Click Here

Side groups on a benzene ring can affect the position on the ring of where substitution reactions will occurThe side groups on a benzene ring can either beelectron-withdrawingorelectron-donating groupsElectron-donating groups, such as -CH3, -OH and -NH2, donateelectron densityintothe system of the benzene ring making itmore reactiveThese groupsactivateattack by electrophiles anddirectthe incoming electrophile to attack the 2 and/or 4 positionsFor example, the methyl group in methylbenzene is an electron-donating groupUpon bromination of methylbenzene, the bromine electrophile will be directed to the 2 and/or 4 positionThe products are 2-bromomethylbenzene and 4-bromomethylbenzeneNitration of methylbenzene will also occur on the 2 and 4 positionNitration of methylbenzeneElectron-withdrawing substituents, such as -NO2, removeelectron densityfromthe system in the benzene ring making itlessreactiveThese groupsdeactivateattack by electrophiles anddirectthe incoming electrophile to attack the 3 positionFor example, the nitro group in nitrobenzene is an electron-withdrawing groupUpon bromination of nitrobenzene, the bromine electrophile will be directed to the 3 positionThe product is 3-bromonitrobenzeneWe can use the directing effect of the substitute groups when planning an organic synthesisDid this page help you?In electrophilic aromatic substitution reactions, existing substituent groups on the aromatic ring influence the overall reaction rate or have a directing effect on positional isomer of the products that are formed. An electron donating group (EDG) or electron releasing group (ERG, Z in structural formulas) is an atom or functional group that donates some of its electron density into a conjugated system via resonance (mesomerism) or inductive effects (or induction)called +M or +I effects, respectivelythus making the system more nucleophilic.[1][2] As a result of these electronic effects, an aromatic ring to which such a group is attached is more likely to participate in electrophilic substitution reaction. EDGs are therefore often known as activating groups, though steric effects can interfere with the reaction. An electron withdrawing group (EWG) will have the opposite effect on the nucleophilicity of the ring. The EWG removes electron density from a system, making it less reactive in this type of reaction,[2][3] and therefore called deactivating groups.EDGs and EWGs also determine the positions (relative to themselves) on the aromatic ring where substitution reactions are most likely to take place. Electron donating groups are generally ortho/para directors for electrophilic aromatic substitutions, while electron withdrawing groups (except the halogens) are generally meta directors. The selectivities observed with EDGs and EWGs were first described in 1892 and have been known as the Crum BrownGibson rule.[4]Diagram showing the ortho, meta and para positions relative to a substituent X on a benzene ringElectron donating groups are typically divided into three levels of activating ability (The "extreme" category can be seen as "strong".) Electron withdrawing groups are assigned to similar groupings. Activating substituents favour electrophilic substitution about the ortho and para positions. Weakly deactivating groups direct electrophiles to attack the benzene molecule at the ortho- and para- positions, while strongly and moderately deactivating groups direct attacks to the meta- position.[5] This is not a case of favoring the meta- position like para- and ortho- directing functional groups, but rather disfavouring the ortho- and para-positions more than they disfavour the meta- position.The activating groups are mostly resonance donors (+M). Although many of these groups are also inductively withdrawing (I), which is a deactivating effect, the resonance (or mesomeric) effect is almost always stronger, with the exception of Cl, Br, and I.Magnitude ofactivationSubstituent Name (in approximate orderof activating strength)StructureType of electronic effectDirecting effectExtremeoxido group-O+I, +M, metal-hydrogen exchangeortho, paraStrong(substituted) amino groups-NH2, -NHR, -NR2I, +Mhydroxy and alkoxy groups-OH,-ORModerateacylamido groups-NHCORacyloxy groups-OCOR(di)alkylphosphino, alkylthio, and sulfhydryl groups[6]-PR2,-SR,-SH+M (weak)Weakphenyl (or aryl) group-C6H5I, +M;[7][8] though other interactions may be involved as well[9]vinyl group-CH=CH2alkyl groups(e.g. -CH3, -C2H5)-Rcarboxylate group[10]-CO2+IIn general, the resonance effect of elements in the third period and beyond is relatively weak. This is mainly because of the relatively poor orbital overlap of the substituent's 3p (or higher) orbital with the 2p orbital of the carbon.Due to a stronger resonance effect and inductive effect than the heavier halogens, fluorine is anomalous. The partial rate factor of electrophilic aromatic substitution on fluorobenzene is often larger than one at the para position, making it an activating group.[11] Conversely, it is moderately deactivated at the ortho and meta positions, due to the proximity of these positions to the electronegative fluoro substituent.While all deactivating groups are inductively withdrawing (I), most of them are also withdrawing through resonance (M) as well. Halogen substituents are an exception: they are resonance donors (+M), they are meta directing groups.Halides are ortho, para directing groups but unlike most ortho, para directors, halides mildly deactivate the arene. This unusual behavior can be explained by two properties:Since the halogens are very electronegative they cause inductive withdrawal (withdrawal of electrons from the carbon atom of benzene).Since the halogens have non-bonding electrons they can donate electron density through pi bonding (resonance donation).The inductive and resonance properties compete with each other but the resonance effect dominates for purposes of directing the sites of reactivity. For nitration, for example, fluorine directs strongly to the para position because the ortho position is inductively deactivated (86% para, 13% ortho, 0.6% meta). On the other hand, iodine directs to ortho and para positions comparably (54% para and 45% ortho, 1.3% meta).[12]Magnitude ofdeactivationSubstituent Name (in approximate orderof deactivating strength)StructureType of electronic effectDirecting effectStrongtrifluoromethylsulfonyl group[13]-SO2CF3I, Mmeta(substituted) ammonium groups[14]-NR3+ (R = alkyl or H)Initro group-NO2I, Msulfonic acids and sulfonyl groups-SO3H,-SO2Rcyano group-CNtrihalomethyl groups (strongest for -CF3 group)-CX3 (X = F, Cl, Br, I)IModeratehaloformyl groups-COX(X = Cl, Br, I)I, Mformyl and acyl groups-CHO,-CORcarboxyl and alkoxycarbonyl groups-CO2H,-CO2R(substituted) aminocarbonyl groups-CONH2,-CONHR,-CONR2Weakfluoro group (ortho, meta positions)-FI, +M (ortho)ortho, paranitroso group-N=OI, +M (dimer) orM (monomer)halo groups-F(para), -Cl, -Br, -I[15]I, +M (weak)Although the full electronic structure of an arene can only be computed using quantum mechanics, the directing effects of different substituents can often be guessed through analysis of resonance diagrams. Specifically, any formal negative or positive charges in minor resonance contributors (ones in accord with the natural polarization but not necessarily obeying the octet rule) reflect locations having a larger or smaller density of charge in the molecular orbital for a bond most likely to break. A carbon atom with a larger coefficient will be preferentially attacked, due to more favorable orbital overlap with the electrophile.[16] The perturbation of a conjugating electron-withdrawing or electron-donating group causes the electron distribution on a benzene ring to resemble (very slightly!) an electron-deficient benzyl cation or electron-excessive benzyl anion, respectively. The latter species admit tractable quantum calculation using Hckel theory: the cation withdraws electron density at the ortho and para positions, favoring meta attack, whereas the anion releases electron density into the same positions, activating them for attack.[17] This is precisely the result that the drawing of resonance structures would predict. For example, aniline has resonance structures with negative charges around the ring system:The amino group can donate electron density through resonance.Attack occurs at ortho and para positions, because the (partial) formal negative charges at these positions indicate a local electron excess. On the other hand, the nitrobenzene resonance structures have positive charges around the ring system:The nitro group can withdraw electron density through resonance.Attack occurs at the meta position, since the (partial) formal positive charges at the ortho and para positions indicate electron deficiency at these positions. Another common argument, which makes identical predictions, considers the stabilization or destabilization by substituents of the Wheland intermediates resulting from electrophilic attack at the ortho/para or meta positions. The Hammond postulate then dictates that the relative transition state energies will reflect the differences in the ground state energies of the Wheland intermediates.[14][18] Because of the full or partial positive charge on the element directly attached to the ring for each of these groups, they all have a moderate to strong electron-withdrawing inductive effect (known as the -I effect). They also exhibit electron-withdrawing resonance effects, (known as the -M effect):The -M effect of nitrobenzeneThus, these groups make the aromatic ring very electron-poor (+) relative to benzene and, therefore, they strongly deactivate the ring (i.e. reactions proceed much slower in rings bearing these groups compared to those reactions in benzene.)Due to the electronegativity difference between carbon and oxygen / nitrogen, there will be a slight electron withdrawing effect through inductive effect (known as the I effect). However, the other effect called resonance add electron density back to the ring (known as the +M effect) and dominate over that of inductive effect. Hence the result is that they are EDGs and ortho/para directors.Phenol is an ortho/para director, but in a presence of base, the reaction is more rapid. It is due to the higher reactivity of phenolate anion. The negative oxygen was 'forced' to give electron density to the carbons (because it has a negative charge, it has an extra +I effect). Even when cold and with neutral (and relatively weak) electrophiles, the reaction still occurs rapidly. The phenolate has a negatively charged oxygen. That is very unstable that the oxygen has a stronger +M effect (compared to phenol) and an extra +I effect.Alkyl groups are electron donating groups. The carbon on that is sp3 hybridized and less electronegative than those that are sp2 hybridized. They have overlap on the carbonhydrogen bonds (or carboncarbon bonds in compounds like tert-butylbenzene) with the ring p orbital. Hence they are more reactive than benzene and are ortho/para directors.Inductively, the negatively charged carboxylate ion moderately repels the electrons in the bond attaching it to the ring. Thus, there is a weak electron-donating +I effect. There is an almost zero -M effect since the electron-withdrawing resonance capacity of the carbonyl group is effectively removed by the delocalisation of the negative charge of the anion on the oxygen. Thus overall the carboxylate group (unlike the carboxyl group) has an activating influence.[10]The negative charge was spread through both oxygens.These groups have a strong electron-withdrawing inductive effect (-I) either by virtue of their positive charge or because of the powerfully electronegativity of the halogens. There is no resonance effect because there are no orbitals or electron pairs which can overlap with those of the ring. The inductive effect acts like that for the carboxylate anion but in the opposite direction (i.e. it produces small positive charges on the ortho and para positions but not on the meta position and it destabilises the Wheland intermediate.) Hence these groups are deactivating and meta directing:They have formal or partial positive charges, which deactivates the ring.Fluorine is something of an anomaly in this circumstance. Above, it is described as a weak electron withdrawing group but this is only partly true. It is correct that fluorine has a -I effect, which results in electrons being withdrawn inductively. However, another effect that plays a role is the +M effect which adds electron density back into the benzene ring (thus having the opposite effect of the -I effect but by a different mechanism). This is called the mesomeric effect (hence +M) and the result for fluorine is that the +M effect approximately cancels out the -I effect. The effect of this for fluorobenzene at the para position is reactivity that is comparable to (or even higher than) that of benzene. Because inductive effects depends strongly on proximity, the meta and ortho positions of fluorobenzene are considerably less reactive than benzene. Thus, electrophilic aromatic substitution on fluorobenzene is strongly para selective.This -I and +M effect is true for all halides - there is some electron withdrawing and donating character of each. To understand why the reactivity changes occur, we need to consider the orbital overlaps occurring in each. The valence orbitals of fluorine are the 2p orbitals which is the same for carbon - hence they will be very close in energy and orbital overlap will be favourable. Chlorine has 3p valence orbitals, hence the orbital energies will be further apart and the geometry less favourable, leading to less donation the stabilize the carbocationic intermediate, hence chlorobenzene is less reactive than fluorobenzene. However, bromobenzene and iodobenzene are about the same or a little more reactive than chlorobenzene, because although the resonance donation is even worse, the inductive effect is also weakened due to their lower electronegativities. Thus the overall order of reactivity is U-shaped, with a minimum at chlorobenzene/bromobenzene (relative nitration rates compared to benzene = 1 in parentheses): PhF (0.18) > PhCl (0.064) ~ PhBr (0.060) < PhI (0.12).[12] But still, all halobenzenes reacts slower than benzene itself.Notice that iodobenzene is still less reactive than fluorobenzene because polarizability plays a role as well. This can also explain why phosphorus in phosphanes can't donate electron density to carbon through induction (i.e. +I effect) although it is less electronegative than carbon (2.19 vs 2.55, see electronegativity list) and why hydroiodic acid (pKa = -10) being much more acidic than hydroflueric acid (pKa = 3). (That's 1013 times more acidic than hydroflueric acid)Due to the lone pair of electrons, halogen groups are available for donating electrons. Hence they are therefore ortho / para directors.Due to the electronegativity difference between carbon and nitrogen, the nitroso group has a relatively strong -I effect, but not as strong as the nitro group. (Positively charged nitrogen atoms on alkylammonium cations and on nitro groups have a much stronger -I effect)The nitroso group has both a +M and -M effect, but the -M effect is more favorable.Nitrogen has a lone pair of electrons. However, the lone pair of its monomer form is unfavourable to donate through resonance. Only the dimer form is available for +M effect. However, the dimer form is less stable in a solution. Therefore, the nitroso group is less available to donate electrons.Oppositely, withdrawing electron density is more favourable: (see the picture on the right).The -M effect of the nitroso groupAs a result, the nitroso group is a deactivator. However, it has available to donate electron density to the benzene ring during the Wheland intermediate, making it still being an ortho / para director.There are 2 ortho positions, 2 meta positions and 1 para position on benzene when a group is attached to it. When a group is an ortho / para director with ortho and para positions reacting with the same partial rate factor, we would expect twice as much ortho product as para product due to this statistical effect. However, the partial rate factors at the ortho and para positions are not generally equal. In the case of a fluorine substituent, for instance, the ortho partial rate factor is much smaller than the para, due to a stronger inductive withdrawal effect at the ortho position. Aside from these effects, there is often also a steric effect, due to increased steric hindrance at the ortho position but not the para position, leading to a larger amount of the para product.The effect is illustrated for electrophilic aromatic substitutions with alkyl substituents of differing steric demand for electrophilic aromatic nitration.[19]Substratetoluene [-CH3]ethylbenzene[-CH2CH3]cumene[-CH(CH3)2]tert-butylbenzene[-C(CH3)3]ortho product58453016meta product56811para product37596273ortho/para ratio1.570.760.480.22The methyl group in toluene is small and will lead the ortho product being the major product. On the other hand, the t-butyl group is very bulky (there are 3 methyl groups attached to a single carbon) and will lead the para product as the major one. Even with toluene, the product is not 2:1 but having a slightly less ortho product.When two substituents are already present on the ring, the third substituent's new location is relatively predictable. If the existing substituents reinforce or the molecule is highly symmetric, there may be no ambiguity. Otherwise:[20]The most-activating substituent usually controls over the less-activating one. Substituents add ortho to the amine in diethyl-(para-methyl)aniline and ortho to the amide in para-cyanobenzamideIn particular, ortho/para directors control over meta ones. Substituents add ortho to the amine in diethyl-(meta-trifluoromethyl)aniline and ortho to the fluoride in para-fluorobenzaldehydeWhen multiple substituents are comparably activating, steric hindrance dominates regioselectivity. Substituents add ortho to the methyl group in para-(tert-butyl)tolueneIn particular, the position between two substituents, each meta to the other, reacts last. New substituents add para to either substituent in meta-chlorotolueneElectrophilic aromatic substitution^ "Electron withdrawing group". Illustrated Glossary of Organic Chemistry. UCLA Department of Chemistry. Retrieved 16 November 2012.^ a b Hunt, Ian. "Substituent Effects". University of Calgary Department of Chemistry. Retrieved 16 November 2012.^ "Electron donating group". Illustrated Glossary of Organic Chemistry. UCLA Department of Chemistry. Retrieved 16 November 2012.^ Brown, A. Crum; Gibson, John (1892). "XXX.A rule for determining whether a given benzene mono-derivative shall give a meta-di-derivative or a mixture of ortho- and para-di-derivatives". J. Chem. Soc. 61: 367369. doi:10.1039/ct8926100367.^ "Substituent Effects". www.mhhe.com. Retrieved 2 April 2015.^ James, Ashenhurst (29 Jan 2018). "Ortho-, Para- and Meta- Directors in Electrophilic Aromatic Substitution". Master Organic Chemistry.^ Norman, Richard O. C.; Coxon, James M. (1993). Principles of Organic Synthesis (3rded.). CRC Press. pp.353354. ISBN9780748761623.^ Salvatella, Luis (October 2017). "The alkyl group is a I + R substituent". Educacin Qumica. 28 (4): 232237. doi:10.1016/j.eq.2017.06.004. hdl:10261/184773. S2CID46641895.^ Hoggett, J. G.; Moodie, R. B.; Penton, J. R.; Schofield, K. (1971). Nitration and aromatic reactivity. London: Cambridge University Press. p.200. ISBN0521080290. OCLC205846.^ a b Smith, Ed (12 February 2018). "LECTURE 2" (PDF). Handouts for Organic Chemistry Lectures given at Imperial College London, Chemistry. p.3.^ Rosenthal, Joel; Schuster, David I. (2003-06-01). "The Anomalous Reactivity of Fluorobenzene in Electrophilic Aromatic Substitution and Related Phenomena". Journal of Chemical Education. 80 (6): 679690. Bibcode:2003JChEd..80..679R. doi:10.1021/ed080p679. ISSN0021-9584.^ a b Jonathan., Clayden (2012). Organic chemistry. Greeves, Nick., Warren, Stuart G. (2nded.). Oxford: Oxford University Press. ISBN9780199270293. OCLC761379371.^ Andrew, D. Abell; Brent, K. Nabbs; Alan, R. Battersby (12 February 1998). "Synthesis and Properties of Ring-Deactivated Deuterated (Hydroxymethyl)pyrroles". Journal of the American Chemical Society. 120 (8). doi:10.1021/ja973656+.^ a b C., Vollhardt, K. Peter (2018-01-29). Organic chemistry: structure and function. Schore, Neil Eric, 1948- (8eed.). New York. ISBN9781319079451. OCLC1007924903.{{cite book}}: CS1 maint: location missing publisher (link) CS1 maint: multiple names: authors list (link)^ "Substitution Reactions of Benzene Derivatives". Chemistry LibreTexts. 2013-10-02. Retrieved 2021-09-18.^ E., Lewis, David (2016). Advanced organic chemistry. New York. ISBN9780199758975. OCLC933277973.{{cite book}}: CS1 maint: location missing publisher (link) CS1 maint: multiple names: authors list (link)^ Fleming, Ian (1976). Frontier orbitals and organic chemical reactions. London: Wiley. ISBN0471018201. OCLC2048204.^ Carey, Francis A. (2013-01-07). Organic chemistry. Giuliano, Robert M., 1954- (Ninthed.). New York, NY. ISBN9780073402741. OCLC822971422.{{cite book}}: CS1 maint: location missing publisher (link)^ Peter, Sykes (1979). "2" (PDF). Some Organic Reaction Pathways. p.32. ISBN0851869998.^ "12.15. Multiple Multiple Substituent Substituent Effects" (PDF). p.7.Retrieved from " this article, we look at how electron-donating and electron withdrawing substituents direct the substitution on a benzene ring. In the synthesis of disubstituted benzenes, the cation resulting from ortho-para addition with electron donors will be more stable than the meta-derived cation. For example, if you brominate anisole, as shown in the first figure, you get substitution of the bromine at the ortho and para positions, but not at the meta position. This is because methoxy groups (OCH3) are pi electron donors, so they direct all incoming electrophile traffic into the ortho and para positions. Bromine addition to anisole You can see why the methoxy group directs to the ortho and para positions by looking at the intermediate carbocation for both the para substitution and the meta addition, shown in the next figure. This figure shows the relative stabilities of intermediate carbocations resulting from meta and para substitution of anisole. With para substitution (and with ortho substitution), a much more stable intermediate carbocation is formed compared to the cation that's formed when the substituent adds in the meta position. The intermediate carbocation that results from para substitution has four resonance structures, as shown in the second figure, with one of these resonance structures being particularly good because all valence octets on all atoms are filled. (This good resonance structure is boxed in the figure.)The carbocation resulting from meta substitution, on the other hand, has only three resonance structures, none of which have all atoms with filled valence octets. Recall the general rule that stability increases as the number of resonance structures increases. Thus, with electron donors on the aromatic ring, ortho-para products are selectively formed. Electron-withdrawing substituents When you synthesize disubstituted benzenes, and the first added group is an electron-withdrawing substituent, this group usually directs incoming electrophiles to the meta position (shown in the first figure). The ortho, meta, and para positions For example, take the bromination reaction of nitrobenzene, shown in the next figure. Nitro groups are electron-withdrawing groups, so bromine adds to the meta position. The bromine substitution of nitrobenzene To see why a meta product is formed instead of ortho-para products, compare the intermediate cation formed as a result of para bromine addition to the cation generated from meta addition (shown here). This figure shows the relative stabilities of intermediate carbocations resulting from para and meta substitution to nitrobenzene The intermediate carbocation resulting from para substitution (or ortho substitution) has three resonance structures, but one of them is a particularly bad resonance structure because the structure has two adjacent positive charges (and like charges repel). Therefore, this bad resonance structure doesn't contribute much to the overall resonance hybrid. The cation resulting from meta substitution also has three resonance structures, but none of them is bad.So, for benzenes substituted with electron-withdrawing groups, the cation resulting from meta substitution is more stable than the cation resulting from either ortho or para substitution. The main point to remember here is that electron-donating groups direct substitution to the ortho and para positions, while pi electron-withdrawing groups direct substitution to the meta position. To clarify what is meant by electron-donating and electron-withdrawing substituents: Any substituent whose first atom (the one that's attached to the benzene ring) has a lone pair will be a pi electron donor to the phenyl ring, as shown in the resonance structure in the next figure. Pi electron donors to the phenyl ring Note that the resonance structures show that substituents that are pi donors add electron density to the ortho and para positions of the ring. So, pi donors activate the benzene ring toward electrophilic attack (attack by incoming electrophiles) at the ortho and para positions. Adding electron density to the benzene ring makes the ring more nucleophilic (that is, more nucleus loving) and activates the ring. Therefore, pi donors are considered ring activators.The only exceptions are the halogens, which are not terribly good pi donors. They deactivate the ring as a result of being highly electronegative groups, pulling electrons away from the benzene ring toward themselves, making the ring less nucleophilic. But even though halogens are ring deactivators, they're still ortho-para directors.Pi-withdrawing groups (such as NO2 groups, carbonyl groups, CN, and so on) pull electrons away from the ring and deactivate it, making the ring less nucleophilic. Pi electron-withdrawers are thus ring deactivators. A deactivator means that the reaction of benzenes substituted with these substituents will be slower than the reaction of unsubstituted benzene. Pi electron-withdrawing substituents are meta directors. The table outlines the nature of different substituents. The Nature of Aromatic Substituents Ortho-Para Directing Meta Directing Strongly activating Weakly activating Deactivating Deactivating OH Alkyl Halogens (F, Cl, Br, I) NO2 OCH3 Phenyl COR (COOH, COOR, CHO, and so on) NH2 CN NR2 SO3H 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 has important effects on further EAS reaction. When substituted benzene undergoes EAS reactions, the substitute that is on the benzene ring has effects on two aspects, that 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., 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. 5.1a 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. 5.1b 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 reasonings 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. 5.1c with the OH group as an example. Fig. 5.1c 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. 5.1d. Fig. 5.1d 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. 5.1e. Fig. 5.1e NH3+ group is electron-withdrawing Electron-donating groups on benzene, such as alkyl groups, donate electron density to the benzene ring, making it more electron-rich and increasing its reactivity towards electrophiles. In contrast, electron-withdrawing groups on benzene, such as nitro or carbonyl groups, withdraw electron density from the benzene ring, making it more electron-poor and decreasing its reactivity towards electrophiles. Overall, electron-donating groups enhance the nucleophilic nature of benzene, while electron-withdrawing groups enhance its electrophilic nature. Benzene, a six-membered ring of carbon atoms with alternating single and double bonds, is a fundamental building block in organic chemistry. The reactivity of benzene can be greatly influenced by the presence of substituents, known as electron-donating groups and electron-withdrawing groups. These substituents can either donate or withdraw electron density from the benzene ring, affecting its chemical properties. In this article, we will compare the attributes of electron-donating groups and electron-withdrawing groups on benzene.Electron-Donating GroupsElectron-donating groups are substituents that release electron density into the benzene ring through inductive or resonance effects. This results in an increase in electron density around the benzene ring, making it more nucleophilic and less electrophilic. Common examples of electron-donating groups include alkyl groups (such as methyl and ethyl), amino groups, and hydroxyl groups. These groups stabilize positive charges on the benzene ring and promote electrophilic aromatic substitution reactions.One of the key characteristics of electron-donating groups is their ability to activate the benzene ring towards electrophilic attack. This is due to the increased electron density around the ring, which makes it more reactive towards electrophiles. Electron-donating groups also enhance the ortho and para directing effects in electrophilic aromatic substitution reactions, leading to regioselective products.Another important aspect of electron-donating groups is their ability to stabilize carbocation intermediates in electrophilic aromatic substitution reactions. The electron-rich nature of these groups allows them to donate electron density to the positively charged carbon, reducing its overall positive charge and stabilizing the intermediate species.Overall, electron-donating groups enhance the reactivity of benzene towards electrophilic aromatic substitution reactions by increasing its electron density and stabilizing reaction intermediates. These groups are commonly found in organic molecules to facilitate various synthetic transformations.Electron-Withdrawing GroupsElectron-withdrawing groups are substituents that withdraw electron density from the benzene ring through inductive or resonance effects. This results in a decrease in electron density around the benzene ring, making it more electrophilic and less nucleophilic. Common examples of electron-withdrawing groups include nitro groups, carbonyl groups, and halogens. These groups destabilize negative charges on the benzene ring and promote nucleophilic aromatic substitution reactions.One of the key characteristics of electron-withdrawing groups is their ability to deactivate the benzene ring towards electrophilic attack. This is due to the decreased electron density around the ring, which makes it less reactive towards electrophiles. Electron-withdrawing groups also enhance the meta directing effects in electrophilic aromatic substitution reactions, leading to regioselective products.Another important aspect of electron-withdrawing groups is their ability to stabilize carbanion intermediates in nucleophilic aromatic substitution reactions. The electron-deficient nature of these groups allows them to accept electron density from the negatively charged carbon, reducing its overall negative charge and stabilizing the intermediate species.Overall, electron-withdrawing groups decrease the reactivity of benzene towards electrophilic aromatic substitution reactions by decreasing its electron density and destabilizing reaction intermediates. These groups are commonly used in organic synthesis to control the regioselectivity and reaction pathways of aromatic substitution reactions.ComparisonWhen comparing electron-donating and electron-withdrawing groups on benzene, several key differences can be observed. Electron-donating groups increase the electron density around the benzene ring, making it more nucleophilic and reactive towards electrophiles. In contrast, electron-withdrawing groups decrease the electron density around the benzene ring, making it more electrophilic and reactive towards nucleophiles.Electron-donating groups activate the benzene ring towards electrophilic attack, while electron-withdrawing groups deactivate the benzene ring towards electrophilic attack. This difference in reactivity can be attributed to the electron-donating or electron-withdrawing nature of the substituents, which affects the overall electron distribution in the benzene ring.Electron-donating groups stabilize positive charges on the benzene ring and promote electrophilic aromatic substitution reactions, while electron-withdrawing groups destabilize negative charges on the benzene ring and promote nucleophilic aromatic substitution reactions. These contrasting effects highlight the importance of substituent effects in controlling the reactivity of benzene in organic chemistry.Overall, electron-donating and electron-withdrawing groups play crucial roles in modulating the reactivity of benzene in various synthetic transformations. Understanding the impact of these substituents on the benzene ring is essential for designing efficient and selective organic reactions. Comparisons may contain inaccurate information about people, places, or facts. Please report any issues. Share copy and redistribute the material in any medium or format for any purpose, even commercially. Adapt remix, transform, and build upon the material for any purpose, even commercially. The licensor cannot revoke these freedoms as long as you follow the license terms. Attribution You must give appropriate credit , provide a link to the license, and indicate if changes were made . You may do so in any reasonable manner, but not in any way that suggests the licensor endorses you or your use. ShareAlike If you remix, transform, or build upon the material, you must distribute your contributions under the same license as the original. No additional restrictions You may not apply legal terms or technological measures that legally restrict others from doing anything the license permits. You do not have to comply with the license for elements of the material in the public domain or where your use is permitted by an applicable exception or limitation . No warranties are given. The license may not give you all of the permissions necessary for your intended use. For example, other rights such as publicity, privacy, or moral rights may limit how you use the material. Last updated: February 7th, 2025 | Activating and Deactivating Groups in Electrophilic Aromatic SubstitutionThe rate of electrophilic aromatic substitution (EAS) reactions is greatly affected by the groups attached to the ring. The more electron-rich the aromatic ring, the faster the reactionGroups that can donate electron density to the ring make EAS reactions faster.If a substituent increases the rate of reaction relative to H it is calledactivating. If it decreases the rate relative to H it is calleddeactivating.(These rates need to be measured by experiment).Important! Groups like OR and NR2 that seem like they should be deactivating because of their electronegativity are actually activating since they can donate a lone pair of electrons into the ring through resonance.Theres a lot to this post, so heres a quick index:Table of Contents 1. Activating And Deactivating GroupsLast post in this series we introduced electrophilic aromatic substitution. Heres the general case:Why is this a substitution reaction, you ask? Because were forming and breaking a bond on the same carbon. We form CE (where E is a generic term for electrophilic atom) and we break CH.[As for the specific identity of E, we mentioned six key electrophilic aromatic substitution reactions in the last post (bromination, chlorination, nitration, sulfonylation, Friedel-Crafts alkylation and Friedel-Crafts acylation) that well eventually dig into in detail. But not yet.]So if thats the summary ofwhat happens, the next obvious question is:how does it happen? In other words, whats the mechanism? Obligatory pre-mechanism speech:You cant determine the mechanism of a chemical reaction merely through logical deduction from first principles. Sure, you can make guesses even good ones! But the ultimate test of a mechanistic hypothesis is how well it fits with experiment, and that typically involves a lot of lab work. What youre taught in an introductory course is the tippy-topmost layer of snow on the iceberg. We give you the best answer, and in retrospect it looks obvious.What you dont see is all the failure, wrong turns, and false hypotheses that happened along the path towards determining the correct mechanism. However, the mechanisms of these reactions that you will learn about werent obvious to most of their discoverers, who were among the brightest and best chemists of their time. Remember that. 2. Measuring Reaction Rates Can Provide Insight Into The MechanismAs far as determining mechanisms is concerned, one of the best tools we have in our experimental arsenal is the ability to measure reaction rates.By measuring the effect that slight tweaks in the experimental conditions (e.g. structure of reactant, temperature, solvent) have upon the rate, we can gather useful insights about how a reaction operates under the hood.Of the parameters mentioned above, changing the substrate (reactant) is probably the most powerful way to probe a mechanism, because it allows you to tune how electron-rich (nucleophilic) or electron-poor (electrophilic) it is.Let me show you what I mean.Lets arbitrarily pick one electrophilic aromatic substitution reaction: nitration.We know that by adding nitric acid and H2SO4, benzene can undergo nitration to form nitrobenzene (break C-H, form C-NO2)We can even measure the rate of this reaction at a given temperature, concentration, and solvent.Using the exact same experimental conditions we can then measure the rate of the reaction when toluene (methylbenzene, C6H5CH3) is used as the substrate instead of benzene.The nitration of toluene is23 times faster than it is for benzene. [Ref 1]Using the exact same experimental conditions, we can also use trifluoromethylbenzene (C6H5CF3) as the substrate, and measure the reaction rate.The nitration of trifluoromethylbenzene is40,000times slower than it is for benzene (2.5 10-5).Bottom line: if we swap a hydrogen on benzene for a methyl group, the reaction is faster.If we swap a hydrogen for a trifluoromethyl group, the reaction is slower.This pattern turns out to be general for other electrophilic aromatic substitution reactions as well (chlorination, bromination, Friedel-Crafts, and others).3. Activating and Deactivating Groups A DefinitionLets call a group activatingthatincreasesthe rate of an electrophilic aromatic substitution reaction, relative to hydrogen. As we just saw, CH3 is a perfect example of an activating group; when we substitute a hydrogen on benzene for CH3, the rate of nitration is increased.Adeactivating group, on the other hand,decreases the rate of an electrophilic aromatic substitution reaction, relative to hydrogen.The trifluoromethyl group, CF3 ,drastically decreases the rate of nitration when substituted for a hydrogen on benzene.This definition is ultimately based onexperimental reaction rate data. It doesnt tell uswhyeach group accelerates or decreases the rate. Activating and deactivating just refers to the effect of each substituent on the rate, relative to H. OK then. So why might CH3 increase the rate of reaction, and CF3 decrease it?4. Sigma () donors and acceptors (otherwise known as inductive effects)Lets quickly think back to what we know about alkyl groups (such as CH3) and haloalkyl groups (such as CF3), and try to address this question.In CH3, the carbon atom is more electronegative (2.5) than hydrogen (2.2). This means that the carbon attracts a bit more than an equal share of electron-density from the covalent bond with H, resulting in a partial negative charge () on carbon and a partial positive charge (+) on hydrogen. This partial negative charge is then available to be donated to an adjacent atom. Hence, we tend to think of CH3 as an electron-rich species; an electrondonor.In CF3 the electrons are pulled in the opposite direction. Three highly electronegative (4.0) fluorine atoms pull electron density away from the carbon atom (2.5), resulting in a partial positive charge (+) on carbon. Rather than donate electron density, the carbon tends toaccept(pull away) electron density from adjacent atoms (this is the familiar inductive effect) We generally consider CF3 to be an electron-poor species; an electron-acceptor.Since these inductive effects operate solely through single bonds (sigma, or bonds) this behaviour is sometimes called sigma donation (as for CH3) or sigma accepting (for CF3).So it seems like a good hypothesis thatactivating groups areelectron-donating (relative to H), anddeactivating groups are electron-withdrawing (relative to H)5. Pi ( ) Donors and Acceptors (otherwise known as Resonance)Sigma donation and acceptance helps us to understand the effect of alkyl groups on electrophilic aromatic substitution. So what about other functional groups? What effect might, say, a hydroxyl group have on the rate of nitration?Quiz time. Do you think OH would be activating (increase the rate) or deactivating (decrease the rate) for electrophilic aromatic substitution (such as nitration)? Guessing is OK!Based on what we just said, its fully understandable if you said, deactivating. After all, oxygen is highly electronegative (3.4) and through induction, pulls away electron density through the bond. In other words, its a sigma-acceptor.The fact is, however, that OHgreatly accelerates the rate,orders of magnitudemore than CH3 does.In fact I couldnt find good rate data comparing OH to CH3 because in the case of -OH, the reaction is whats called, diffusion controlled. That roughly means, as soon as the reactant comes in contact with the electrophile, a reaction occurs. In other words, the OH group ishighly activating.Clearly, something else must be going on here besides the inductive effect of oxygen!6. Oxygen And Nitrogens Containing Lone Pairs Are Highly Activating When Bonded Directly To The RingAs we saw in our chapter way back on resonance, hydroxyl groups are excellent pi donors. The lone pairs on the oxygen atom can form a pi bond with an adjacent atom containing an available p-orbital.This donation effect (or resonance) must outweigh electron-withdrawal via inductive effects, otherwise wed observe that hydroxyl groups are deactivating.The same is true for nitrogen groups with lone pairs, such as amines and amides (below).[One measure of the importance of pi-donation in the activating nature of amines is seen in their behavior under strongly acidic conditions. If the nitrogen lone pair is either protonated with strong acid or undergoes a substitution reaction to form NR3+ , pi-donation is impossible and the group becomes strongly deactivating (see table below).]7. Halogens (F, Cl, Br, I) Are DeactivatingNot all groups capable of pi donation are activating groups. For example, halogens (F, Cl, Br, I)