

STUDY GUIDE AND SOLUTIONS MANUAL

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ORGANIC CHEMISTRY

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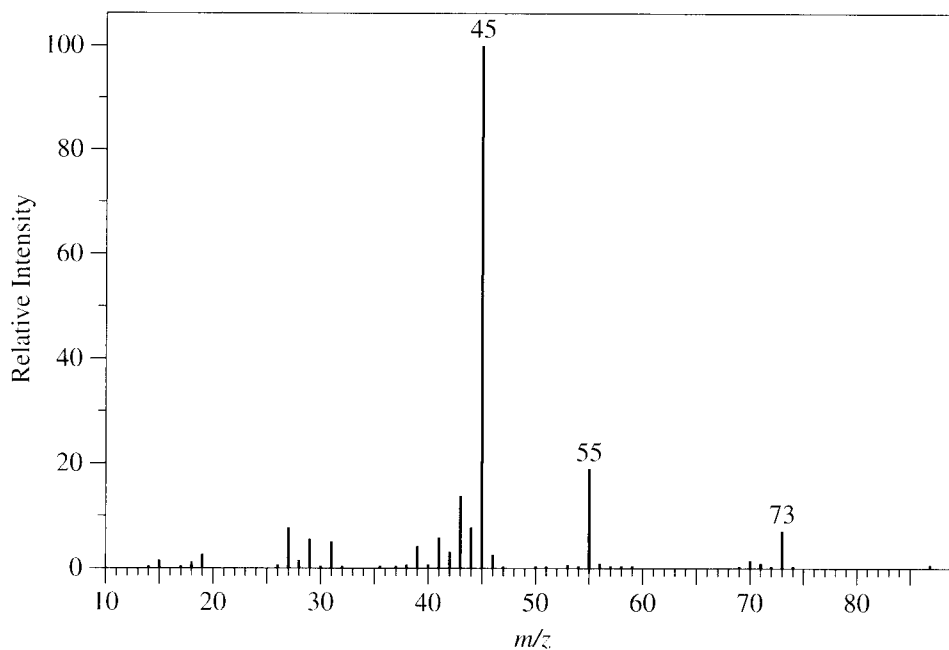
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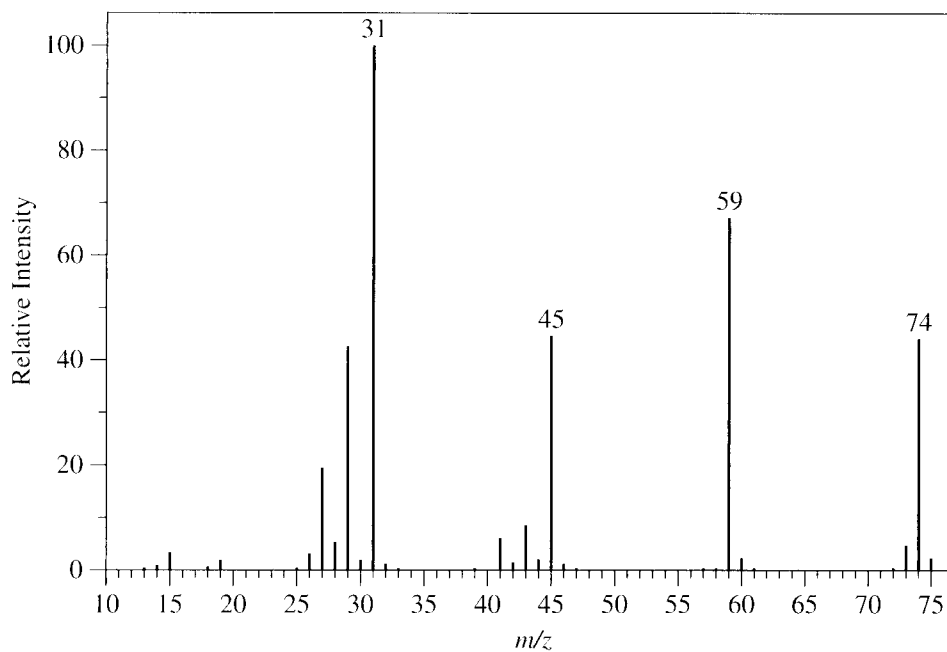
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Spectroscopy Problems

1. Determine the structure of the straight-chain pentanol that produces the mass spectrum shown here.



2. The mass spectrum of an ether is shown here. Determine the molecular formula of the ether that would produce this spectrum and then draw possible structures for it.



Strong Acids

A strong acid is one that dissociates completely in solution. Strong acids have pK_a values < 1 .

Because a strong acid dissociates completely, the concentration of hydrogen ions is the same as the concentration of the acid: a 1.0 M HCl solution contains 1.0 M $[H^+]$; a 1.5 M HCl solution contains 1.5 M $[H^+]$. Therefore, to determine the pH of a strong acid, the $[H^+]$ value does not have to be calculated; it is the same as the molarity of the strong acid.

<u>Solution</u>	<u>$[H^+]$</u>	<u>pH</u>
1.0 M HCl	1.0 M	0
1.0×10^{-2} M HCl	1.0×10^{-2} M	2.0
6.4×10^{-4} M HCl	6.4×10^{-4} M	3.2

Strong Bases

Strong bases are compounds such as NaOH or KOH that dissociate completely in water.

Because they dissociate completely, the $[HO^-]$ is the same as the molarity of the strong base.

pOH describes the basicity of a solution. The smaller the pOH, the more basic the solution; just like the smaller the pH, the more acidic the solution.

$$pOH = -\log [HO^-]$$

$[HO^-]$ and $[H^+]$ are related by the ionization constant for water (K_w).

$$K_w = [H^+][HO^-] = 10^{-14}$$

$$pH + pOH = 14$$

<u>Solution</u>	<u>$[HO^-]$</u>	<u>pOH</u>	<u>pH</u>
1.0 M NaOH	1.0 M	0	$14.0 - 0 = 14.0$
1.0×10^{-4} M NaOH	1.0×10^{-4} M	4.0	$14.0 - 4.0 = 10.0$
7.8×10^{-2} M NaOH	7.8×10^{-2} M	1.1	$14.0 - 1.1 = 12.9$

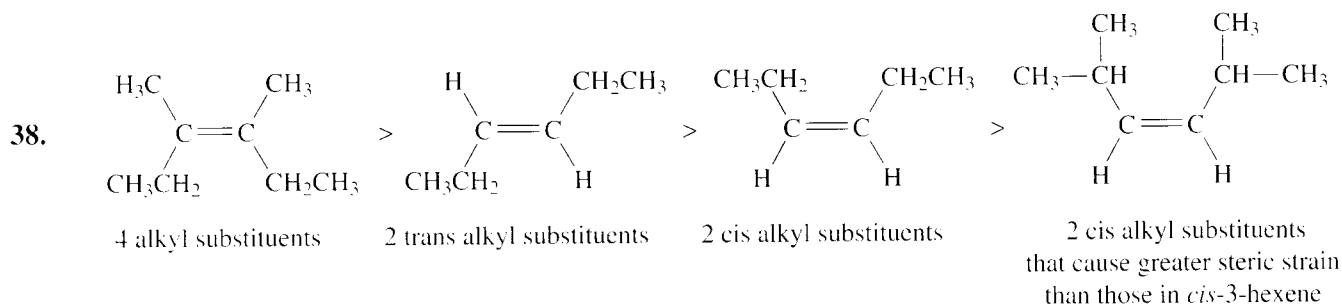
Weak Acids

A weak acid does not dissociate completely in solution. Therefore, $[H^+]$ must be calculated before the pH can be determined.

Acetic acid (CH_3COOH) is an example of a weak acid. It has an acid dissociation constant of 1.74×10^{-5} ($pK_a = 4.76$). The pH of a 1.00 M solution of acetic acid can be calculated as follows:

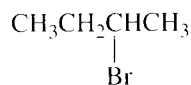


$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$



39. The reactant must have *E,Z* stereoisomers or *R,S* stereoisomers.

40. a. No, because only one constitutional isomer can be formed as a product since 2-butene is a symmetrical alkene.



b. No, because it forms a racemic mixture.

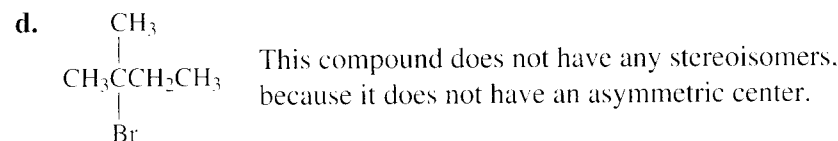
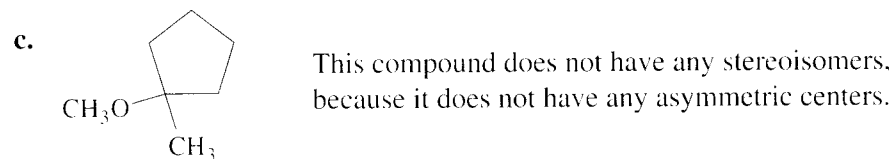
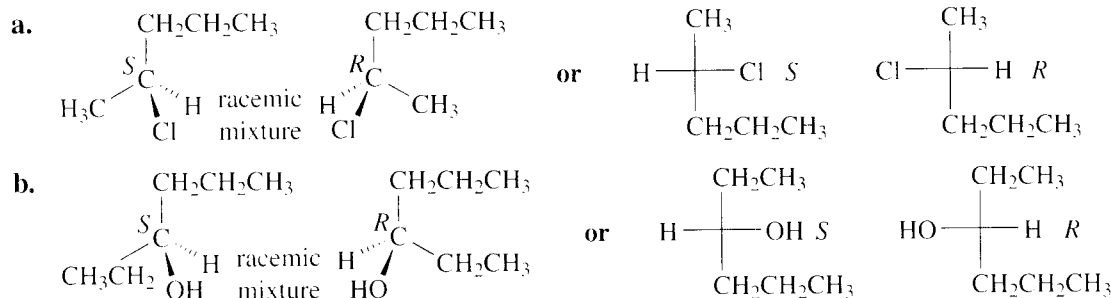
c. No, because *cis*-butene and *trans*-butene form the same product.

d. Yes, because two constitutional isomers are possible, but only one is formed.

e. No, because it forms a racemic mixture.

f. No, because *cis*-butene and *trans*-butene form the same product.

41. Only the stereoisomers of the major product of each reaction are shown.



42. Solved in the text.

43. Solved in the text.

44. Solved in the text.

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12. Solved in the text.

13. a. $\text{CH}_3\text{CH}_2\text{Br} + \text{HO}^-$ HO^- is a better nucleophile than H_2O .
 b. $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Br} + \text{HO}^-$ This alkyl halide has less steric hindrance toward nucleophilic attack.
 c. $\text{CH}_3\text{CH}_2\text{Cl} + \text{CH}_3\text{S}^-$ CH_3S^- is a better nucleophile than CH_3O^- in a protic solvent (a solvent that can form hydrogen bonds).
 d. $\text{CH}_3\text{CH}_2\text{Br} + \text{I}^-$ Br^- is a weaker base than Cl^- , so Br^- is a better leaving group.

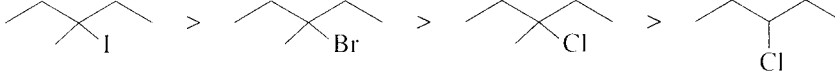
14. These are all $\text{S}_{\text{N}}2$ reactions.

- a. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ c. $\text{CH}_3\text{CH}_2\text{N}^+(\text{CH}_3)_3 \text{Br}^-$
 b. $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_3$ d. $\text{CH}_3\text{CH}_2\text{SCH}_2\text{CH}_3$

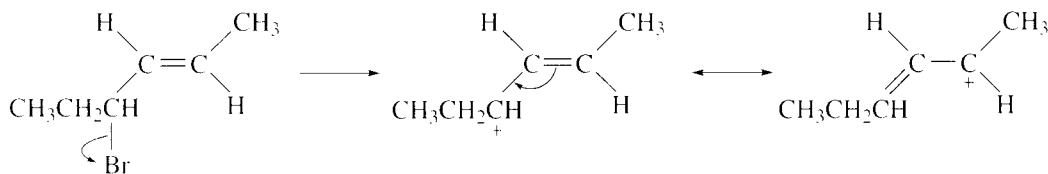
15. Solved in the text.

16. a. Reaction of an alkyl halide with ammonia gives a low yield of primary amine, because as soon as the primary amine is formed, it can react with another molecule of alkyl halide to form a secondary amine; the secondary amine can react with the alkyl halide to form a tertiary amine, which can then react with an alkyl halide to form a quaternary ammonium salt. (See Problem 15 on page 415.)
 b. The alkyl azide is not treated with hydrogen until after all the alkyl halide has reacted with azide ion. Therefore, when the primary amine is formed, there is no alkyl halide for it to react with to form a secondary amine.

17. a.  one product because the leaving group was not attached to an asymmetric center
 b.  *R* and *S* because the leaving group was attached to an asymmetric center

18. 

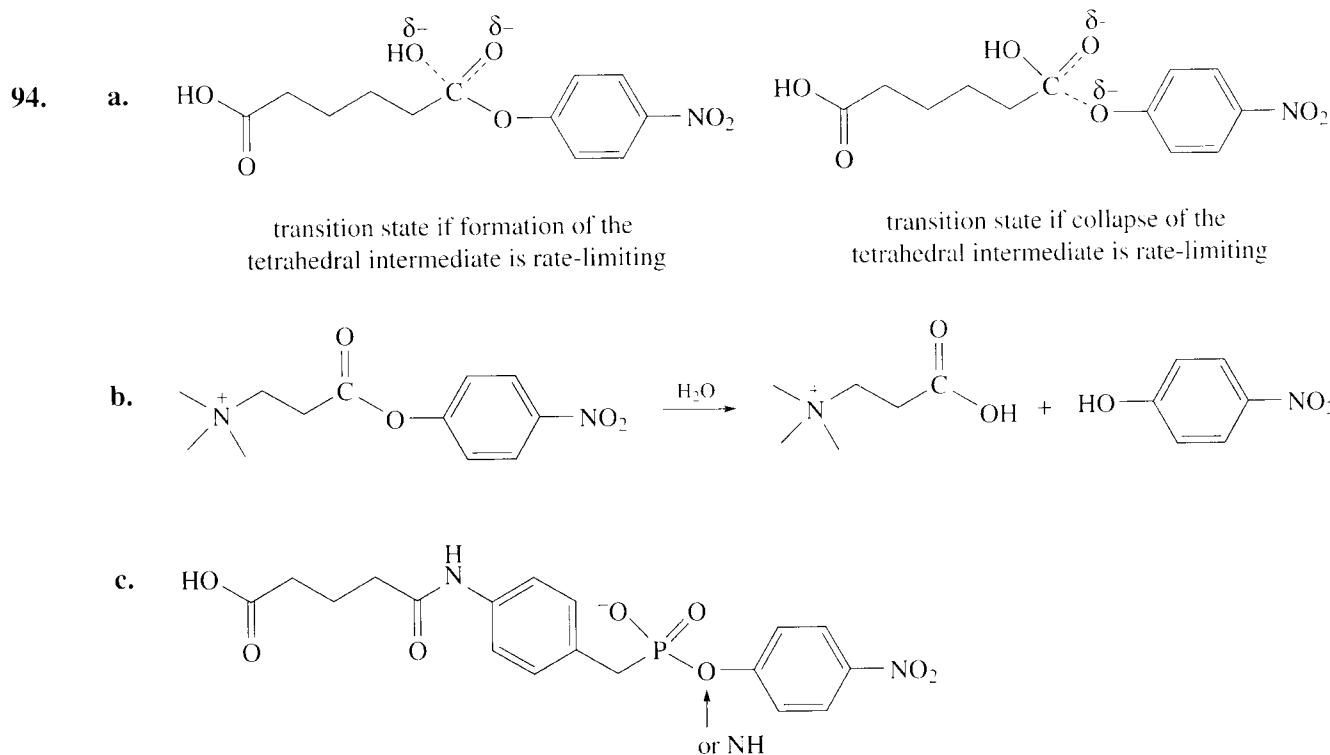
19. *trans*-4-Bromo-2-hexene (the compound on the right) is more reactive in an $\text{S}_{\text{N}}1$ solvolysis reaction, because the carbocation that is formed is stabilized by electron delocalization. (It is a secondary allylic cation.) The other alkyl halide is a secondary alkyl halide and does not undergo an $\text{S}_{\text{N}}1$ solvolysis reaction.



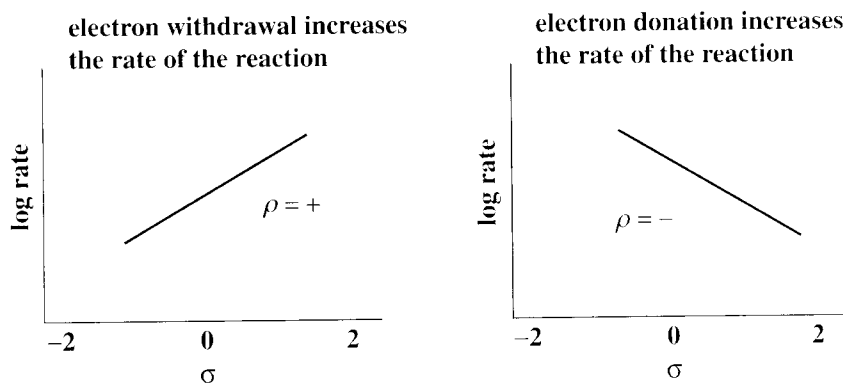
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radical initiator	a compound that creates radicals.
radical substitution reaction	a substitution reaction that has a radical intermediate.
reactivity-selectivity principle	the greater the reactivity of a species, the less selective it will be.
saturated hydrocarbon	a hydrocarbon that contains only single bonds (it is saturated with hydrogen).
secondary alkyl radical	an alkyl radical with the unpaired electron on a secondary carbon.
termination step	two radicals combine to produce a molecule in which all the electrons are paired.
tertiary alkyl radical	an alkyl radical with the unpaired electron on a tertiary carbon.

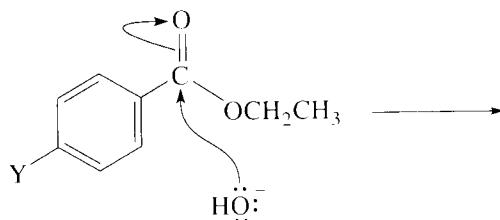
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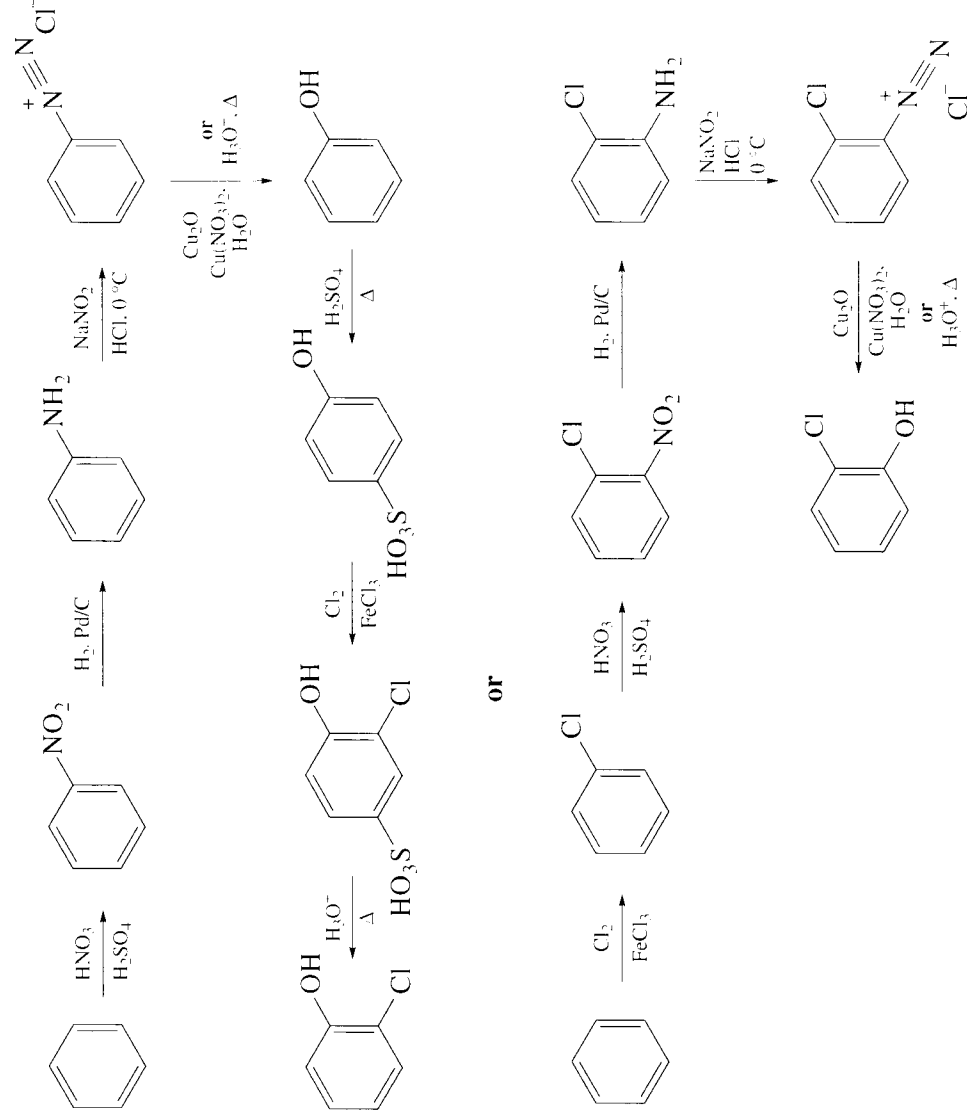
95. Because electron-withdrawing substituents have positive substituent constants and electron-donating substituents have negative substituent constants, a reaction with a positive ρ value is one in which compounds with electron-withdrawing substituents react more rapidly than compounds with electron-donating substituents, and a reaction with a negative ρ value is one in which compounds with electron-donating substituents react more rapidly than compounds with electron-withdrawing substituents.



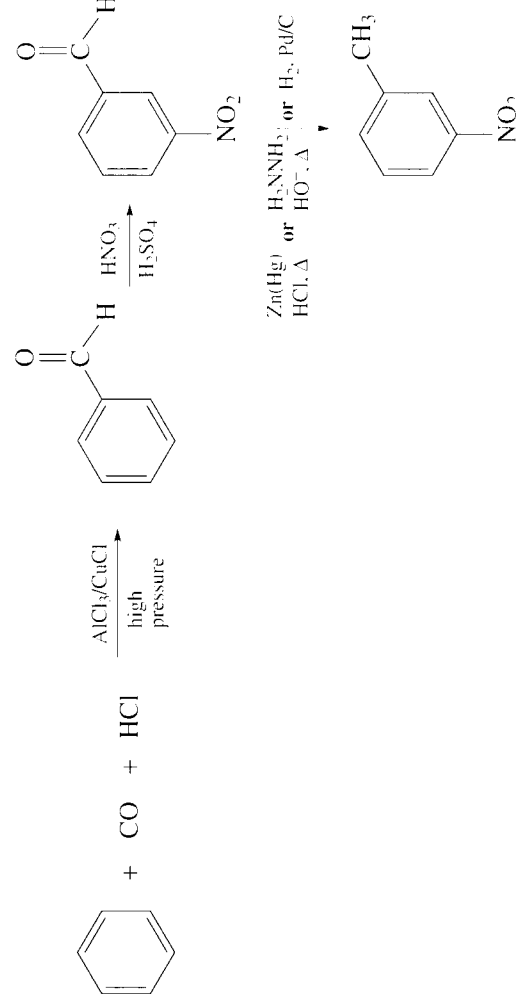
- a. In the hydroxide-ion-promoted hydrolysis of a series of ethyl benzoates, electron-withdrawing substituents increase the rate of the reaction by increasing the amount of positive charge on the carbonyl carbon, thereby making it more readily attacked by hydroxide ion. The ρ value for this reaction is, therefore, positive.



c. The first approach is longer, but it will generate a higher yield of the ortho isomer.



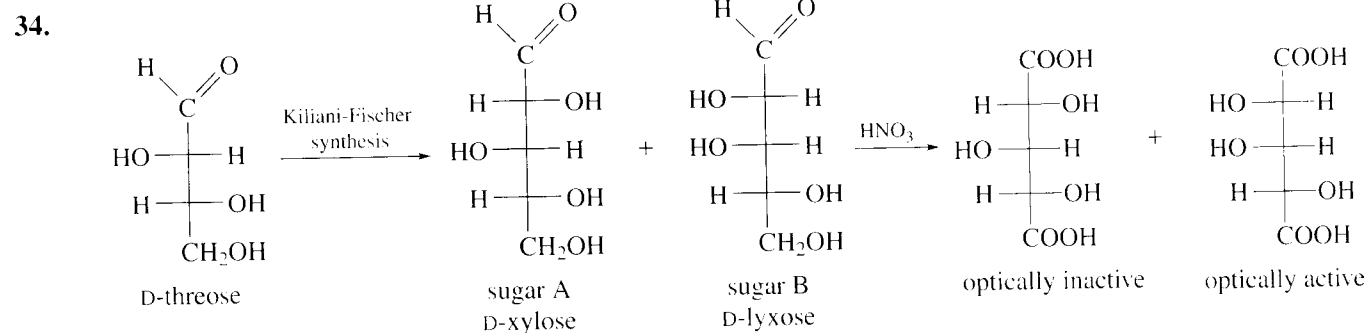
d. The nitro group cannot be placed on the benzene ring first, because a Friedel-Crafts reaction cannot be carried out on a ring with a meta director. Because formyl chloride is too unstable to be purchased, benzaldehyde is prepared by the Gatterman-Koch reaction (page 919 in the text).



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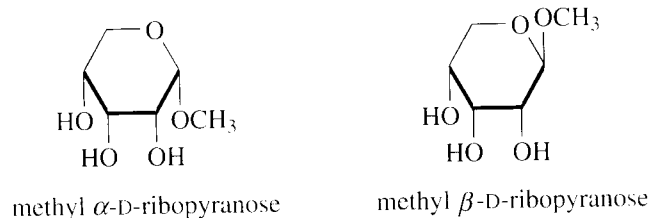
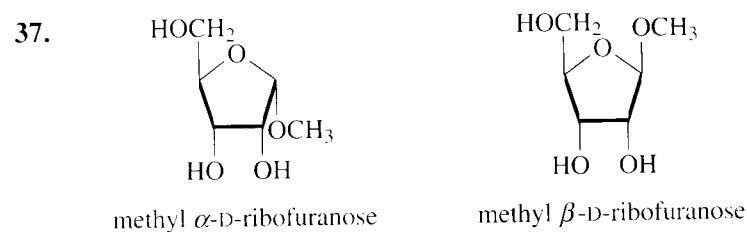
32. C-2 epimer = D-mannose C-4 epimer = D-galactose
 C-3 epimer = D-allose C-5 epimer = L-idose

33. a. D-lyxose b. D-talose c. D-psicose



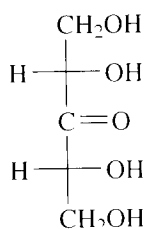
35. a. D-ribose and L-ribose, D-arabinose and L-arabinose, D-xylose and L-xylose, D-lyxose and L-lyxose
 b. D-ribose and D-arabinose, D-xylose and D-lyxose, L-ribose and L-arabinose, L-xylose and L-lyxose
 c. D-arabinose, L-arabinose, D-lyxose, and L-lyxose

36. a. $2R,3S,4R,5R$ b. $2R,3S,4S,5R$ c. $2R,3R,4R$ d. $2R,3S,4R$ e. $3R,4S,5R$

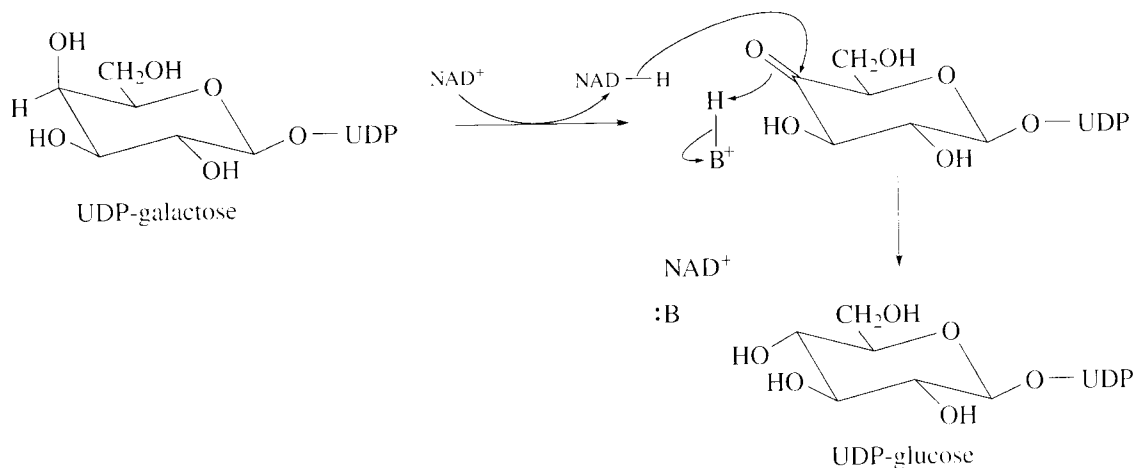


38. a. methyl β -D-sorbose b. ethyl β -D-guloside c. methyl α -D-idoside

39. A monosaccharide with a molecular weight of 150 must have five carbons (five C's = 60, five O's = 80, and 10 H's = 10 for a total of 150). All aldopentoses are optically active. Therefore, the compound must be a ketopentose. The following is the only ketopentose that would not be optically active.



63. a. UDP-galactose and UDP-glucose are C-4 epimers. NAD^+ oxidizes the C-4 OH group of UDP-galactose to a ketone. When NADH reduces the ketone back to an OH, it attacks the sp^2 carbon from above the plane, forming the C-4 epimer of the starting material.

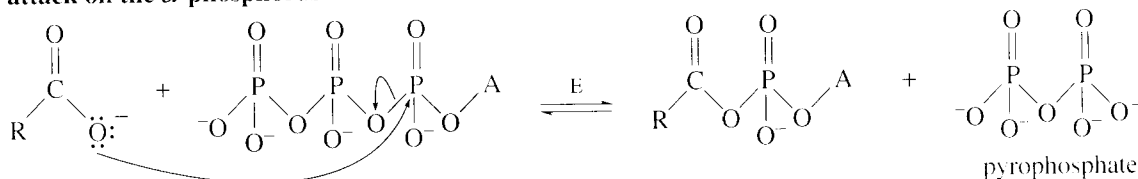


- b. The enzyme is called an epimerase because it converts a compound into an epimer (in this case, a C-4 epimer).
64. Because the compound that would react in the second step with the activated carboxylic acid group is excluded from the incubation mixture, the reaction between the carboxylate ion and ATP will come to equilibrium.

If radioactively labeled pyrophosphate is put into the incubation mixture, ATP will become radioactive if the mechanism involves attack on the α -phosphorus because pyrophosphate is a reactant in the reverse reaction that forms ATP.

ATP will not become radioactive if the mechanism involves attack on the β -phosphorus because pyrophosphate is not a reactant in the reverse reaction that forms ATP. (In other words, because pyrophosphate is not a product of the reaction, it cannot become incorporated into ATP in the reverse reaction.)

attack on the α -phosphorus



attack on the β -phosphorus

