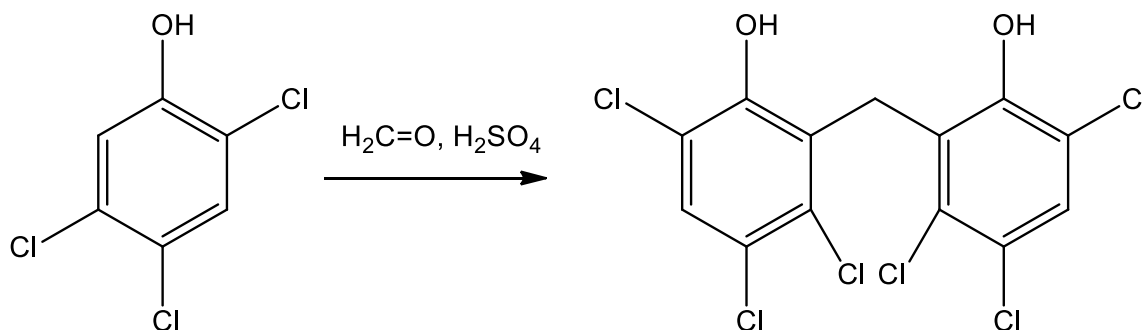


### Problem Set 4 – Electrophilic aromatic substitution

- 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.
  - What is the species actually undergoing nitration to give the *meta* product?
  - How is it formed?
  - What is its relative reactivity to that of benzene?
  - Why does this species undergo *meta* substitution?
- The nitroso group,  $-N=O$ , is *ortho-para* directing but deactivating. Explain in terms of resonance and inductive effects.
- 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.



- Propose a synthesis of 2-bromo-4-nitrotoluene from benzene.
- 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".
- Propose a mechanism for the following reaction:

