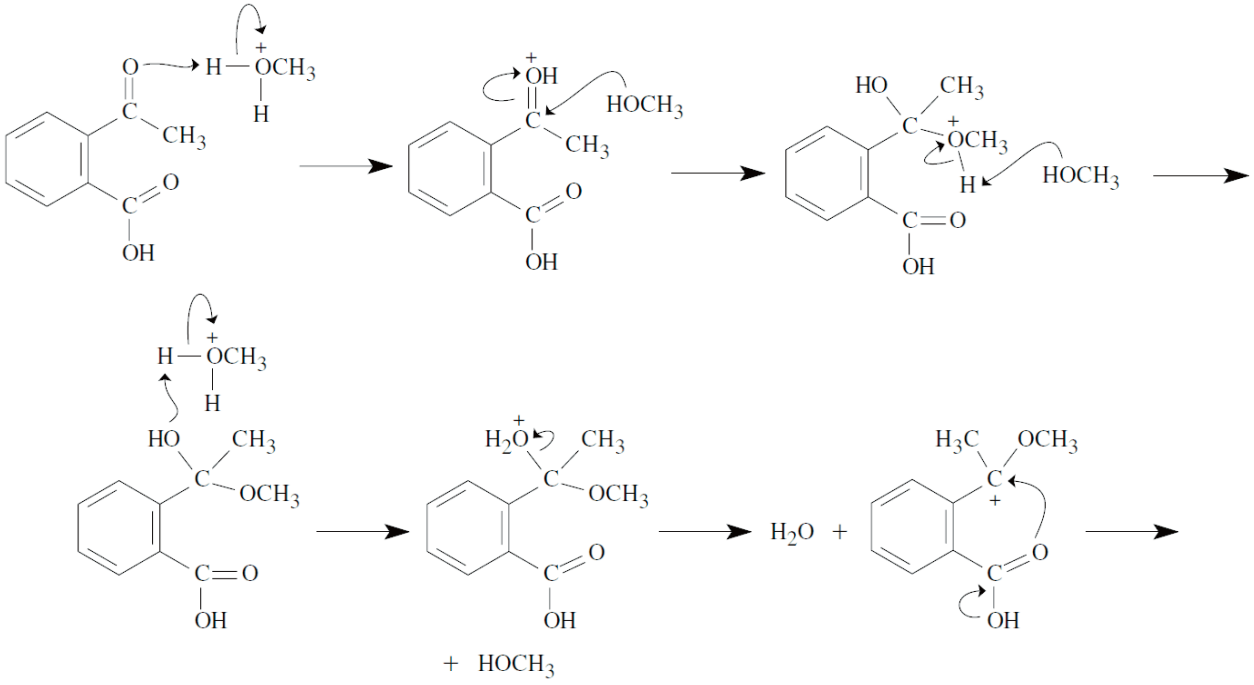


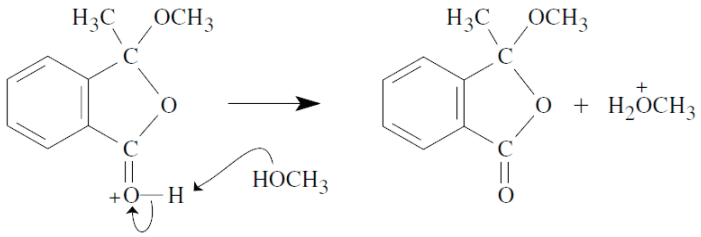
(h) Chlorosulfonation of chlorobenzene gives electrophilic aromatic substitution at the para position. (See Eq. 20.28a–b on text p. 972.)



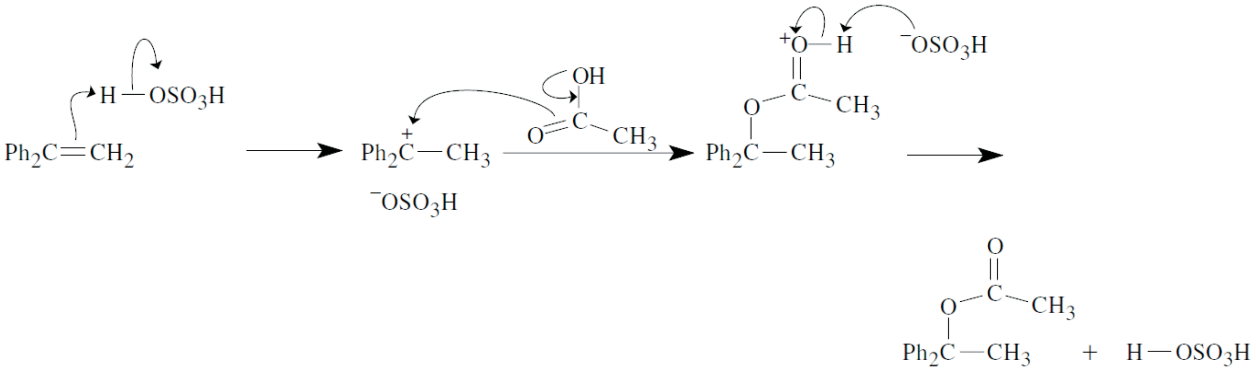
p-chlorobenzenesulfonyl chloride

20.51 (b) The mechanism is much like that for acetal formation, except that the carboxy group rather than a second alcohol molecule reacts with the α-alkoxy carbocation intermediate. (Recall that many intramolecular reactions that form small rings are faster than related intermolecular reactions; see Sec. 11.7A–B, text p. 510.)

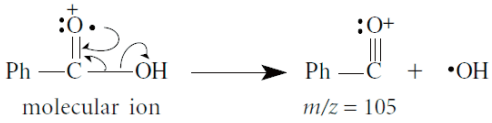




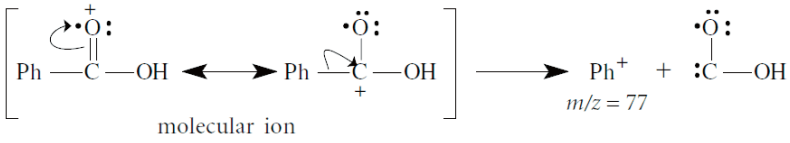
(d) The pattern is much like that in the solution to part (c), except that acetic acid rather than carbon monoxide reacts with the carbocation intermediate.

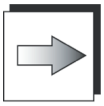


20.52 (b) The molecular mass of benzoic acid is 122; therefore, the $m/z = 105$ peak in its mass spectrum represents a mass loss of 17 units, which corresponds to loss of an —OH group. This loss can occur by an α-cleavage mechanism.



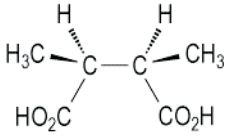
The $m/z = 77$ peak corresponds to a phenyl cation, which can be lost by inductive cleavage at the other side of the carboxy group.





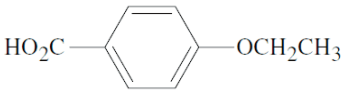
You may recall that aryl cations are very unstable. (See Fig. 18.2, text p. 827.) The high electron energies involved in mass spectroscopy enable the formation of such intermediates that would ordinarily not form in solution.

20.53 (b) The meso stereoisomer isomer would have ^{1}H and ^{13}C NMR spectra that are almost identical to that of *A*. Because it is a diastereomer of *A*, it has a different melting point.



***meso*-2,3-dimethylbutanedioic acid**

20.55 (b) The IR spectrum indicates the presence of a carboxylic acid, and the NMR indicates the presence of an ethoxy group (—OCH_2CH_3) and a *para*-disubstituted benzene ring. The compound is 4-ethoxybenzoic acid.



4-ethoxybenzoic acid