

## LECTURE 2

Category 2: NO<sub>2</sub>, CN, SO<sub>3</sub>H, CHO, COR, CO<sub>2</sub>H, CONH<sub>2</sub>

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, -I:

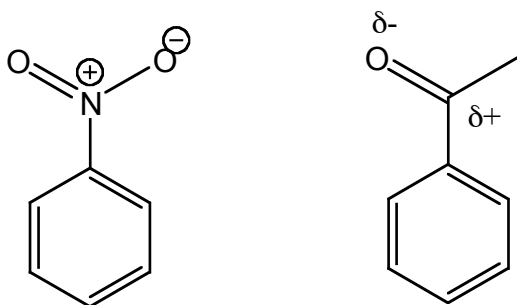
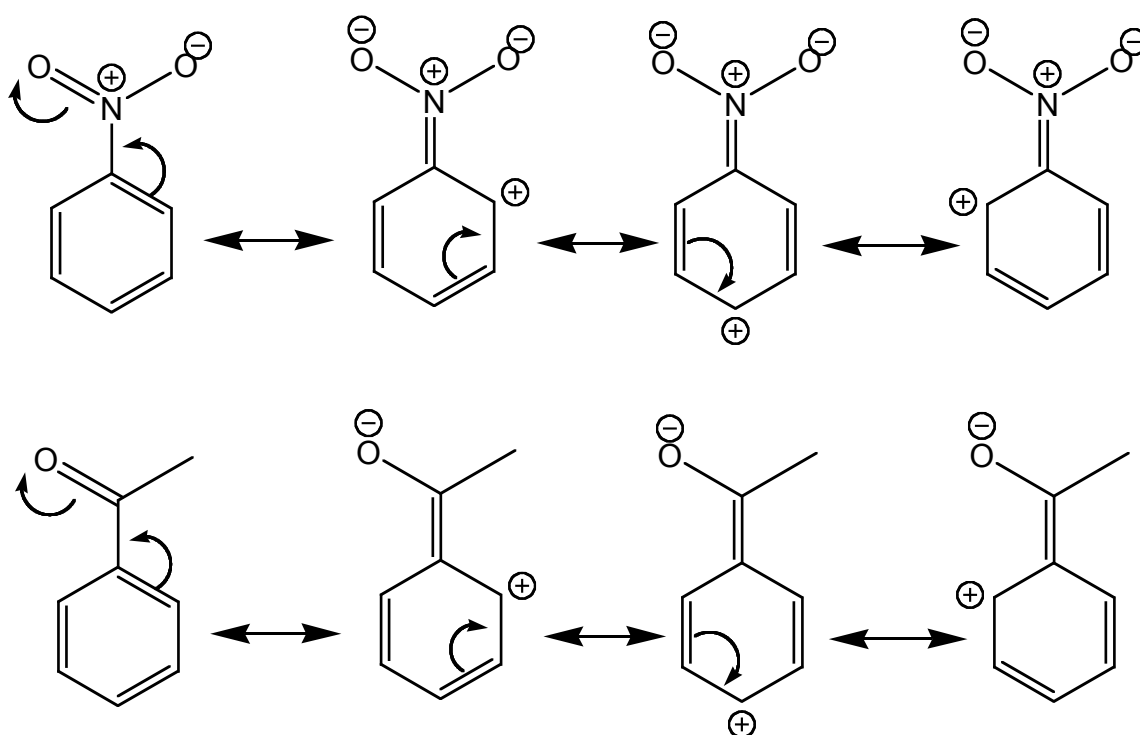


Fig. 1

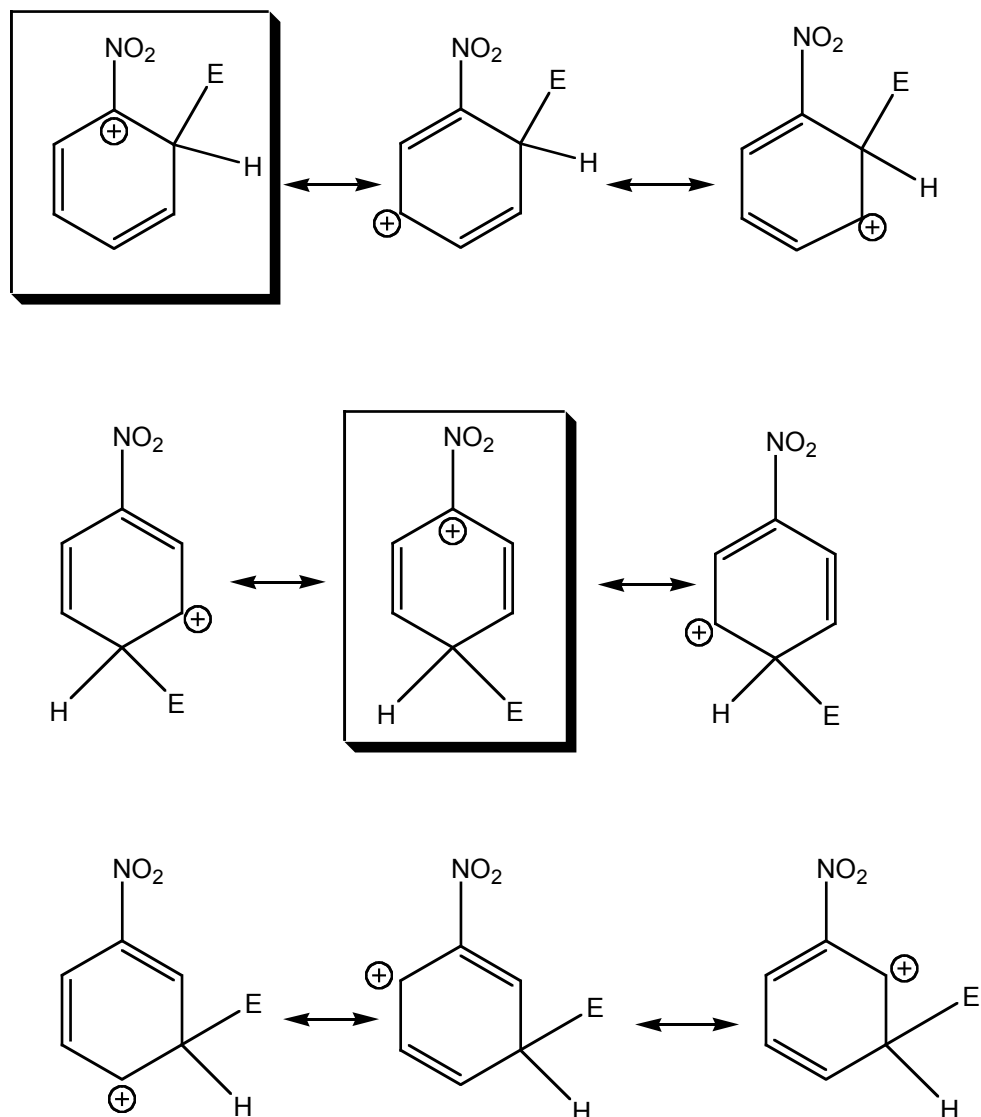
They also exhibit electron-withdrawing resonance effects, -Re:



Thus, 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.

We see that the resonance contribution in the starting material places positive charges at the *ortho* and *para* positions and these will deter

attack at those positions by electrophiles i.e. these groups are **meta (m) directing**. The same conclusion is reached by looking at the stability of the Wheland intermediates:



In these cases attack at the *ortho* or *para* positions must lead to one canonical form in which a positive charge is situated adjacent to the positively charged substituent, which is electrostatically unfavourable. Such a situation is avoided by *meta* attack.

### Category 3: Alkyl (R)

Because the element directly attached to ring is a carbon with no partial charge on it, the electronegativity difference between it and the ring carbon is small and hence the inductive effect is almost zero.

Weak resonance effects increasing the electron density in the ring come from  $\sigma$ -conjugation (hyperconjugation) (weak +Re effect):

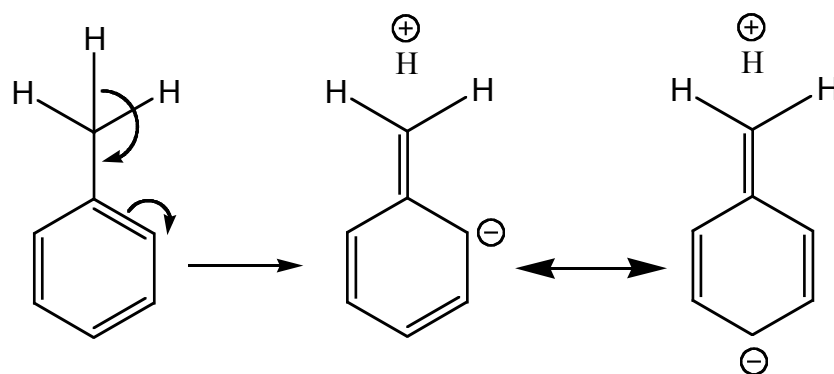


Fig. 2

Thus alkyl groups should be mildly **activating**. The  $\sigma$ -conjugation in the starting material and  $\sigma$ -conjugative stabilisation of the Wheland intermediates also make alkyl groups **o/p directing** (ortho only shown):

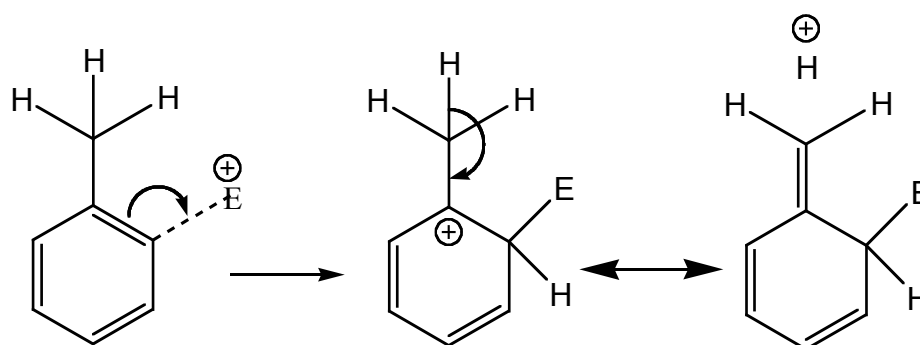
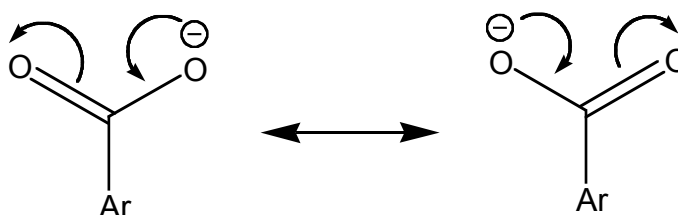


Fig. 3

#### Category 4: Carboxylate Anions, $\text{CO}_2^-$

Inductively, the negatively charged carboxylate ion moderately repels the electrons in the bond attaching it to the ring. Thus, there is moderate electron-donating +I effect. There is an almost zero Re effect since the electron withdrawing resonance capacity of the carbonyl group is effectively removed by the delocalisation of the negative charge of the anion:

Fig. 4



Thus overall the carboxylate group (unlike the carboxylic acid group) has an **activating** influence.

The inductive effect in the starting material is quite small but the repulsion of the electrons in the ring is best transmitted by the less tightly held  $\pi$ -electrons thereby producing small negative charges on the *ortho* and *para* positions but not on the *meta* position:

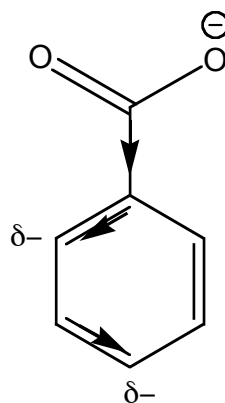


Fig. 5

The same argument may be applied to the stabilisation of the Wheland intermediate. Hence carboxylate groups are **o/p directing**.

Category 5: <sup>+</sup>NR<sub>3</sub>, <sup>+</sup>NH<sub>3</sub>, CCl<sub>3</sub>, CF<sub>3</sub>

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 **m-directing**:

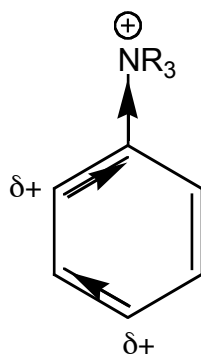


Fig. 6

## Category 6: F, Cl, Br, I

These elements are powerfully withdrawing inductively because they are so electronegative; thus there is a strong  $-I$  effect. This electronegativity affects their lone pairs which, although they should be available for a  $+Re$  effect as we have seen with other groups bearing lone pairs, are held so tightly that there is a negligible resonance effect in the starting material. Thus,  $-I \gg +Re$  and these groups are **deactivating**.

However, in the Wheland intermediate the carbocation centre is itself very electronegative (by virtue of its positive charge) and this forces the halogen atom to release its lone pair in a resonance fashion just like Category 1 groups. Thus these groups are **o/p directing**.

Summary:

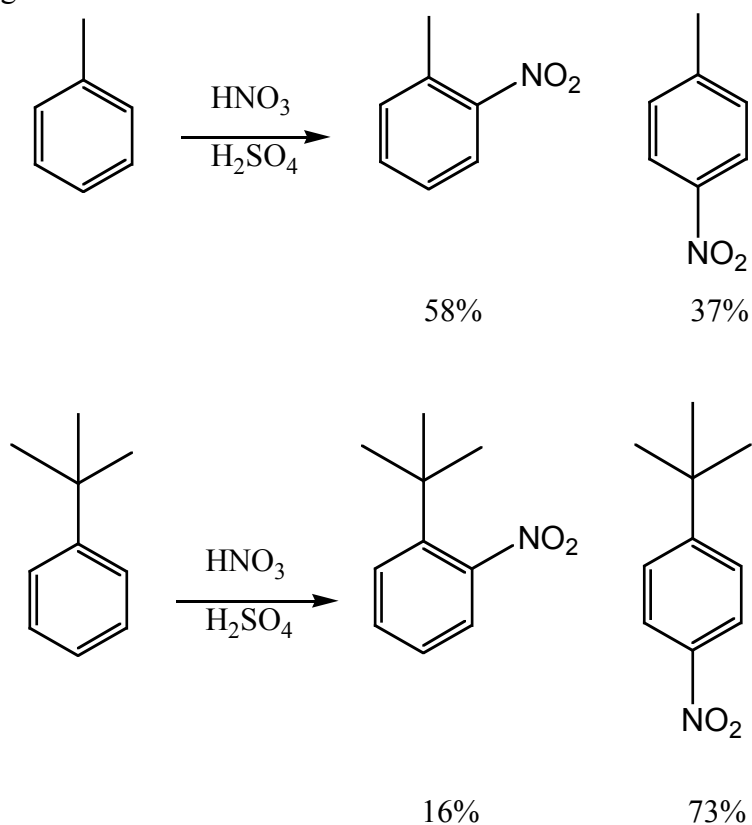
- Electron-donating groups (EDGs) are **activating** and **o/p directing**
- Electron-withdrawing groups (EWGs) are **deactivating** and **m directing**

The exception is the halogen group which is **deactivating** and **o/p directing**.

### Ortho / Para Ratio

It is usually difficult to predict how much of the product from an o/p directing group aromatic will be *ortho* and how much *para*. Indeed, it depends greatly on the conditions of the reaction. For example, the chlorination of toluene gives an o/p ratio anywhere between 62:38 and 34:66. Although the reasons for these changes are largely unknown, there is one factor which does allow us to predict o/p ratios more reliably; that factor is steric hindrance. The greater the size of the group the less of the more hindered *ortho* product is formed e.g.:

Fig. 7



(d) Orientation in benzene rings containing more than one substituent

It is often possible to predict the correct isomer of monosubstitution especially when groups on the ring reinforce their directing abilities e.g. in the molecule **A** below where both the carboxyl group (*meta*-directing) and the chlorine (*o/p* directing) will guide the incoming electrophile to one of the positions *ortho* to the chlorine. When the groups oppose each other, as in molecule **B**, it is more difficult and one

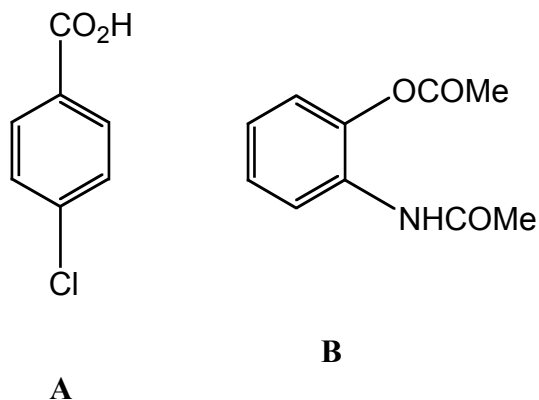


Fig. 8

often gets a mixture (both groups are *o/p* directing but the *ortho* position to one is *meta* to the other).

Nevertheless, there are three general, predictive rules:

- The groups can be arranged in the following order of influence:  
 $O^-$ ,  $NR_2$ ,  $NHR$ ,  $NH_2$ ,  $OH$ ,  $OR$  >  $NHCOR$ ,  $OCOR$  >  $R$  >  $F$ ,  $Cl$ ,  $Br$ ,  $I$  > all *meta* directing groups
- All other things being equal a third group is less likely to enter between two groups for steric reasons
- When a *meta* directing group is *meta* to an *o/p* directing group the incoming electrophile goes predominantly *ortho* to the *meta* directing group rather than para to it (there is currently no good explanation of why this is so).

The following molecule illustrates these points:

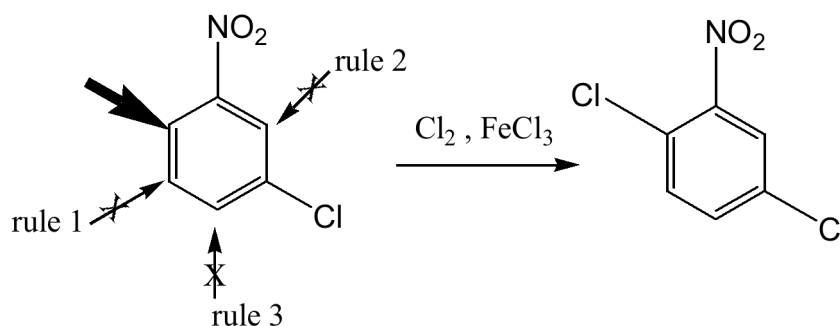


Fig. 9