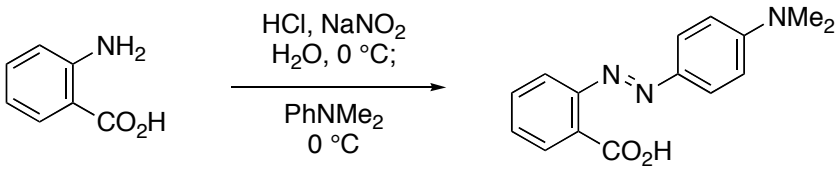
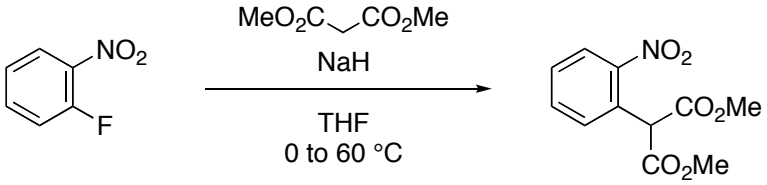
2020 有機化学演習-４ (1/21)

以下の反応の反応機構を電子の流れがわかるように、別紙に矢印を使って記せ。

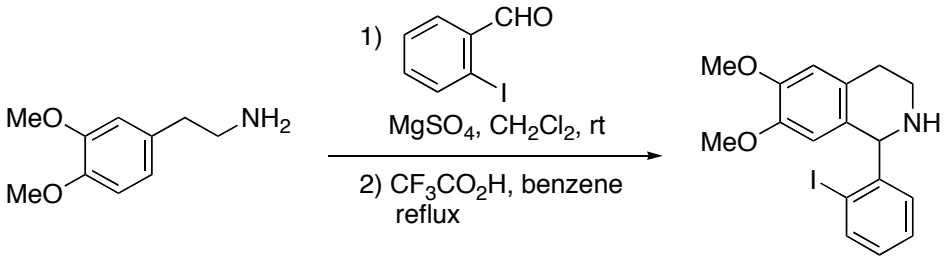
１９.



２０.



２１.



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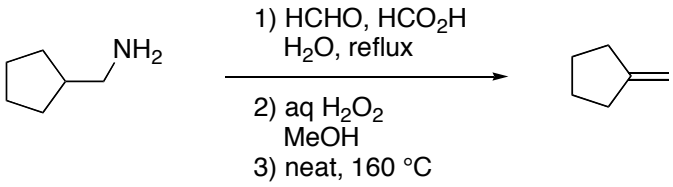
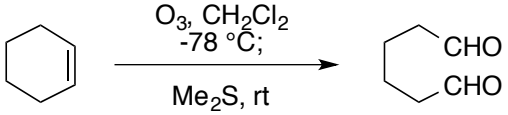
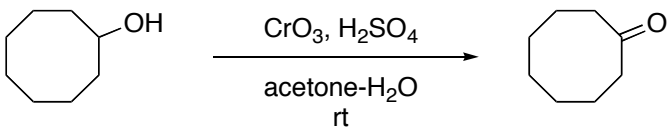


２３.



２４.



１９.

ヒント：A: Formation of nitrous anhydride.　B: Addition of the aniline to nitrous anhydride.　C: Proton transfer followed by elimination of water to form a diazonium salt.　D: Addition of electron-rich dimethylaniline to the diazonium salt.　E: Aromatization.

２０.

ヒント：A: Deprotonation of the malonate to form an enolate (pKa $RO_2CCH_2CO_2R = 13$, $H_2 = 35$).　B: Nucleophilic addition of the enolate to the electron-deficient aromatic ring.　C: Elimination of fluoride ion.

２１.

ヒント：Pictet-Spengler reaction.　A: Formation of an imine.　B: Addition of an electron-rich aromatic ring to the iminium ion followed by aromatization.

２２.

ヒント：Eschweiler-Clarke methylation (A-C) and Cope elimination (D-E).　A: Addition of the amine to formaldehyde followed by dehydration to form an iminium ion.　B: Hydride transfer from a formate anion to the iminium ion with generation of CO_2.　C: Iteration of the same steps.　D: Oxidation of the tertiary amine to form an *N*-oxide.　E: *syn*-Elimination.

２３.

ヒント： A: 1,3-Dipolar cycloaddition of ozone to the olefin.　B: Heterolytic cleavage of the initial ozonide.　C: Recombination of the resulting 1,3-dipole and the aldehyde to form an ozonide.　D: Reductive cleavage of the O-O bond of the ozonide with Me_2S.

２４.

ヒント：Jones oxidation.　A: Hydration of CrO_3.　B: Attack of the alcohol to H_2CrO_4.　C: Elimination of H_2CrO_3.