

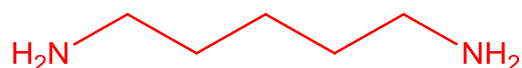
Problem Set 10 – Reactions of amines

1. Putrescine and cadaverine are found in rotting flesh. Putrescine ($C_4H_{12}N_2$) may be synthesized by treating 1,2-dibromoethane with KCN followed by hydrogenation. Treatment of 1,5-dibromopentane with ammonia gives cadaverine ($C_5H_{14}N_2$).

- a. What is the structure of putrescine?

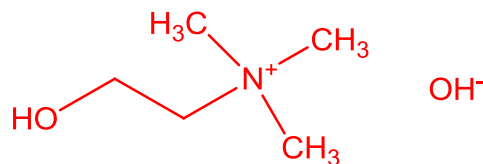


- b. What is the structure of cadaverine?

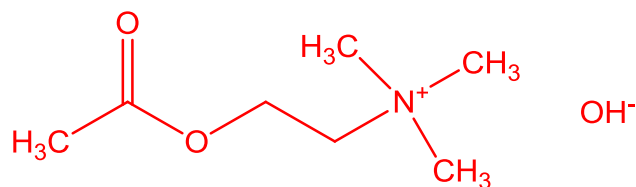


2. Choline, $C_5H_{15}O_2N$, is a constituent of phospholipids. It dissolves in water to give a basic solution. It can be prepared by reaction of ethylene oxide with trimethylamine in the presence of water. Acetylcholine, $C_7H_{17}O_3N$, is its acetyl derivative.

- a. What is the structure of choline?

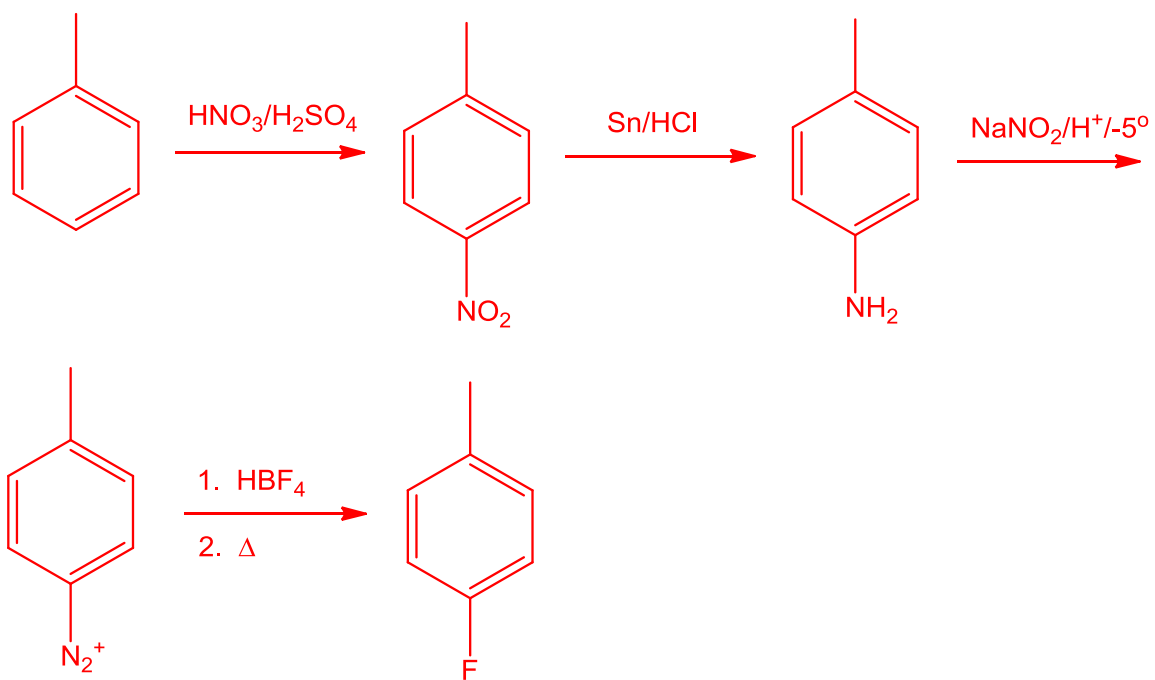


- b. What is the structure of acetylcholine?

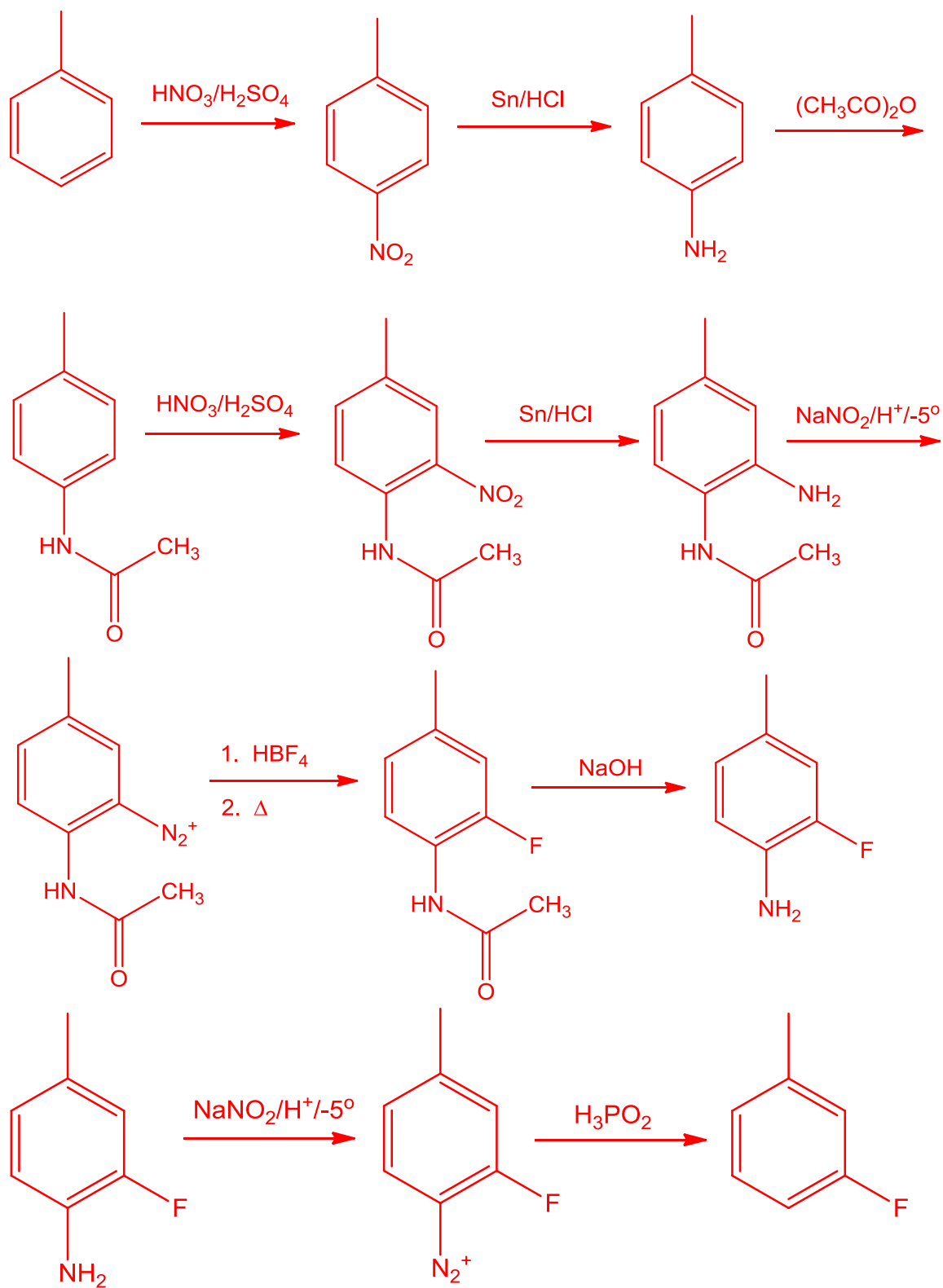


3. Write equations for each step in the following syntheses:

- a. toluene \rightarrow *p*-fluorotoluene

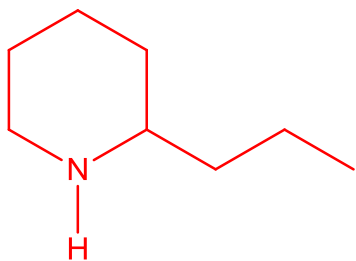


b. toluene \rightarrow *m*-fluorotoluene

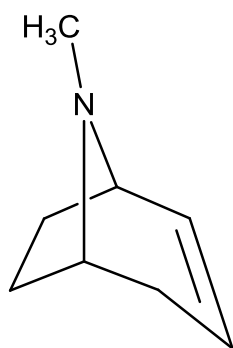


4. Coniine, $\text{C}_8\text{H}_{17}\text{N}$, is the toxic ingredient of poison hemlock, drunk by Socrates. When subject to exhaustive methylation and Hofmann elimination, coniine

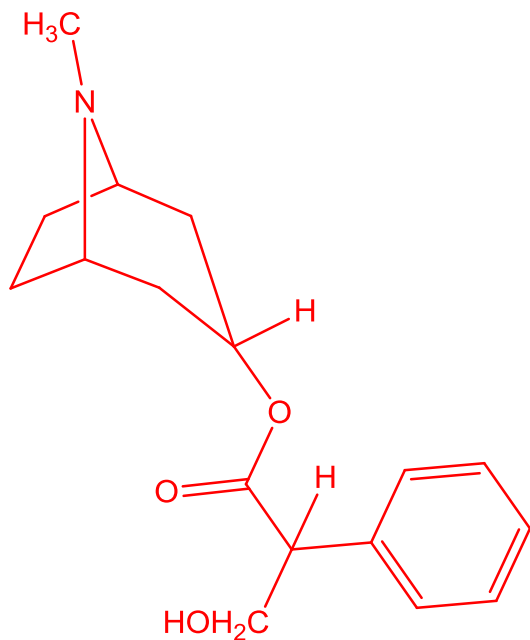
gives 5-(*N,N*-dimethylamino)-1-octene. If coniine is a secondary amine, what is its structure?



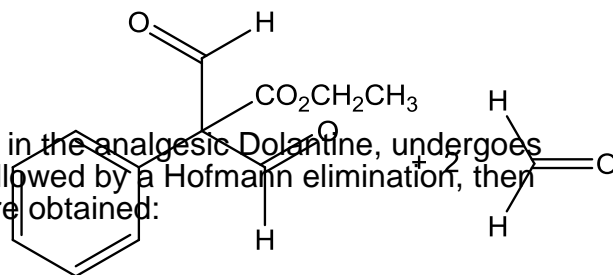
5. Atropine, $C_{17}H_{23}NO_3$, is a poisonous alkaloid isolated from *Atropa belladonna*, deadly nightshade. Base hydrolysis gives tropic acid, $C_6H_5CH(CH_2OH)CO_2H$, and tropine, $C_8H_{15}NO$. Tropic acid, an optically inactive alcohol reacts with H_2SO_4 to give tropidene:



What is the structure of atropine?



6. When pethidine, the active ingredient in the analgesic Dolantin, undergoes two exhaustive methylations, each followed by a Hofmann elimination, then an ozonolysis, the following results are obtained:



Propose a structure for pethidine.

