Quadrant II – Transcript and Related Materials

Programme: T.Y.B.Sc. (Chemistry)

Subject: Chemistry

Paper Code: CHC 107

Paper Title: Core Course Organic Chemistry

Unit: 01- Aromaticity, Aromatic hydrocarbons and Reactivity

Module Name: Deactivating groups

Module No: 08

Name of the Presenter: Ms. Anuja B. Naik

Notes

Transcript of the video

This is Anuja Naik from Ganpat Parsekar College of Education, Harmal, Pernem Goa and I will be dealing with 'DEACTIVATING GROUPS'. The lecture deals with,

- What are deactivating groups?
- Different deactivating groups.
- Effect of substituents on orientation, and
- Electrophilic aromatic substitution reactions with emphasis on deactivating groups.

So, at the end of the lecture, the student will be able to:

- Define deactivating groups.
- Identify the various deactivating groups.
- Explain the directive effects of deactivating groups, and
- Predict the product of the reaction.

What are deactivating groups?

Deactivating groups are the groups that deactivate a benzene ring towards electrophilic attack. They are also called electron-withdrawing groups and meta directors. Deactivating groups destabilize the carbocation intermediates and increase the energy of the transition state and therefore decrease the rate of the reaction, thereby making electrophilic aromatic substitution reaction slower.

Deactivating groups are categorized into strongly deactivating substituents, moderately deactivating substituents and weakly deactivating substituents.

List of deactivating groups

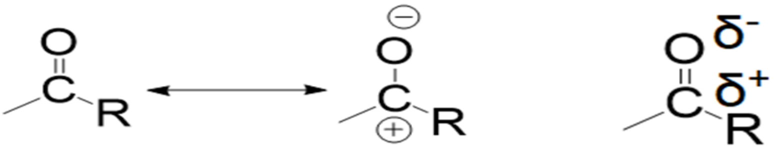
- Strongly deactivating substituents

  -NO_2, -CN, -SO_3H,
- Moderately deactivating substituents

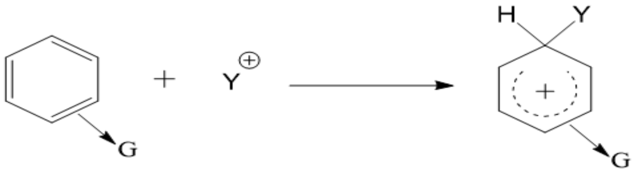
  -CHO, -COR, -COOR, -COOH, -COCl
- Weakly deactivating substituents

  -F, -Cl, -Br, -I

Consider an example of a deactivating group, carbonyl group. In this case, oxygen is more electronegative than carbon. Therefore, Oxygen will pull the electrons towards itself making the carbon electrophilic. So Oxygen will carry a delta negative charge and carbon will carry a delta positive charge.

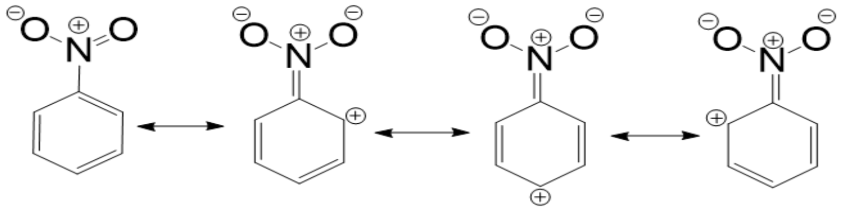


Electrophilic aromatic substitution – Let us consider G as the electron-withdrawing group. The electron-withdrawing group withdraws the electrons and deactivates the ring. Once the electron-withdrawing group withdraws the electrons, it destabilizes carbocation and deactivates the ring. The same is true when chlorine is present as a substituent.

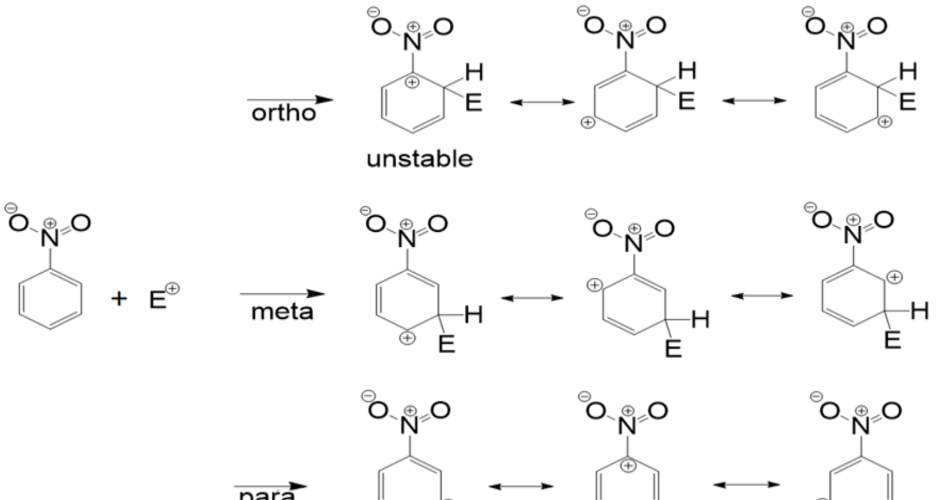


G withdraws electrons: destabilizes carbocation, deactivates the benzene ring

Withdrawal of electrons by Resonance-Various resonating structures for nitrobenzene are drawn, involving the delocalization of electrons.

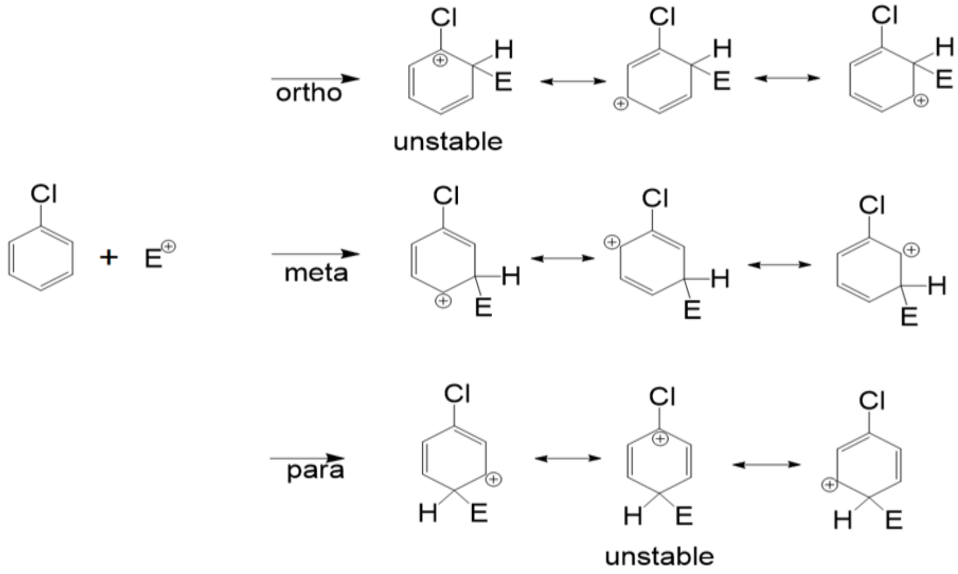


Directive effects of –NO_2 group

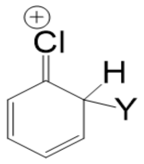


The different resonating structures formed after showing ortho, meta and para attack are shown. In the case of a meta attack, three resonating structures are possible. In the case of ortho and para attack, one unstable structure is formed and does little to help stabilize the ion. The ion for para and ortho attack is virtually a hybrid of only two structures. It is less stable than the ion resulting from attack at meta position which is a hybrid of three structures. Therefore, para and ortho substitution occur more slowly than meta substitution.

Effect of halogen

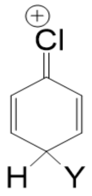


In this case, Chlorine through its inductive effect withdraws electrons most from the carbon to which it is joined. Through its resonance effect chlorine tends to release electrons and thus to stabilize the intermediate carbocation. Halogen can share more than a pair of electrons and can accommodate a positive charge giving halonium ion. In which chlorine bears a positive charge and is joined to the ring by a double bond. This structure is comparatively stable since in it every atom has a complete octet of electrons. No such structure is possible for the ion resulting from a meta attack. The resonance effect tends to oppose the inductive effect at the ortho and para positions and hence makes the deactivation less for ortho, para attack than for meta.



ortho attack

Halonium ion

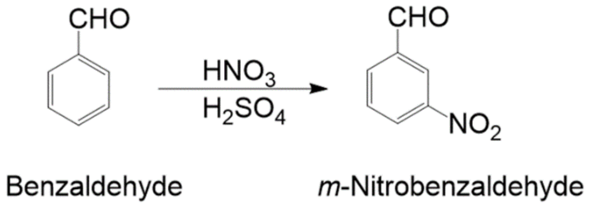


para attack

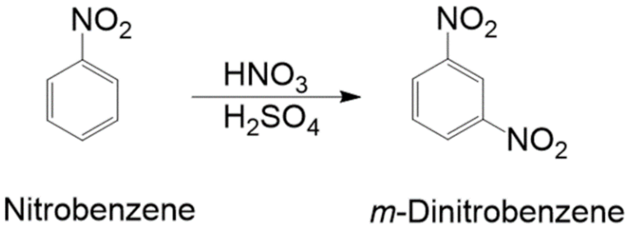
Halonium ion

Different Electrophilic Aromatic Substitution reactions

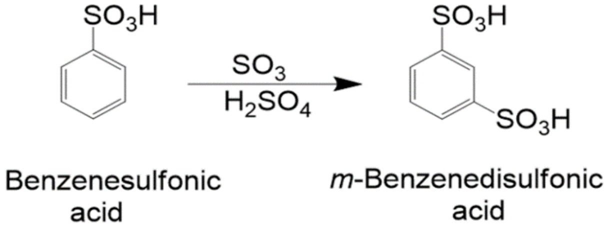
1) Nitration of Benzaldehyde - Benzaldehyde on Nitration gives *m*-Nitrobenzaldehyde



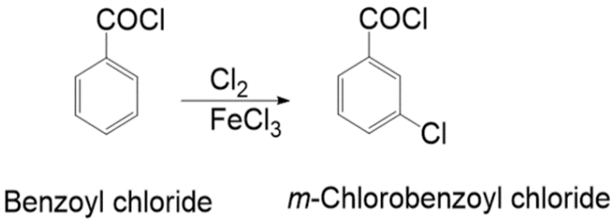
2) Nitration of Nitrobenzene- Nitrobenzene on nitration gives *m*-Dinitrobenzene



3) Sulphonation of Benzene sulphonic acid- Benzene sulphonic acid on sulphonation gives *m*-Benzenedisulfonic acid



4) Chlorination of Benzoyl chloride- Benzoyl chloride on chlorination gives *m*-Chlorobenzoyl chloride



Summary of the video (Abstract of the transcript)

- **Deactivating groups**
- Are the groups which withdraw electrons and deactivate a benzene ring towards electrophilic attack.
- Electron-withdrawing groups.
- Meta directors.
- Destabilize the carbocation intermediates.
- Increase the energy of the transition state.
- Decrease the rate of reaction.
- Make electrophilic aromatic substitution reactions slower.

- **List of deactivating groups**
  - Strongly deactivating substituents

    $-NO_2$, -CN, $-SO_3H$
  - Moderately deactivating substituents

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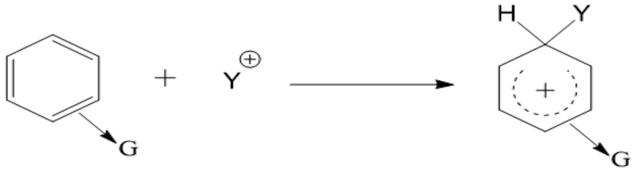
- **Electrophilic Aromatic Substitution**

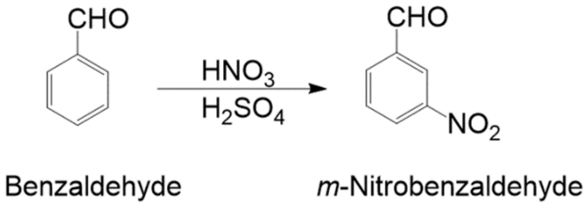


G withdraws electrons: destabilizes carbocation, deactivates the benzene ring

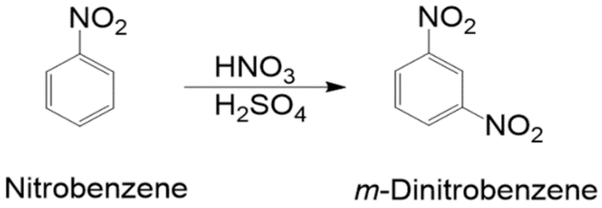
- Meta substituted product is the major product.

- **Different Electrophilic Aromatic Substitution reactions:**

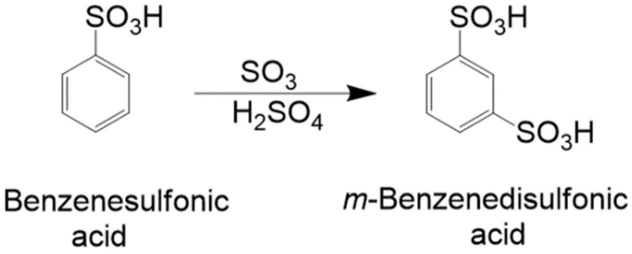
1) Nitration of Benzaldehyde



2) Nitration of Nitrobenzene



3) Sulphonation of Benzene sulphonic acid



4) Chlorination of Benzoyl chloride