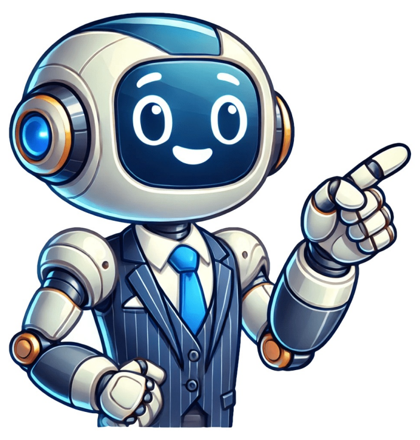

As you saw in Section 16.4, a substituent on a benzene ring can be an activator or a deactivator. At the same time, a substituent can also be a meta director or an ortho/para director. Of the four possible combinations, only three are knownthere are no meta directing activators. If you look at the data for the nitration of toluene, you will see that the yield of onitrotoluene is 63% and that of pnitrotoluene is 34%. Statistically, we should expect to obtain twice as much ortho product as para product, because the former is produced by attack at either of two carbon atoms whereas the latter is produced by attack at only one carbon atom (see Figure 16.1, below). Figure 16.1: Proportions of onitrotoluene and pnitrotoluene produced by the nitration of toluene In this instance, the observed ortho/para ratio is almost 2:1, as we might expect. However, if we study the ortho/para ratio found in the nitration of a number of other arenes, we see that this is not always the case. Note that the data for the nitration of toluene given in the table below differ from those presented elsewhere. The variation may result from a difference in temperature, reaction conditions or reagent, and emphasizes the point that it is the trends which are important, not the numbers themselves. Substrate % ortho % para ortho/para ratio toluene 58 37 1.57:1 ethylbenzene 45 49 0.92:1 isopropylbenzene 30 62 0.48:1 tert-butylbenzene 16 73 0.22:1 [Source: These data were taken from the audiocassette Some Organic Reaction Pathways, by Peter Sykes. London: Educational Techniques Subject Group, The Chemical Society, 1975.] Table 16.1: Nitration of arenes The table above shows us that as the size of the alkyl substituent already present in the ring increases, attack at the ortho position becomes more difficult, and the percentage of ortho isomers in the mixture of products decreases. This is an example of a steric effectan effect caused by the size of the substituentand we would say that as the size of the alkyl group increases, attack at the ortho position becomes less favourable as a result of steric hindrance. Note that the size of the electrophile can also be a factor in determining the ortho/para ratio: the larger the electrophile, the less able it is to attack at the ortho position, particularly if the substituent already present in the ring is itself quite bulky. When drawing the resonance contributors to the carbocation formed during an electrophilic aromatic substitution, bear in mind that those of the type are particularly important, because in such structures each atom possesses a complete octet of electrons. Note that, as do the hydroxyl and amino groups, the halogens have an inductive electron-withdrawing effect and a resonance electron-releasing effect on a benzene ring. The difference in behaviour during electrophilic substitutions arises because, with the hydroxyl and amino groups, the resonance effect completely swamps the inductive effect, whereas with the halogens, there is a much finer balance. In the case of the latter, the inductive effect reduces the overall reactivity, but the resonance effect means that this reduction is felt less at the ortho and para positions than at the meta position.An important element in organic chemistry is the influence of substituents. The properties of a molecule change depending on what functional group is attached to the alkyl chain or benzene ring.Two particularly important effects of the substituents are the inductive effect (I effect) and the resonance effect (R effect). The acidity of the molecule will be different depending on the substituents that are bonded to it. It also depends on whether the substituent is bound to an alkyl chain or a benzene ring.There are two types of substituents: electron-donating and electron-withdrawing. Electron-donating groups provide electrons, and electron-withdrawing groups pull electrons. By identifying these, we can infer the reactivity of the molecule.So make sure you understand the principles of the inductive and resonance effects. Once you understand the nature of the substituents and learn how to distinguish between electron-donating and electron-withdrawing groups, youll be able to figure out what the acidity of the molecule is.Differences Between the Inductive Effect (I Effect) and the Resonance Effect (R Effect)First, what is the inductive effect (I effect)? And what is the resonance effect (R effect)? Lets think of them both as effects caused by the functional groups attached to the molecule. Depending on what substituents are bonded to the molecule, there will be many differences, such as different acidity.The differences between the two are as follows.Inductive effect: effect of -bond (single bond)Resonance effect: Effect of -bond (double and triple bonds)Electronic orbitals include s and p orbitals, and these orbitals form bonds. Among the bonds formed by these s and p orbitals, the single bond is the -bond. The substituent effect of the -bond is the inductive effect.On the other hand, some molecules form double or triple bonds. The part of the molecule that forms a double or triple bond is called a bond; if a pi bond is present, you can write resonance structures. The resonance effect is the result of resonance by the substituent, which changes the orientation (reactivity on the benzene ring) and the acidity of the molecule.Roughly speaking, understand that the inductive effect (I effect) affects the alkyl chain, and the resonance effect (R effect) affects the benzene ring.The Acidity Varies with the Degree of Electronegativity Due to the Inductive EffectThe inductive effect affects the single bond (-bond). When does the inductive effect appear? It occurs when an atom (or molecule) with a high degree of electronegativity is attached.Particularly important is when it is bonded to an alkyl chain. An alkyl chain without double or triple bonds will not cause resonance. Therefore, for alkyl chains, we only need to consider the inductive effect.When an atom with a high degree of electronegativity bonds together, it will strongly attract electrons. As a result, the molecule will produce a positive and negative charge, even if it is the same molecule. This is known as polarization. Water, ammonia and hydrogen chloride are known to be polarized.Polarization due to differences in electronegativity also occurs in alkyl chains. When a substituent with high electronegativity is attached to an alkyl chain, it causes a difference in acidity.For example, acetic acid is known as an acidic substance. When a carboxylic acid is present, it shows acidic properties. However, even if it is the same carboxylic acid, the acidity varies depending on what substituents are present on the surrounding carbon.For example, what happens if one chlorine atom, a halogen, is bonded to acetic acid (CH3COOH)? In this case, the result is as follows.When a chlorine atom is bonded, electrons are attracted to the chlorine atom. As a result, chloroacetic acid is more negatively charged than carboxylic acid. This means that the acidity of chloroacetic acid is higher.The electrons are pulled by the halogen, and as a result, the chloroacetic acid is more acidic than the carboxylic acid.The effect of the substituent pulling the electrons is an inductive effect. This effect is responsible for the strength of the acidity. Of course, the more halogens that are bonded, the greater the acidity.As explained in the example of acidity, it also affects basicity in the same way. The inductive effect is related to the degree of basicity.For functional groups with strong electronegativity, the inductive effect is involved in many cases. When an oxygen or nitrogen atom or a halogen is bonded to an alkyl chain, it causes an inductive effect and lowers the electron density.Nitro group (-NO2)Amino group (-NH2)Cyano group (-CN)Carbonyl group (-CO)Carboxy group (-COOH)Sulfone group (-SO3H)Methoxy group (-OCH3)Hydroxy group (-OH)Halogen (-Cl, -Br, -I)All of these attract electrons by binding to the alkyl chain, causing the inductive effect. In functional groups with oxygen or nitrogen atoms or halogens, they are all electronwithdrawing groups.Limited Influence of ElectronWithdrawing GroupsWhat is the extent of the inductive effect of the electronwithdrawing group? Lets understand that this is limited.Even though the electronegativity attracts electrons, the effect is small when the distance is large. For the neighboring carbon atoms that the electron-withdrawing group is bonded to, there is an effect due to the inductive effect. However, as the distance increases, the effect of electronegativity decreases.Although the inductive effect reduces the electron density, the range of influence is small.-The More Carbon Atoms There Are, the Higher the Electron DensityFor reference, the presence of carbon atoms increases the electron density. Unlike oxygen and nitrogen atoms and halogens, carbon atoms push out electrons. This is the opposite of electronwithdrawing.Therefore, if there are multiple carbon atoms bonded together, the electron density will be higher.Resonance Effects Take Into Account the Delocalization of ElectronsThe inductive effect in alkyl chains is simple. The inductive effect (I effect) is the lowering of the electron density due to the bonding of functional groups with a high degree of electronegativity. This results in a higher degree of acidity (or basicity).The resonance effect (R effect), on the other hand, is a bit more complicated. In contrast to the inductive effect, which only requires considering the effects of single bonds, the resonance effect requires considering the effects of double and triple bonds. The effect of the -bond is the resonance effect.Among these double bonds, the resonance effect has a strong influence on the orientation and acidity of aromatic compounds (compounds involving benzene rings). It is also responsible for the reaction rates of organic chemical reactions.For compounds with conjugated structures, the resonance effect should be taken into account. Roughly speaking, we can think of resonance effects as those related to the reactivity of the benzene ring.The Resonance Effect Is Stronger than the Inductive EffectOxygen and nitrogen atoms are typical examples of electron-withdrawing groups. So when hydroxy groups (-OH), methoxy groups (-OCH3) and amino groups (-NH2) are attached to the alkyl chain, they become electron-withdrawing groups. Any of these substituents can be considered to be an electron-withdrawing group.In aromatic compounds, on the other hand, the situation is different. Sometimes the substituent becomes an electron-donating group, and sometimes it becomes an electron-withdrawing group. This is because they resonate.The more you can write resonance structures, the more stable the compound is. If there is resonance, the electrons can move to many places with it. This is called the delocalization of electrons. The greater the degree of delocalization, the more stable the electron state becomes.In order to draw resonance structures, it is essential that the compound has a double bond. Since the benzene ring has double bonds, we can draw resonance structures for any aromatic ring compound. For example, here is the resonance of aniline.If we focus on the nitrogen atom of aniline, we can see that electrons are pushed out from the nitrogen atom toward the benzene ring. In other words, the nitrogen of aniline acts as an electron-donating group.Because it is a nitrogen atom, there is a force that attracts electrons through the inductive effect. However, compared to the inductive effect, the effect of the delocalization of electrons due to resonance is much stronger. As a result, the amino group on the benzene ring becomes an electron-donating group.How to Distinguish Between Electron-Donating and Electron-Withdrawing Groups in Aromatic RingsHow do we distinguish between the electron-donating and the electron-withdrawing group on the benzene ring? To do this, look for double (or triple) bonds in the substituents.For example, the following substituents are involved as electron-donating groups on the benzene ring.Methoxy group (-OCH3)Hydroxy group (-OH)Amino group (-NH2)If we focus on the atoms directly bonded to the benzene ring (oxygen and nitrogen atoms), we find that they are all single bonds. As a result, these substituents are electron-donating groups on the benzene ring.On the other hand, what if there is a double (or triple) bond in the substituent? In this case, they act as electron-withdrawing groups.Carbonyl group (-CO)Carboxy group (-COOH)Sulfone group (-SO3H)Nitro group (-NO2)Cyano group (-CN)The presence of a double bond (or triple bond) allows electrons to be drawn into the substituent group by resonance. As a result, it becomes an electron-withdrawing group.When an oxygen or nitrogen atom is bonded to the substituent, it becomes an electron-donating group if the substituent has only single bonds. On the other hand, when a substituent that has a double bond (or triple bond) is bonded, it becomes an electron-withdrawing group. Although there are exceptions, this is a rough understanding.The Acidity of the Benzene Ring Depends on the SubstituentsEven if it is an electron-withdrawing group in an alkyl chain, it can be an electron-donating group in an aromatic ring compound. This fact must be understood first. In the resonance effect, it can be more complicated than in the inductive effect.So why is it important to understand the resonance effect (R effect) in aromatic compounds? This is because it relates to acidity. Although the orientation (which part of the benzene ring causes the chemical reaction) also changes, we will focus on the acidity.Even for the same aromatic compound, the acidity changes depending on the substituents. For example, phenolic compounds are listed in the following order of acidity.Why does this difference appear?Halogens attract electrons through an inductive effect. Therefore, it is understandable that they would be more acidic than phenol. Carbon atoms also push out electrons. Since a carbon atom is an electron-donating group, its acidity is lower than that of phenol.On the other hand, what should we think of nitro and methoxy groups? These two functional groups should not be considered in terms of their inductive effects alone. Since the resonance effect is very strong, we need to consider the acidity by taking the resonance into account.Resonance Structures Change the Stability of ElectronsIn order for phenol to be acidic, we can expect that the more stable it is after becoming an ion, the stronger the acidity will be. In this case, the nitro group (p-nitrophenol) resonates as follows.Thus, after phenol becomes an acid, several resonance structures can be written. The electrons are also delocalized to the nitro group. The acidity of p-nitrophenol is high because of its stability when it becomes an acid. The presence of an electron-withdrawing group increases the acidity.On the other hand, what about the presence of a methoxy group? The methoxy group in the aromatic ring acts as an electron-donating group. As a result, the acidity becomes lower, contrary to the previous example.In the case of resonance with the methoxy group providing electrons, the result is as follows.The methoxy group pushes electrons into the benzene ring, resulting in a negatively charged carbon and an oxygen atom next to each other. When they become ions in this state, the negative charges exist next to each other.The negative and negative charges repel each other. This means that the resonance structure is unfavorable, considering that phenol shows acidity when it becomes an ion. For this reason, the presence of an electron-donating group in the benzene ring reduces its acidity.-Resonance Effect Changes the Orientation of Ortho, Meta, and ParaIt is not only the acidity that is affected by the resonance effect, but also the orientation. Orientation is a tool for predicting which part of the benzene ring will undergo an organic chemical reaction.In the benzene ring, there are ortho, meta, and para positions starting from the substituents. Where the substituents bind in an aromatic compound depends on the electron-donating and electron-withdrawing groups. Also, if the orientation is different, the reactivity of the aromatic compound will change.These are also affected by the resonance effect (R effect).Electronegativity and Resonance Contribute to the Stability of the CompoundMolecules have various substituents attached to them. Depending on the type of functional group, the molecule will have different properties.The most obvious one is the inductive effect (I effect). The higher the electronegativity, the more electrons the substituent attracts. As a result, the acidity of the molecule will differ. The difference in acidity is very important because it causes not only a difference in the strength of acidity and basicity, but also a difference in reactivity.However, a substituent that is involved as an electron-withdrawing group in the inductive effect may act as an electron-donating group in aromatic compounds. So, it is important to be able to distinguish the difference between an electron-donating group and an electron-withdrawing group.The resonance effect is stronger than the inductive effect. So, depending on what substituents are on the benzene ring, the acidity and orientation of the molecule can vary greatly.The nature of the molecule is largely related to the substituents. Depending on whether the substituent is bonded to an alkyl chain or a benzene ring, the properties of the substituent will change. It is important to understand this fact.The substituents on a benzene ring can influence its chemical behavior in two ways: through inductive effects and resonance effects. 1. Inductive Effect:This is a property of the substituent to donate or pull electron density through bonds. Electronegative substituents withdraw electron density, making the benzene ring less electron-rich, and hence less susceptible to electrophilic attack. This effect is seen with groups like -NO2, -CN, -COOH etc. In contrast, electropositive substituents like alkyl groups donate electron density, making the benzene ring more susceptible to electrophilic attack. 2. Resonance Effect:Some substituents can donate or withdraw electron density via bonds. Groups capable of donating electrons through resonance, for example -OH, -OR, -NH2, etc., enhance the electron density in the benzene ring, making it more susceptible to electrophilic attacks. On the other hand, groups that can withdraw electron density via resonance (like -COOH, -NO2, -CHO, -CF3, etc.) reduce the electron density of the benzene ring, making it less susceptible to electrophilic attack. These two effects also control the Directing Effects of substituents. Electron-donating groups (EDGs) direct incoming electrophiles to the ortho- and para- positions due to enhanced electron density at these locations. Electron-withdrawing groups (EWGs), on the other hand, direct incoming electrophiles to the meta- position as they reduce the electron density at the ortho- and para- positions. There are two main effects of substituents. The substituent will affect the rate of reaction (aka reactivity) of the ring, and it will also affect the position of attack (called directing effects) on the ring by the incoming electrophile. Thus we need to answer the following questions:Does the substituent activate or deactivate the aromatic ring?Where will the incoming group go?Reactivity: Activation and deactivationBecause benzene acts as a nucleophile in electrophilic aromatic substitution, substituents that make the benzene more electron-rich can accelerate the reaction. Substituents that make the benzene moor electron-poor can retard the reaction. In the mid-twentieth century, physical organic chemists including Christopher Ingold conducted a number of kinetic studies on electrophilic aromatic substitution reactions. In table 1, you can see that some substituents confer a rate of reaction that is much higher than that of benzene (R = H). Phenol, C6H5OH, undergoes nitration a thousand times faster than benzene does. Nitrobenzene, C6H5NO2, undergoes the reaction millions of times more slowly.Table : Rate of nitration in benzene derivativesR in C6H5RRelative rateOH1,000CH325H1CH2Cl0.71I0.18F0.15Cl0.033Br0.030CO2Et0.0037NO26 x 10-8NMe3+1.2 x 10-8These observations are consistent with the role of the aromatic as a nucleophile in this reaction. Substituents that draw electron density away from the aromatic ring slow the reaction down. These groups are called deactivating groups in this reaction. Substituents that readily donate electron density to the ring, or that effectively stabilize the cationic intermediate, promote the reaction. These groups are called activating groups in this reaction.The roles of these groups are related to their electronic interactions with the electrons in the ring. Some groups (e.g., H2N-, HO-, RO-) have lone pairs and act as -donors, providing additional electron density to the benzene ring via resonance. This is often called a +R (for resonance) effect, and this activates the ring towards EAS.Other groups contain an electronegative atom attached via a-bond (e.g., C=O) that makes the group electron-withdrawing. These groups act as -acceptors, drawing electron density away from the ring via resonance. This may be called a R effect, and this deactivates the ring towards EAS.Some groups act only through the sigma bonds via the inductive effect (I), which is based purely on electronegativity without any resonance. These effects are usually less than resonance effects, but they are still significant. Since an sp3 carbon is less electronegative than an sp2 carbon, a methyl or similar sp3 alkyl (R) group can act as a -donor, putting some extra electron density into the ring, giving a +I effect (activating). Groups based on more electronegative atoms (O, F, Cl) may be -acceptors, drawing electron density away from the ring via a simple inductive effect which arises from the electronegativity of the substituent. This deactivates the ring, and is often referred to as a I effect.In some cases (e.g., OH, Cl), there may be multiple effects, and the overall influence of the substituents is determined by the balance of the R and I effects. One effect may be stronger in one case than the other, so it wins out in one case and loses in another. The substituent effects on reactivity have been studied experimentally, and the following chart summarizes the reactivity order, with strongest activators (in green) on the left and strongest deactivators (in red) on the right. Thus amino groups are the strongest activators listed, and nitro groups are the strongest deactivators.Directing EffectsIn addition to exerting an effect on the speed of reaction, substituents on the benzene ring also influence the regiochemistry of the reaction. That is, they control where the new substituent appears in the product.Remember, there are three different positions on the benzene ring where a new substituent can attach, relative to the original substituent. Substitution could actually occur on five positions around the ring, but two pairs are related by symmetry. Isomerism in disubstituted benzenes can be described by numbering the substituents (1,2- etc) or by the relationships ortho-, meta and para-. There are two positions ortho to the initial substituent and two positions meta to it. Ingold and colleagues investigated the question of regiochemistry in nitration. They reported the following observations:Table : Substitution patterns during nitration of benzene derivativesR in C6H5R% o product% m product% p productCH356341Cl30070Br38062OH10090CHO19729CO2Et28683CN17812NO26940In looking at the table, you might see that there are two groups of substituents. One group reacts to make mixtures of ortho and para products. There may be different ratios of ortho to para and there may be small amounts of meta-, but dont get bogged down in the details. Focus on the bigger picture. Some groups are ortho/para directors.The other group reacts to make mostly meta-substituted products. Here may be small amounts of ortho and para products, but these groups are best described as meta-directors. These regiochemical effects are very closely related to the activating and directing effects we have already seen. If we want to understand these data, we need to think about things like -donation, -acceptance, inductive effects and cation stability. As seen above, the reactivity of aromatic pi bonds in EAS reactions is very sensitive to the presence of electron-donating groups (EDGs) and electron-withdrawing groups (EWGs) on the aromatic ring. This is due to the carbocation nature of the intermediate, which is stabilized by electron-donating groups and destabilized by electron-withdrawing groups.Alkyl groups are weakly ring-activating groups, as their electron-donating ability stems only from weak inductive effects. Substituents with heteroatoms connected to the aromatic ring are significantly more ring-activating than alkyl groups, because resonance electron-donating effects are possible. Amines, for example, are very powerful ring-activating substituents, due to the ability of the lone pair on the nitrogen to stabilize the carbocation intermediate through resonance:Other ring-activating groups are shown below (in these figures, the R group can be a hydrogen). All of these groups are able, in varying degrees, to stabilize the carbocation intermediate in an electrophilic aromatic substitution reaction. Notice that plain old alkyl groups are also (weakly) ring-activating.Substituent groups that are ring-activating due to resonance effects also tend to exert a strong regiochemical influence on further substitution reactions. Specifically, substitution tends to occur in the ortho and para positions relative to the existing group. This is known as the ortho-para directing effect. The effect can be explained by drawing resonance contributors for the carbocation intermediate of the SEAr reaction: the positive charge is in position to be delocalized by resonance only in reactions leading to ortho or para substitution.The carbocation which leads to the meta-substituted product, however, cannot be stabilized by resonance with the ring-activating group:As an example, the Friedel-Crafts alkylation of methoxy benzene would be expected to produce a mixture of the ortho and para substituted products, but no meta-substituted product.In addition, the para product would be expected to be preferred over the ortho product, due to steric considerations.Electron-withdrawing substituents on an aromatic ring are ring-deactivating, making it harder for further substitution reactions to occur. These are mostly carbonyl-containing groups, as well as alkyl halides.When substitution does occur on an aromatic ring with deactivating group already attached, it tends to occur specifically at the meta position deactivating groups are generally meta-directing. The exception to this rule is the halogens, which are ring-deactivating but ortho-para directing (see next section).Halogens: A Special CaseHalogens are very electronegative. This means that inductively they are electron-withdrawing. However, because of their ability to donate a lone pair of electrons in resonance forms, they are ortho/para directing. Resonance effects win out in directing ortho-para, but the inductive effect is stronger in determining the reactivity: Because (on balance) they are electron withdrawing, halogens are very weak deactivators.Table 1: Common SubstituentsOrthe- and Para-DirectingMeta DirectingStrong ActivatingModerately ActivatingWeakly ActivatingWeakly DeactivatingModerately DeactivatingStrongly Deactivating-NH2 -NHR -OH -OCH3-NHCOR -OCOR-CH3 -phenyl-F -Cl -Br -I-COH -COCH3 -COOCH3 -SO3H-NO2 -CF3 -CCl3Bohm, S., and O. Exner. Interaction of two functional groups through the benzene ring: Theory and Experiment. Journal of Computational Chemistry (2008) (p. 1) , William H., Foote, Christopher S., Iverson, Brent L. Organic Chemisty. 4th ed.Belmont, CA: Thomson Learning Inc./ Brooks/Cole, 2005. (pp. 868-872)Schore, Neil E., Vollhardt, Peter C. Organic Chemistry, Structure and Function. 5th ed. NewYork: W.H. Freeman &Company, 2007. (pp. 724-728)Laali, Kenneth K., and Volkar J. Gettwert. Electrophilic Nitration of Aromatics in Ionic Liquid Solvents.The Journal ofOrganic Chemistry66 (Dec. 2000): 35-40. American Chemical Society.Malhotra, Ripudaman, Subhash C. Narang, and George A. Olah.Nitration: Methods and Mechanisms. New York: VCH Publishers, Inc., 1989.Sauls, Thomas W., Walter H. Rueggeberg, and Samuel L. Norwood. On the Mechanism of Sulfonation of the Aromatic Nucleus and Sulfone Formation.The Journal of Organic Chemistry66 (1955): 455-465. American Chemical Society.Vollhardt, Peter.Organic Chemistry : Structure and Function. 5th ed. Boston: W. H. Freeman & Company, 2007. We have had thorough discussions about EAS reactions on the benzene rings in Chapter 4. EAS reaction also takes place on substituted benzenes, and the substituent already present on the benzene ring affects the position in which further EAS occurs, and the rate of the reaction. Fig 5.1a What happens when the 2nd group is introduced?When substituted benzene undergoes EAS reactions, the substitute that is on the benzene ring has effects on two aspects, which will be discussed here and in section 5.2.Activating or deactivating effect: change the reactivity of the ring toward EAS;Directing effect: affects the orientation of the incoming group on the ring.The activating group is the substituent that makes the ring more reactive than benzene towards EAS, i.e., it reacts faster.Electron-donating groups make the benzene ring more electron-rich and more reactive towards the electrophile, so electron-donating groups are activating groups.Fig. 5.1b Common electron-donating (activating) groupsThe deactivating group is the substituent that makes the ring less reactive than benzene towards EAS, i.e., reacts more slowly.Electron-withdrawing groups make the benzene ring electron-poor, and less reactive towards the electrophile, so electron-withdrawing groups are deactivating groups.Fig. 5.1c Common electron-withdrawing (deactivating) groupsHow to Identify a Group Is Electron-Donating or Electron-Withdrawing Group?A quick hint to tell if a group is electron-donating or electron-withdrawing is to check whether the atom that connects directly to the benzene ring has lone-pair electrons. The group that has lone-pair electrons on the atom attached directly to the benzene ring is an electron-donating group.The group that does not have lone-pair electrons on the atom attached directly to the benzene ring is an electron-withdrawing group. The above trends dont apply to alkyl group (electron-donating) and halogens (electron-withdrawing).The above trend provides a quick hint for us to memorize the properties of groups, however, understanding the actual reasoning behind them is more important. Understanding the Electronic Property of a Group Alkyl groups are electron-donating because of the hyperconjugation effect, the effect we have learned in section 7.4 in Book I. The orbitals of the sigma bonds in the alkyl group overlap partially with the p orbital of the sp2 carbon in the benzene ring, so the electron density of the ring increases. The hyperconjugation effect is a rather weak effect to donate electrons, so alkyl groups are weak electron-donating groups.Groups with heteroatom that contain lone-pair electronsFor groups with heteroatoms, most commonly N and O, there are two effects that work the opposite way. The inductive effect of the electronegative atom makes the group electron-withdrawing, while the resonance effect from the lone-pair electrons of the atom makes the group electron-donating. For most groups, the contribution through the resonance effect is stronger than the inductive effect, so most such groups (except halogens) are electron-donating. This is demonstrated in Fib. 5.1d with the OH group as an example. Fig. 5.1d OH group is electron-donatingHalogensDetailed discussions on halogens will be given in section 5.2.Groups with multiple bondsFor substituents with multiple bonds, for example, -CN, -NO2, SO3H, and -C=O, resonance structures are available because of the multiple bonds. Such resonance effect works in the way of pulling electron density away from the benzene ring, therefore the groups with multiple bonds are electron-withdrawing. The example of the carbonyl group is shown in Fig. 5.1e. Fig. 5.1e Carbonyl group is electron-withdrawingGroups with Heteroatom that does not contain lone-pair electronsInductive effect (because of the high electronegativity of the heteroatom, and positive charge for some groups) is the only effect involved for such groups since there are no lone-pair electrons available. Such groups are strongly electron-withdrawing groups, as the example ofNH3+in Fig. 5.1f. Fig. 5.1f NH3+ group is electron-withdrawing

Does benzene ring show inductive effect. Benzene ring shows which inductive effect. Benzene ring angle.

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