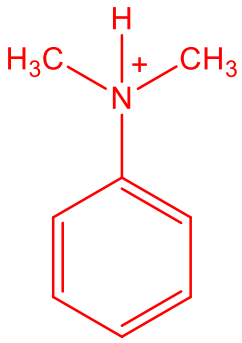
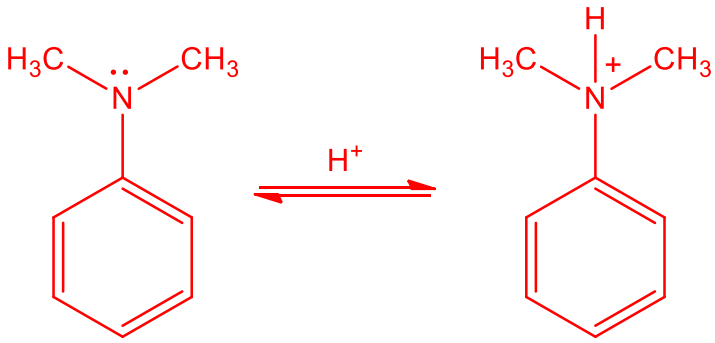
Problem Set 4 – Electrophilic aromatic substitution

1. The nitration of *N*,*N*-dimethylaniline, $C_6H_5N(CH_3)_2$, in 85% H_2SO_4 gives 45% *m*-nitro product and 38% *p*-nitro product.

   a. What is the species actually undergoing nitration to give the *meta* product?

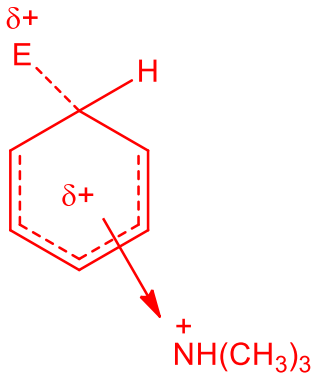


   b. How is it formed?



   c. What is its relative reactivity to that of benzene?

   It is less reactive than benzene as electron withdrawal by the nitrogen destabilizes the transition state, thereby increasing the activation energy for carbocation formation:

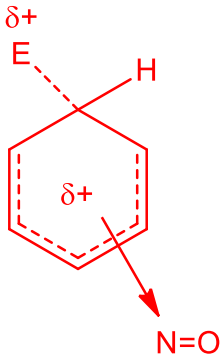


d. Why does this species under go *meta* substitution?

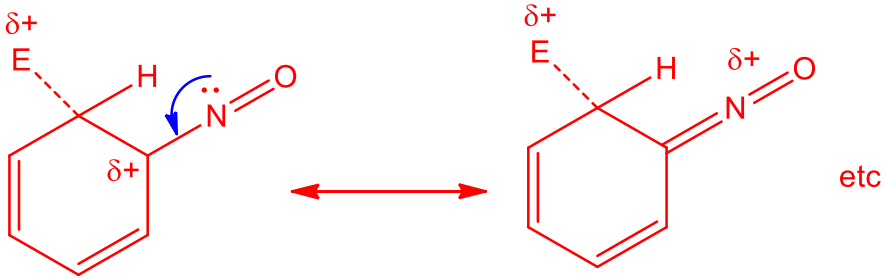
The nitrogen has no ability to donate electrons as there is no lone pair on the nitrogen.

2. The nitroso group, -N=O, is *ortho-para* directing but deactivating. Explain in terms of resonance and inductive effects.

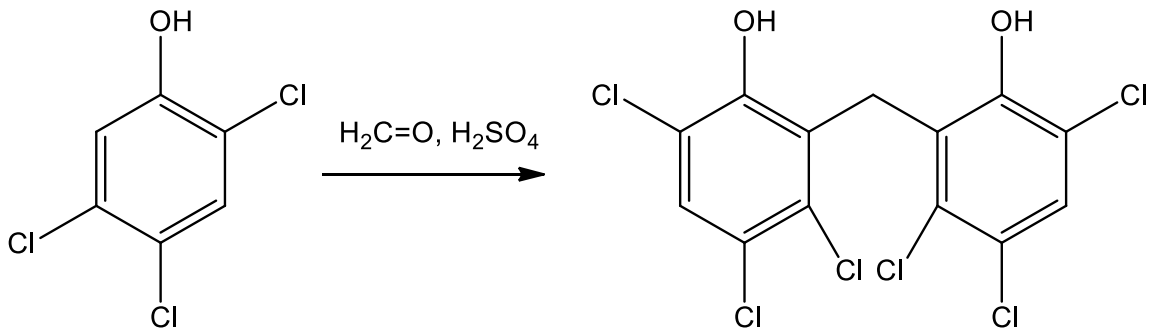
The group is electronegative and therefore attracts electrons through the inductive effect. It destabilizes the transition state and is therefore deactivating:

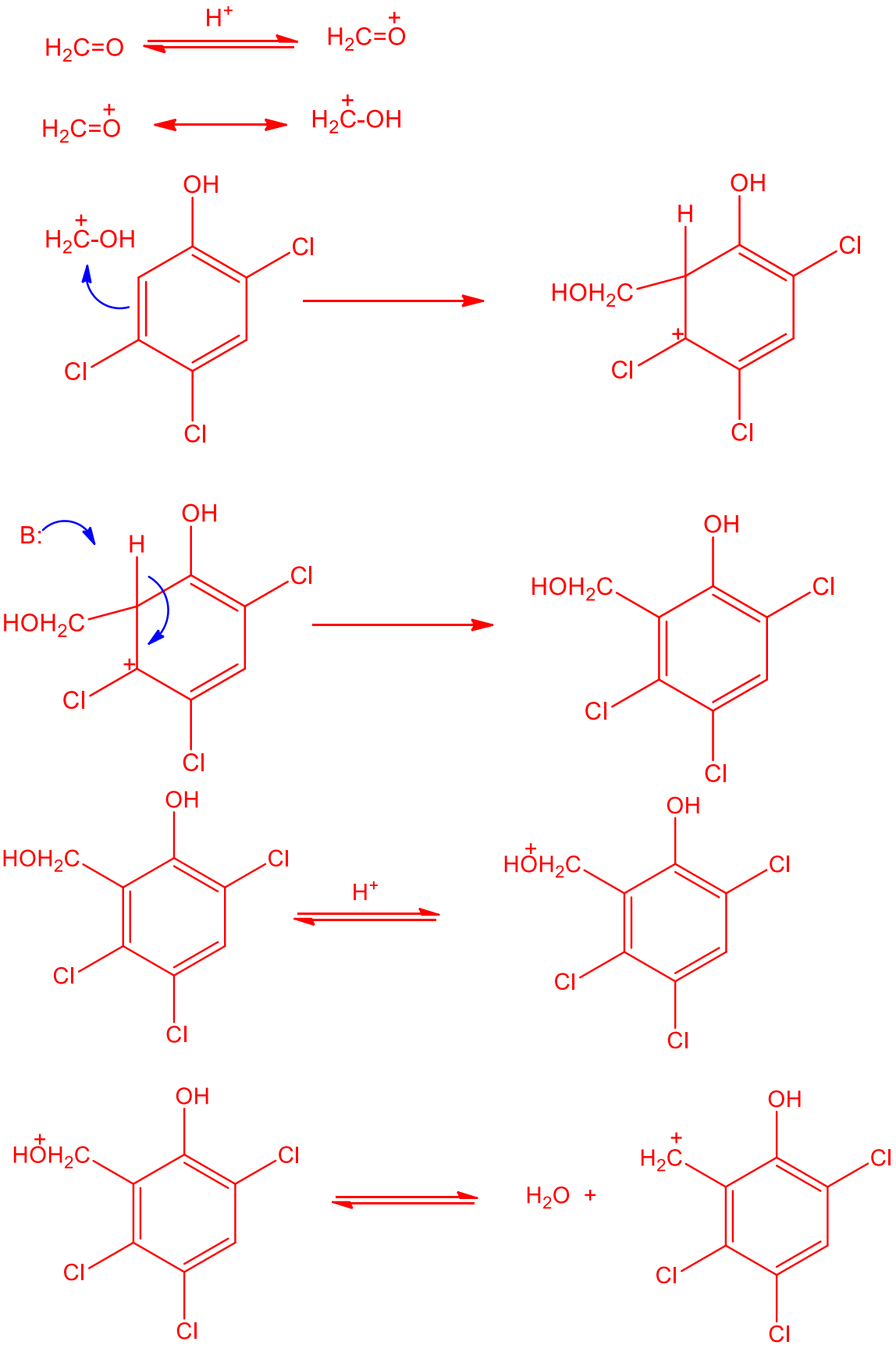


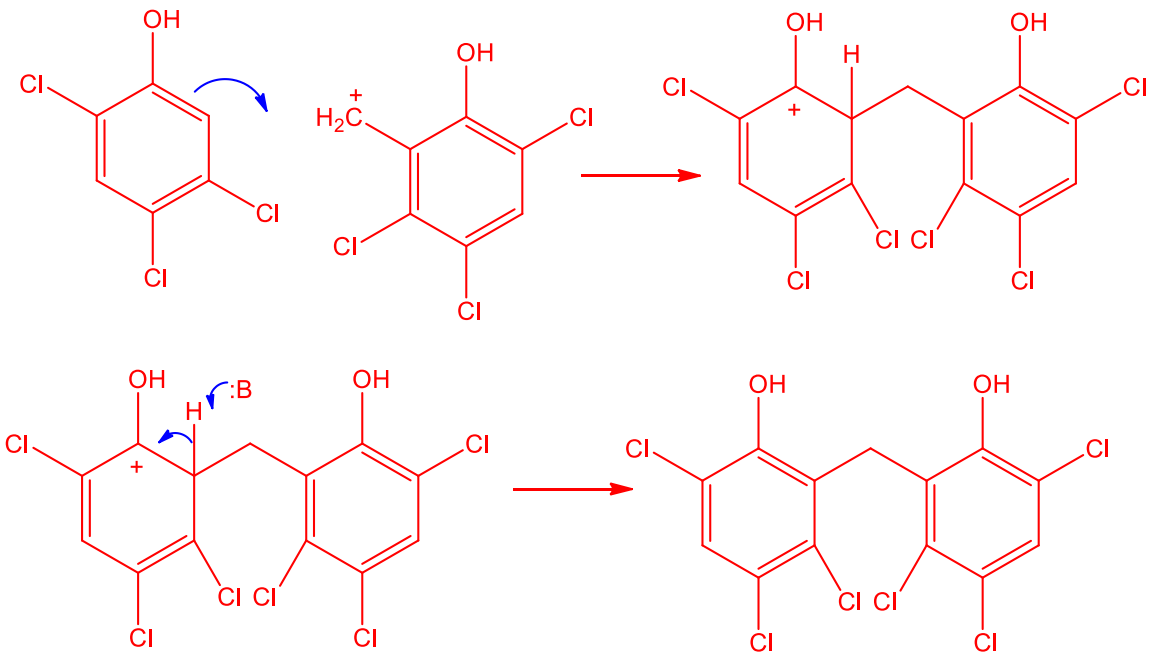
It is also electron donating through resonance thereby stabilizing the transition state for ortho and para attack and results in the observed directing effect.



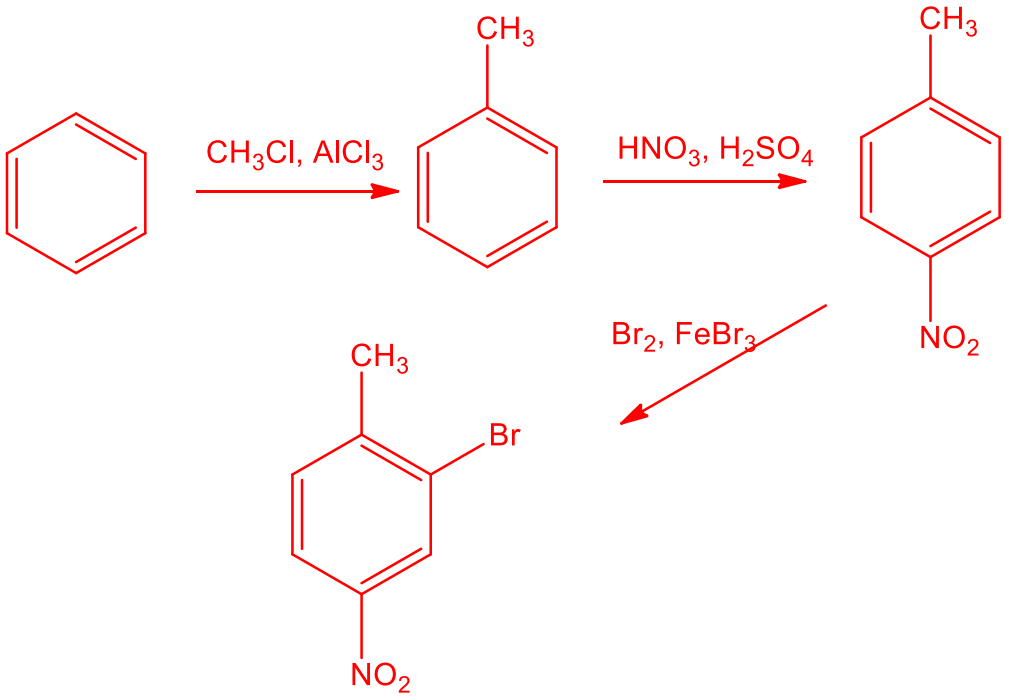
3. Hexachlorophene, a substance used in the manufacture of germicidal soaps, is prepared by reaction of 2,4,5-trichlorophenol with formaldehyde in concentrated sulfuric acid. Propose a mechanism.


OH
Cl
Cl
Cl
H2C=O, H2SO4
OH
OH
Cl
Cl
Cl
Cl
Cl
Cl
Cl


H+
H2C=O
H2C=O+
H2C=O+
H2C-OH+
OH
H2C-OH+
Cl
Cl
Cl
OH
H
HOH2C
Cl
+
Cl
Cl
B:
OH
H
Cl
HOH2C
+
Cl
Cl
OH
HOH2C
Cl
Cl
Cl
OH
HOH2C
Cl
Cl
Cl
H+
OH
HOH2C+
Cl
Cl
Cl
OH
HOH2C+
Cl
Cl
Cl
H2O +
OH
H2C+
Cl
Cl
Cl



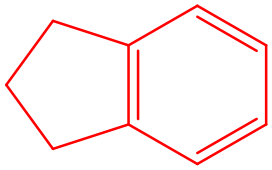
4. Propose a synthesis of 2-bromo-4-nitrotoluene from benzene.



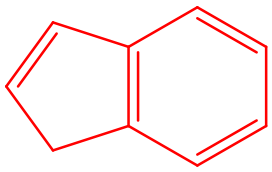
5. Two alcohols, “A” and “B”, have the same molecular formula $C_9H_{10}O$ and react with sulfuric acid to give the same hydrocarbon “C”. Compound “A” is optically active and compound “B” is not. Catalytic hydrogenation of “C” gives a hydrocarbon “D”, C_9H_{10}, which gives two and only two products

when nitrated once with HNO_3/H_2SO_4. Give the structures of “A”, “B”, “C”, and “D”.

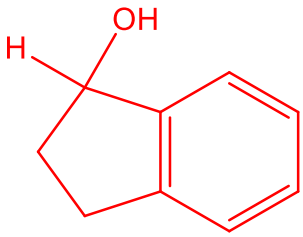
C_9H_{10} has five units of unsaturation. Nitration indicates an aromatic ring. The fact that there are only two mononitrated products indicates that there are only two different types of hydrogen on the aromatic ring. D must be:



Thus, C must be

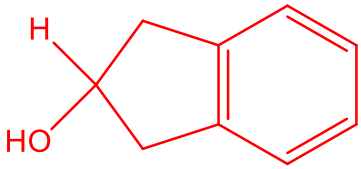


And A must be:

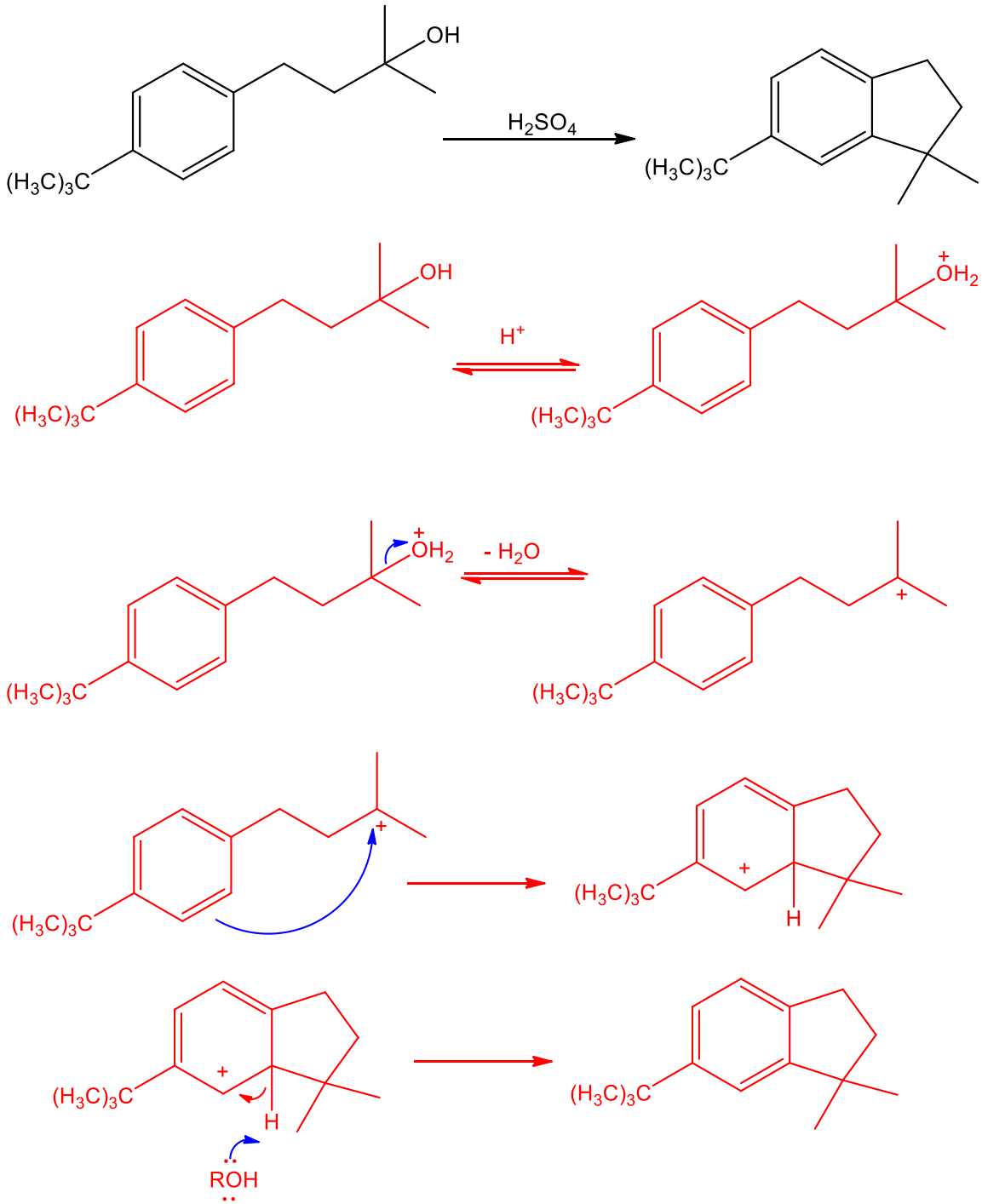


As it is chiral.

And optically inactive B must be:



6. Propose a mechanism for the following reaction:


OH
H_2SO_4
$(H_3C)_3C$
H^+
OH_2
- H_2O
H
ROH