
OpenCourseWare (2023)

CHEMISTRY II

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SOLUTIONS OF ORGANIC CHEMISTRY: INTRODUCTION EXERCISES



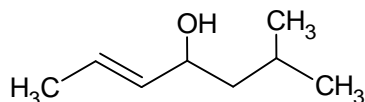
CHARACTERISTIC GROUPS AND NOMENCLATURE OF ORGANIC CHEMISTRY

Exercise 1. Arrange the following characteristic groups in decreasing order and write the formula for each group in order of decreasing seniority: acid halides, alcohols, aldehydes, amines, amides, carboxylic acids, carboxylates, esters, ketones, nitriles and thiols.

SOLUTION

Class	Formula
Carboxylates	-COO-
Carboxylic acids	-COOH
Esters	-COOR
Acid halides	-COX
Amides	-CONH ₂
Nitriles	-C≡N
Aldehydes	-CHO
Ketones	=O
Alcohols	-OH
Thiols	-SH
Amines	-NH ₂

Exercise 2. Indicate the steps required for the formation of a systematic name. Use the following compound as an example:

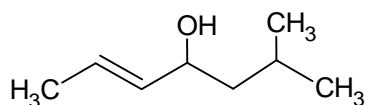
**SOLUTION**

The steps for the formation of a systematic name will be taken (when they are applicable) in the following order:

1. Identify the primary characteristic group to be mentioned as the suffix.
2. Identify the senior parent among those structural components attached to a primary characteristic group.
3. Designate the parent hydride and specify any unsaturation.
4. Unite the designation of the parent hydride with the suffix for the primary characteristic group.
5. Recognize the substituents and organize the corresponding prefixes in alphabetical sequence.
6. Introduce multiplicative prefixes, maintaining the existing order, and include locants.

7. Determine chirality centers and other stereogenic units, such as double bonds, and append stereodescriptors.

Example:

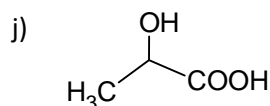
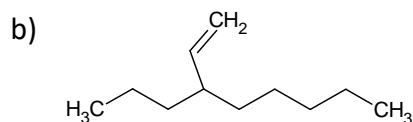
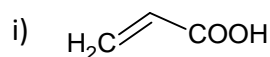
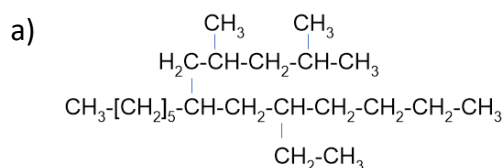


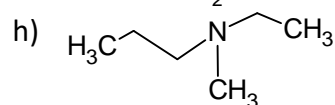
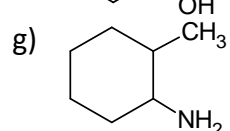
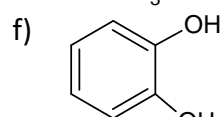
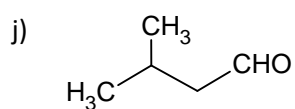
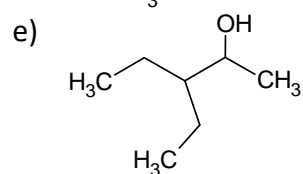
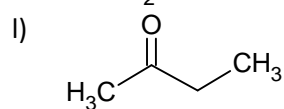
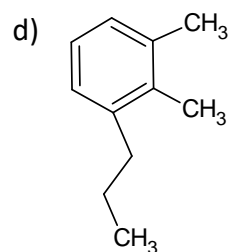
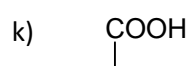
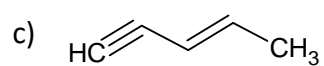
- Identify the primary characteristic group (functional group): alcohol, suffix -ol.
- Determine the base compound or functional base compound: seven-carbon chain: heptane.
- Determine the unsaturation: double bond at position 2.
- Name and locate the substituents: position 6: substituent -CH₃: 6-methyl.
- Write the complete compound name: 6-methylhept-2-en-4-ol.
- Determine the stereoisomerism of the double bond: (2E)-6-methylhept-2-en-4-ol.

Exercise 3. Formulate the following organic compounds from the preferred IUPAC name (PIN).

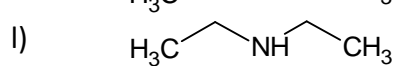
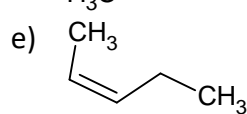
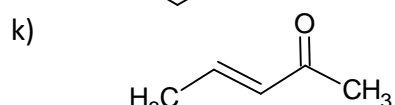
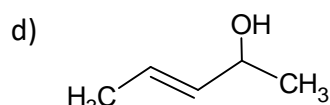
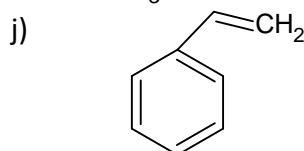
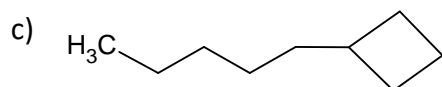
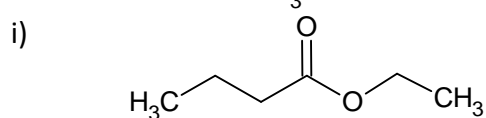
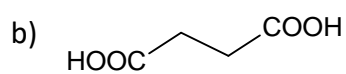
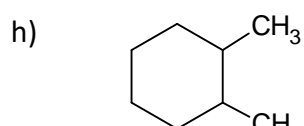
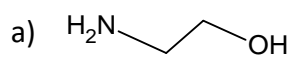
- a) 7-(2,4-dimethylpentyl)-5-ethyltridecane
- b) 4-ethenylnonane
- c) pent-3-en-1-yne
- d) 1,2-dimethyl-3-propylbenzene
- e) 3-ethylpentan-2-ol
- f) benzene- 1,2-diol
- g) 2-methylcyclohexan-1-amine
- h) N-ethyl-N-methylpropan-1-amine
- i) 1-bromo-2-(2-chloroethoxy)ethane
- j) prop -2-enoic acid
- k) 2-hydroxypropanoic acid
- l) 4-aminobenzoic acid
- m) butan-2-one
- n) 3-methylbutanal

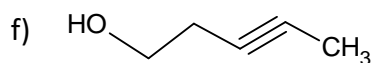
SOLUTION



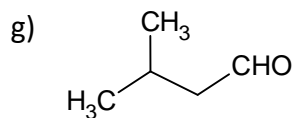
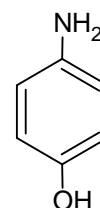


Exercise 4. Give IUPAC names for the following compounds:

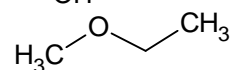




m)



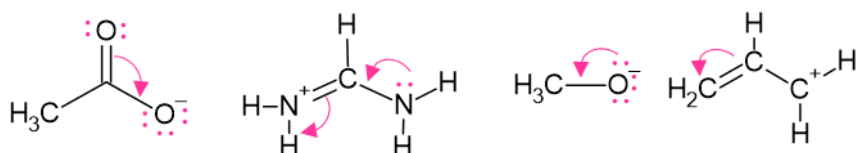
n)

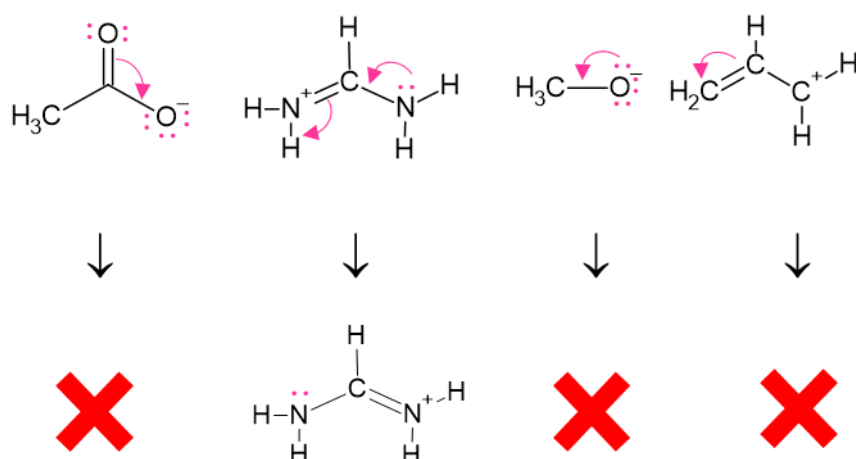
**SOLUTION**

- a) 2-aminoethan-1-ol
- b) butanedioic acid
- c) pentylcyclobutane
- d) (3E)-pent-3-en-2-ol
- e) (2Z)-pent-2-ene
- f) pent-3-yn-1-ol
- g) 3-methylbutanal
- h) 1,2-dimethylcyclohexane
- i) ethyl butanoate
- j) ethenylbenzene
- k) (3E)-pent-3-en-2-one
- l) N-ethylethanamine
- m) 4-aminophenol
- n) methoxyethane

PROPERTIES, STRUCTURE AND REACTIVITY

Exercise 5. Consider the following molecules. Evaluate whether the arrow pushing in each structure leads to an acceptable resonance form. If so, draw it and explain your answer.



SOLUTION

No, one of the oxygens would have 10 e⁻

Yes, every atom has an octet.

No, the atom carbon would have 10 e⁻.

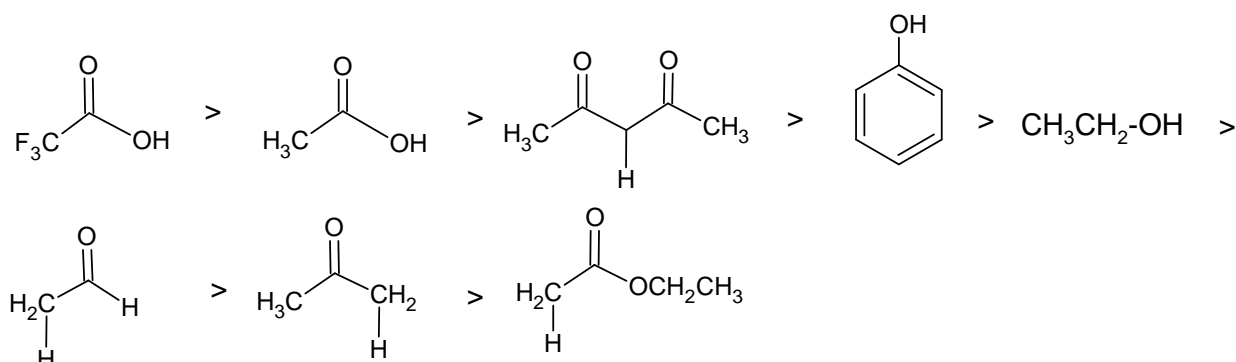
No, there will be two adjacent positive charges.

Exercise 6. Arrange in order of acidity the following compound: acetic acid, acetone, phenol, acetaldehyde, ethanol, ethyl acetate, 2,4-pentanedione, trifluoroacetic acid.

SOLUTION

Trifluoroacetic acid is the most acidic because the trifluoroacetate ion formed is the most stable. Phenol exhibits a pronounced acidic character due to the resonance stabilization of the phenolate ion. This phenomenon does not occur in the ethoxide ion (it lacks resonant forms, and the negative charge is concentrated on the oxygen atom). Therefore, phenol is more acidic than ethanol despite both being alcohols.

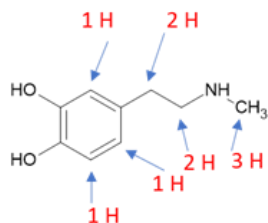
More crucial than the number of resonant forms is their significance. The acetate ion has only two resonant forms, while the phenolate ion has four. However, acetic acid is a stronger acid than phenol. In the case of the acetate ion, the negative charges are located on oxygen atoms, which are more electronegative than carbon. In the case of the phenolate ion, three resonant forms have negative charges on carbon atoms, and these resonant forms are not aromatic.



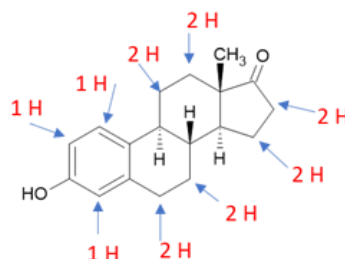
Exercise 7. Tell how many hydrogens are bonded to each carbon in the following compounds and give the molecular formula of each substance: a) adrenalin; b) estrone; c) tryptophan; d) serotonin; e) melatonin.

SOLUTION

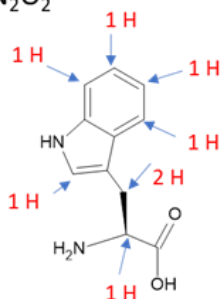
Adrenalin: $C_9H_{13}NO_3$



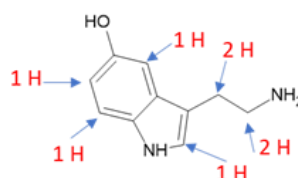
Estrone: $C_{18}H_{22}O_2$



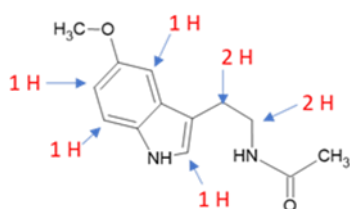
Tryptophan: $C_{11}H_{12}N_2O_2$



Serotonin: $C_{10}H_{12}N_2O$

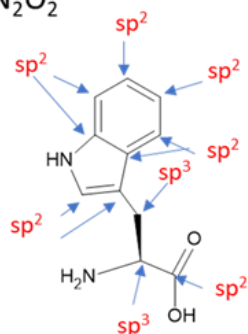
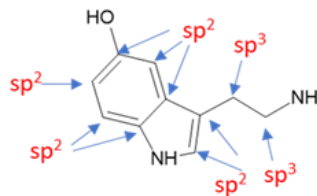
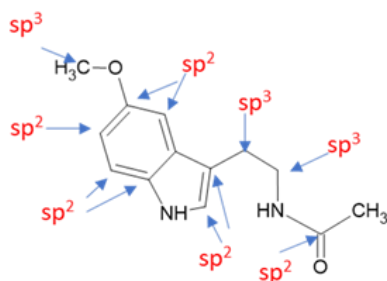


Melatonin: $C_{13}H_{16}N_2O_2$



Exercise 8. For the molecules from the previous exercise, how many sp^3 and sp^2 -hybridized carbons does each molecule have?

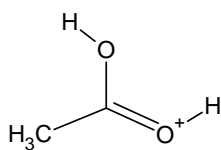
SOLUTION

Tryptophan: $C_{11}H_{12}N_2O_2$ Serotonin: $C_{10}H_{12}N_2O$ Melatonin: $C_{13}H_{16}N_2O_2$ 

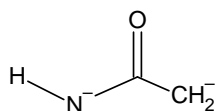
Exercise 9. Draw octet resonance forms for the following molecules. Indicate the strongest resonance contributor (if any) in each case.

(a) CNO^- (b) NO^-

(c)

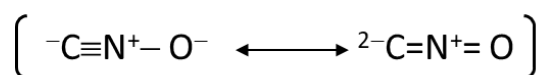


(d)

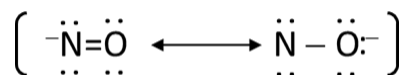


SOLUTION

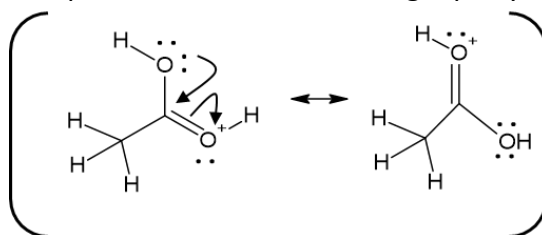
(a) The left-hand structure is preferred because the charges are more evenly distributed, and a negative charge resides on the relatively more electronegative oxygen.



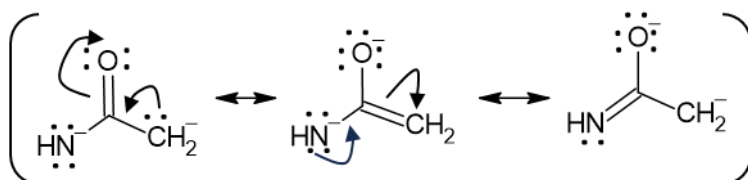
(b) The left-hand structure is preferred because the right-hand structure has no octet on nitrogen.



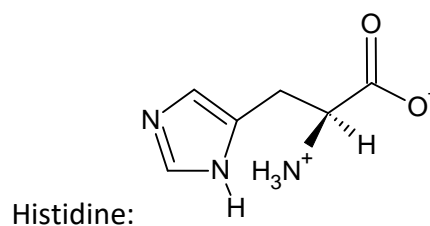
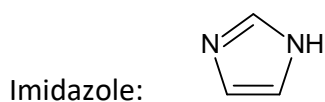
(c) The two structures are equal, therefore contributing equally.



(d) The best structure is at the center, featuring the negative charges at the more electronegative atoms. The best second form is on the right, with the charge on oxygen, better than the first, since oxygen is more electronegative than nitrogen.

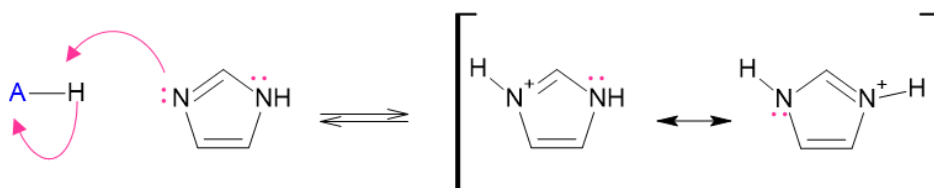


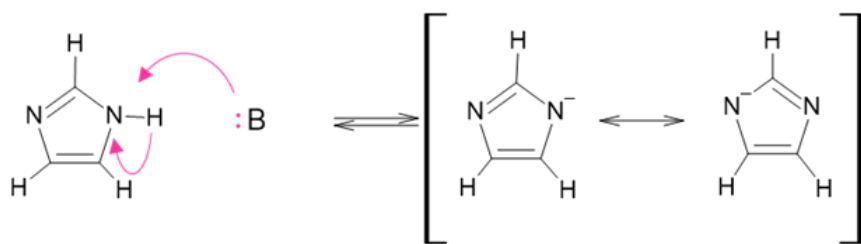
Exercise 10. Imidazole forms part of the structure of the amino acid histidine and can act as both an acid and a base. Draw structures for the resonance forms of the products that result when imidazole is protonated by an acid and deprotonated by a base.



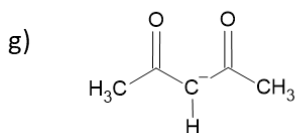
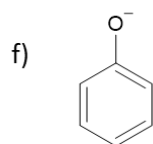
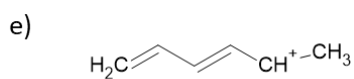
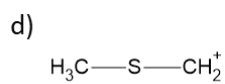
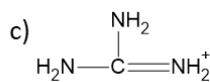
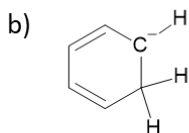
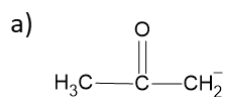
Hint: The most basic nitrogen atom is the N which forms part of the double bond. The most acidic hydrogen atom is the H bonds to N.

SOLUTION

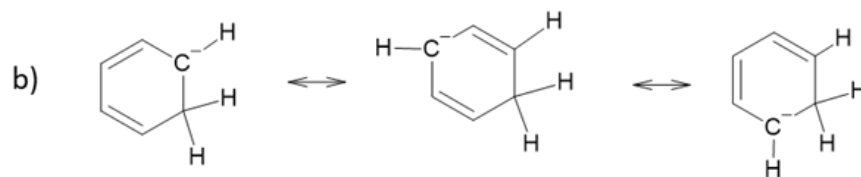
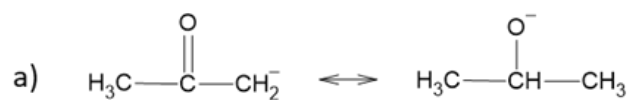


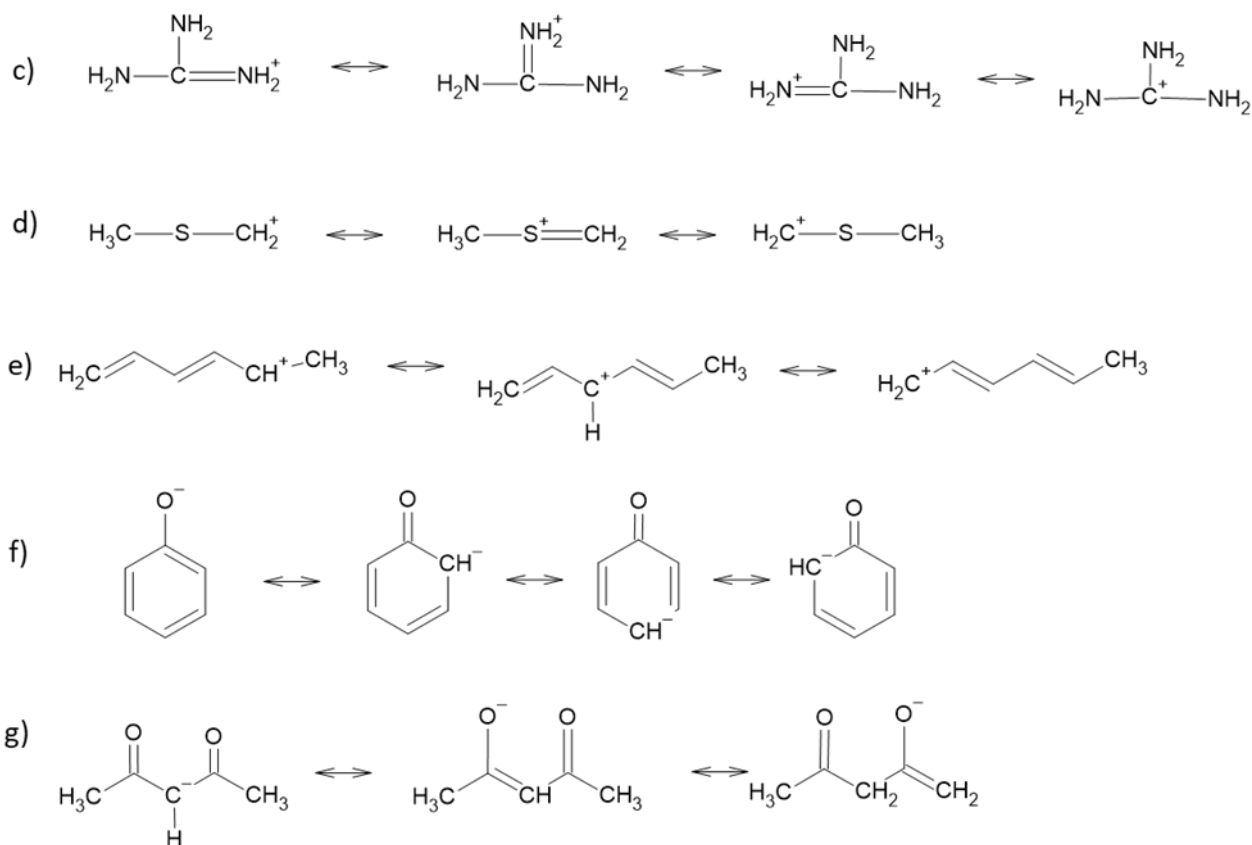


Exercise 11. Draw as many resonance structures as you can for the following species:



SOLUTION



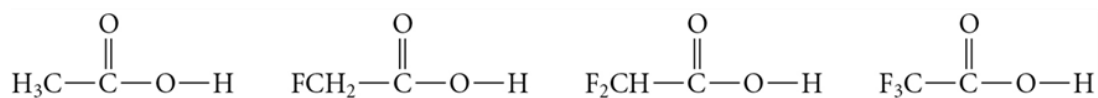
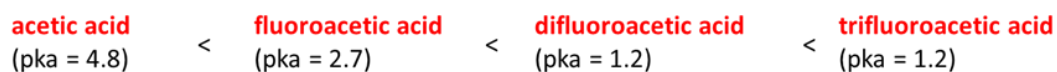


Exercise 12. Based on its structure, arrange in increasing order of acidity each series

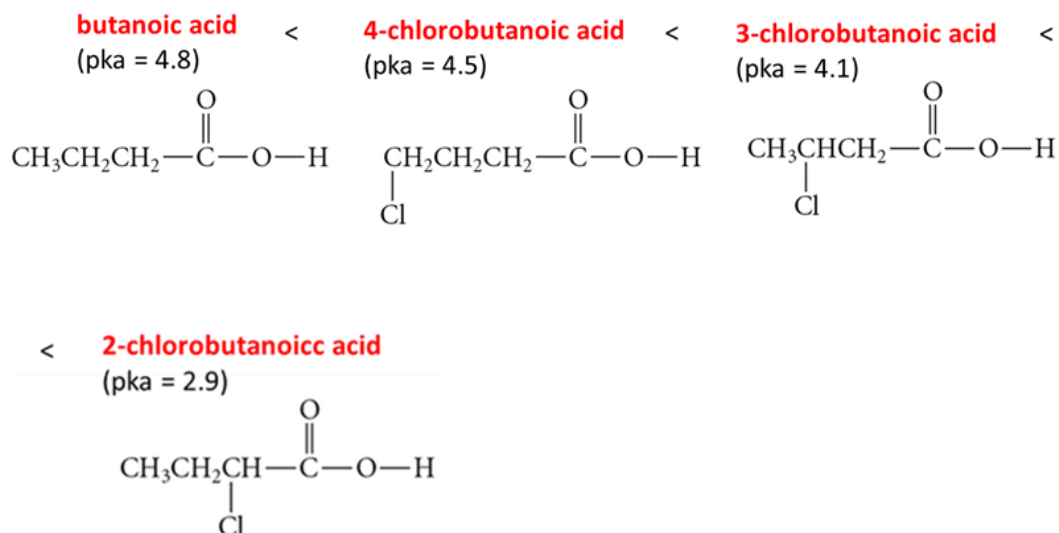
- a) acetic acid, fluoroacetic acid, difluoroacetic acid, and trifluoroacetic acid.
 b) butanoic acid, 4-chlorobutanoic acid, 3-chlorobutanoic acid, and 2-chlorobutanoic acid.

SOLUTION

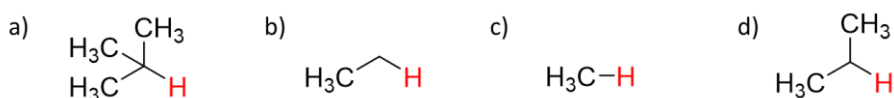
a) Effect polar of F atoms: - increasing the number of nearby electronegative atoms to the acid H, the anion is stabilized (the acid's conjugate base).



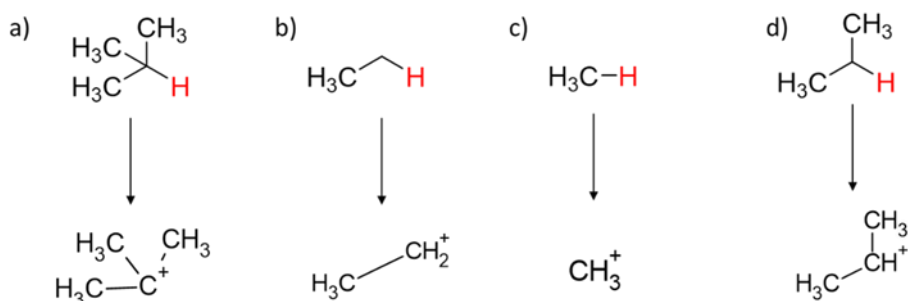
b) Effect polar of Cl atoms: - Varying the distance of the electronegative atom to the acidic H, the anion is stabilized (the acid's conjugate base).



Exercise 13. Explain which of follow C-H bond is the weakest:



SOLUTION



Order of stability for carbocations is as follows: tertiary > secondary > primary > methyl. The C-H weakest is a).

Exercise 14. Order the following series in increasing order of acidity, explaining the response, and when necessary, draw the resonant structures.

- methanol, acetic acid (CH_3COOH), and chloroacetic acid (ClCH_2COOH)
- methanol, ethanol, isopropanol ($(\text{CH}_3)_2\text{CHOH}$), and tert-butanol ($(\text{CH}_3)_3\text{COH}$)
- ethanol and phenol ($\text{C}_6\text{H}_5\text{OH}$).

SOLUTION

a) Increasing order of acidity: methanol (CH_3OH) < acetic acid (CH_3COOH) < chloroacetic acid (ClCH_2COOH)

Explanation: The order of acidity is based on the stability of the conjugated anions. The more stable the conjugated anion, the higher the acidity. In the case of these substances: methanol does not have an acidic group and is therefore not acidic. Acetic acid forms an acetate ion that is stabilized by resonance in the carboxyl group. Chloroacetic acid is more acidic than acetic acid due to the greater electronegativity of chlorine, which stabilizes the conjugated anion.

b) Increasing order of acidity: tert-butanol ($(\text{CH}_3)_3\text{COH}$) < isopropanol ($(\text{CH}_3)_2\text{CHOH}$) < ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) < methanol (CH_3OH).

Explanation: acidity increases with the ease with which alcohol donates a proton. As the number of alkyl groups increases, the acidity decreases. In this case: tert-butanol is the least acidic due to the large amount of methyl groups. Isopropanol is less acidic than ethanol due to the presence of an additional methyl group. Ethanol is less acidic than methanol due to the lack of stability of the ethoxide ion ($\text{CH}_3\text{CH}_2\text{O}^-$).

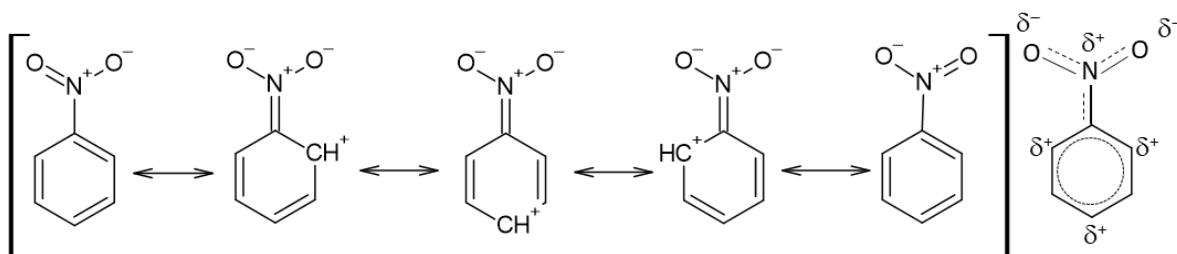
c) Increasing order of acidity: ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) < phenol ($\text{C}_6\text{H}_5\text{OH}$)

Explanation: the acidity in this case is based on the stability of the phenoxide anion. The order is explained by the greater stability of the phenoxide anion, which is formed in phenol due to resonance in the aromatic ring, which disperses the negative charge.

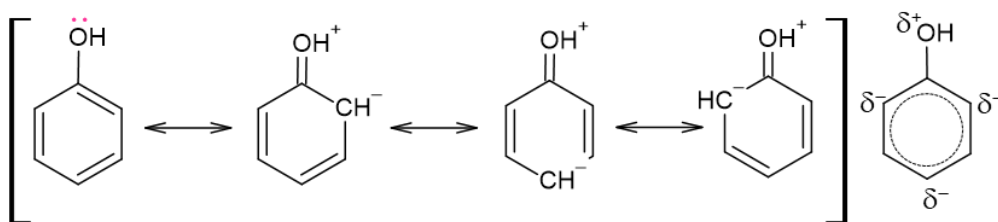
Exercise 15. Indicate, based on the corresponding resonant forms, how the functional group (electron-donor or electron-acceptor of charge) affects the hydrocarbon structures: a) nitrobenzene; b) phenol; c) aniline; d) toluene.

SOLUTION

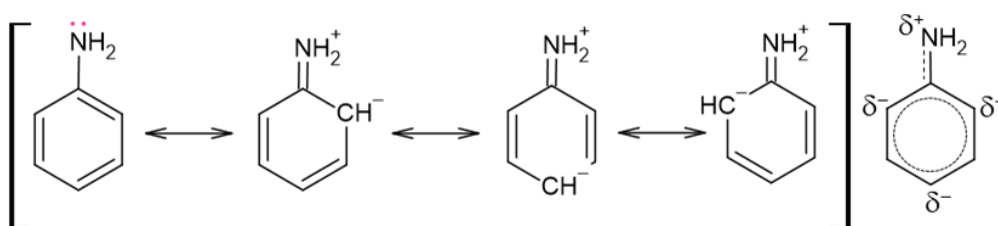
a) The nitro group reduces the electron density of the aromatic ring through delocalization of π electrons (resonance effect being more significant than the inductive effect):



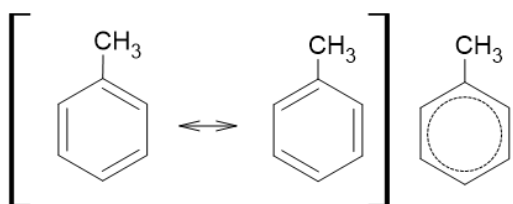
b) The $-\text{OH}$ group exerts a positive resonance effect (delocalization of negative charge) and an inductive effect $-I$ due to the electronegativity of O . However, the resonance effect is more dominant than the inductive effect. Therefore, electron density increases at the ortho and para positions.



c) Similar to phenol. In this case, it is important to highlight that it decreases the basicity compared to alkyl amines because the lone pair of electrons on nitrogen is delocalized in the aromatic ring.

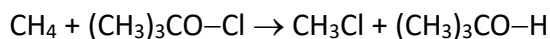


d) Resonance structure of toluene: those generated by the aromatic ring, as the $-\text{CH}_3$ group lacks unpaired electrons to conjugate with the π electrons of the aromatic ring.



The methyl group is a weak activator, and although it is evenly distributed on all aromatic C atoms in the ring, the orientation for electrophilic aromatic substitution is preferably at the ortho and para positions (explained in the topic of benzene and aromaticity).

Exercise 16. An alternative to chlorine in radical halogenations of methane is tert-butyl hypochlorite, $(\text{CH}_3)_3\text{COCl}$:



(a) Using the bond-dissociation energies provided, calculate the ΔH^0 value for the reaction.

(b) The reaction is initiated by the photolytic cleavage of the O–Cl bond. Formulate the two propagation steps of the radical chain leading to the products.

Data: Bond-dissociation energies ($\Delta H^0/\text{Kcal mol}^{-1}$): (O–Cl) = 55; (O–H) = 118; ($\text{CH}_3\text{--H}$) = 105; ($\text{CH}_3\text{--Cl}$) = 85.

SOLUTION

(a) $\Delta H^\circ = (105+55) - (118+85) = -43 \text{ kcal mol}^{-1}$

(b) Propagation step 1 features H abstraction by the *tert*-butoxyl radical rather than $\cdot\text{Cl}$, because the H–O bond is stronger than the H–Cl bond.

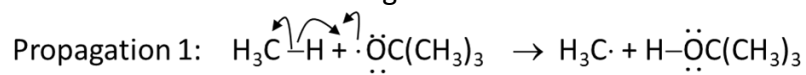


IMAGE CREDITS

- Images of all exercises were made by authors.