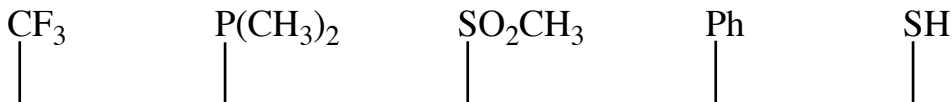


Exercise 115 - Directing/Activation

Question

Classify each of the following as either ortho/para or meta-directing groups.



CF_3 : Meta directing group. The fluorines on this substituent are strongly electron-withdrawing making the carbon very positively polarized. This will destabilize the sigma complex intermediate in the case of ortho and para. As an electron-withdrawing group it will be deactivating.

$\text{P}(\text{CH}_3)_2$: Ortho/para directing group. The P atom bears a lone pair that will stabilize an adjacent charge. Activating group.

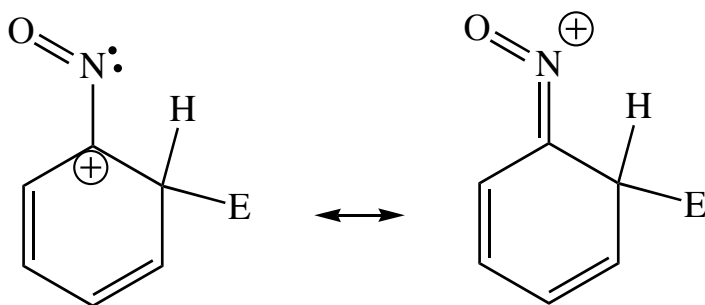
SO_2CH_3 : Meta directing group. This is a sulfone, analogous to the sulfonic acid functional group. Deactivating.

Ph: This is an ortho/para directing group. The phenyl ring will stabilize an adjacent positive charge by delocalization. Activating.

SH: Thiophenol is an o/p director just as OH is due to the lone pair. Activating.

Question

i) This functional group has a lone pair and it is possible to use this lone pair to stabilize an adjacent positive charge in the o/p carbocation intermediates:



On this basis, this would appear to be an ortho/para directing group.

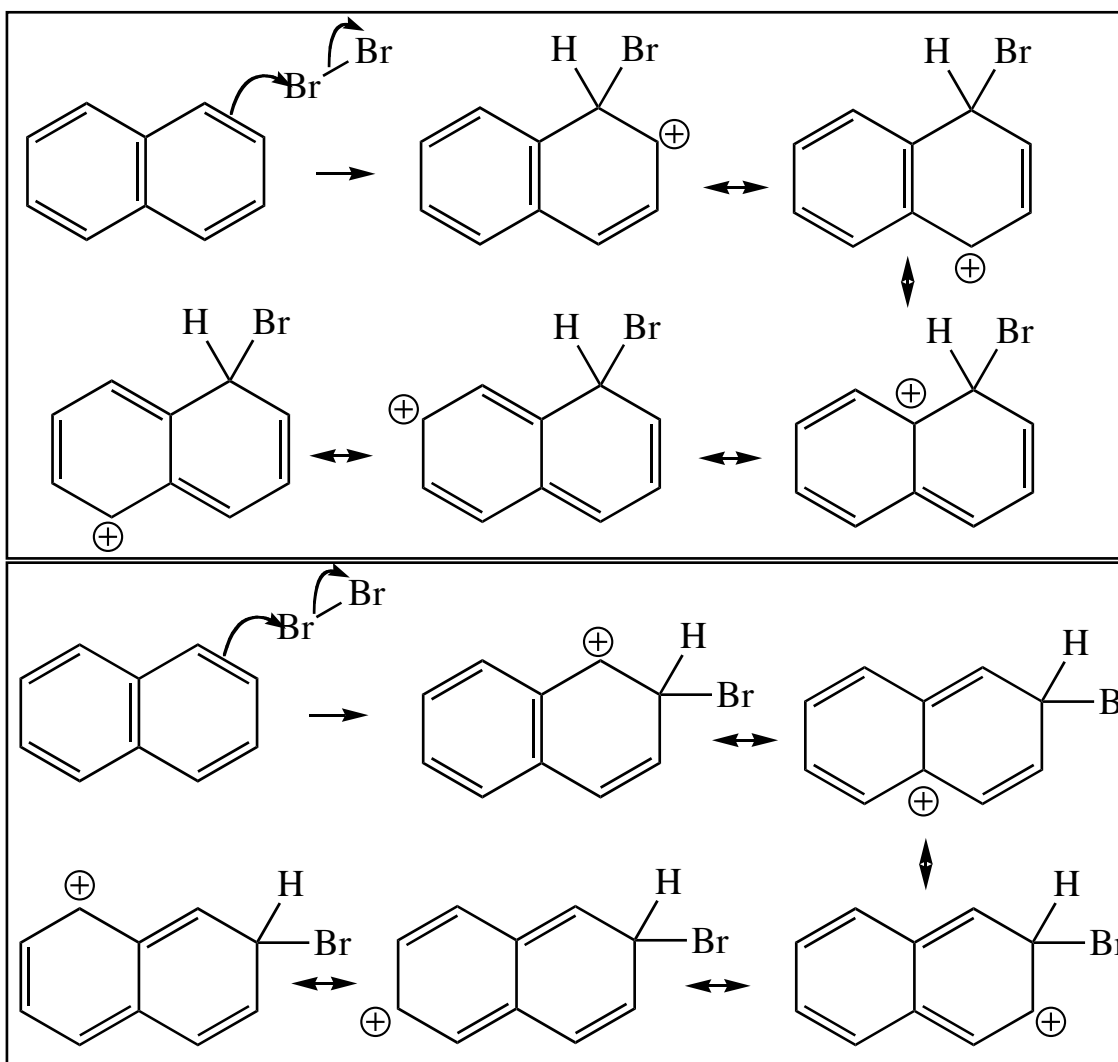
ii) Like the CO (carbonyl) bond, the NO bond is polarized toward oxygen making the N electron poor. N is more electronegative than C so this N atom will be strongly electron-withdrawing. On this basis, one might expect that it would destabilize an adjacent positive charge making this a meta directing group.

iii) The NO group deshields the o, m and para positions almost equally. If the o,p protons were further upfield than the meta protons, then that would suggest that lone pair donation to the ring is operating. The data indicates that this is not the case. I would suspect that this group does not direct to any position and that a mixture of all three products would be formed.

iv) The fact that this group deshields all protons indicates that electron-withdrawing dominates and therefore this is a deactivating group.

Question

To answer this, we must look at the (many) resonance structures of the two possible sigma complex intermediates:



Each intermediate has a set of five resonance structures. The distinction is that in the upper case, two of these structures retain the aromatic ring and its attendant resonance energy thereby making this a more stable carbocation than the second, in which only one structure retains the aromatic ring.

The sigma complex formed from the EAS of naphthalene is stabilized by resonance to a greater extent (over five structures compared to three) than that of benzene suggesting that this would be a faster reaction.