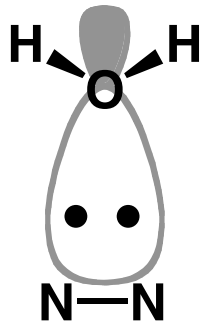
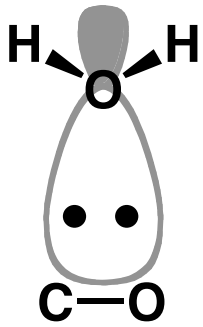
Discussion Problem

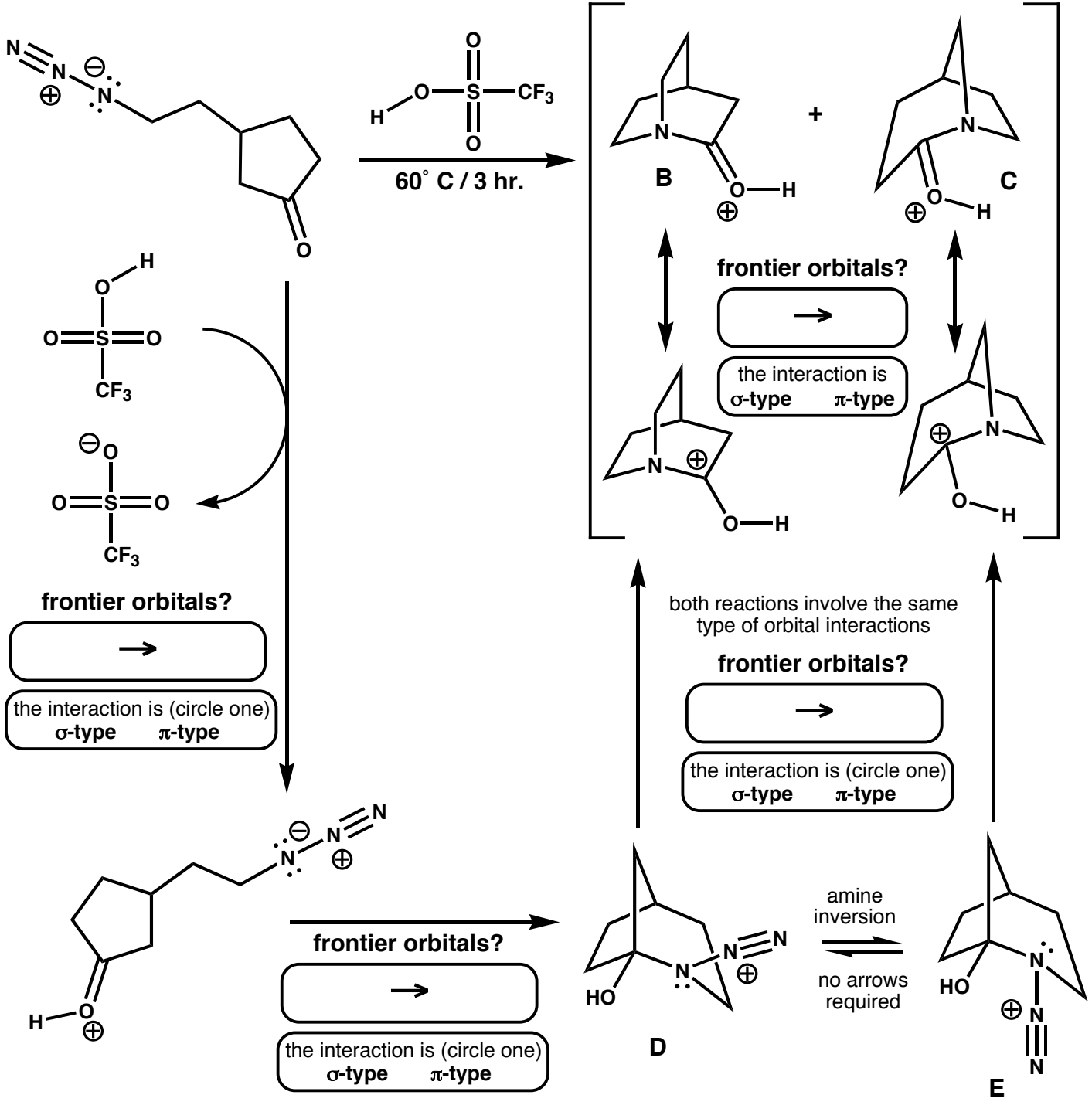
Draw orbital pictures to illustrate why n→π* orbital overlap is zero for the tee-shaped geometry of H_2O with nitrogen (N_2), but nonzero for H_2O with carbon monoxide (CO). Reference: *Chem. Rev.* (1988), *88*, 899.





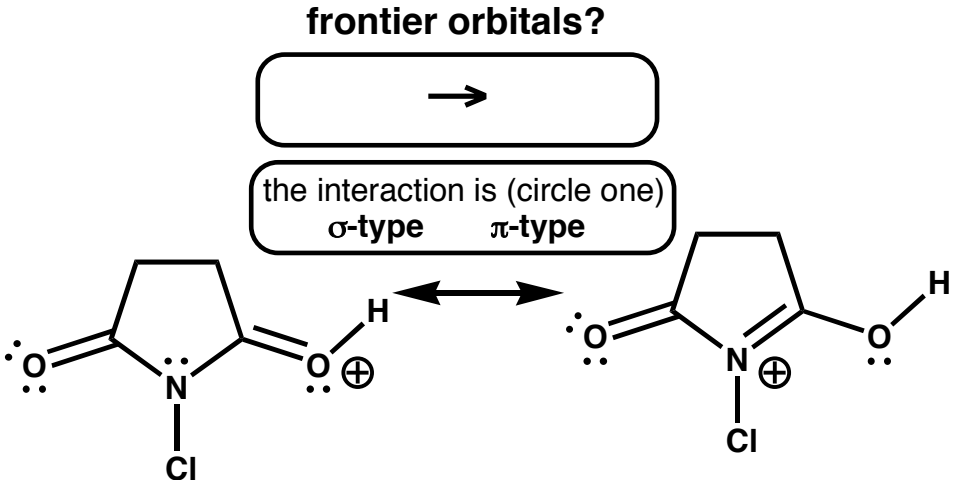
Discussion Problem

Amide **B** was recently prepared as shown; another amide (**C**) was produced in the process (note the products are shown in their protonated forms). A mechanism to account for these products is provided. **Draw curved arrows to show the flow of electrons for each step and for each resonance contributor.** Indicate the frontier orbitals involved based on the arrows that you draw. Your answers should be one of the nine possible combinations of filled→empty orbital pairs (e.g., π → π*). Where requested, indicate the type of frontier orbital interaction (i.e., σ-type or π-type). (Ref: *Nature* **2006**, *441*, 731)

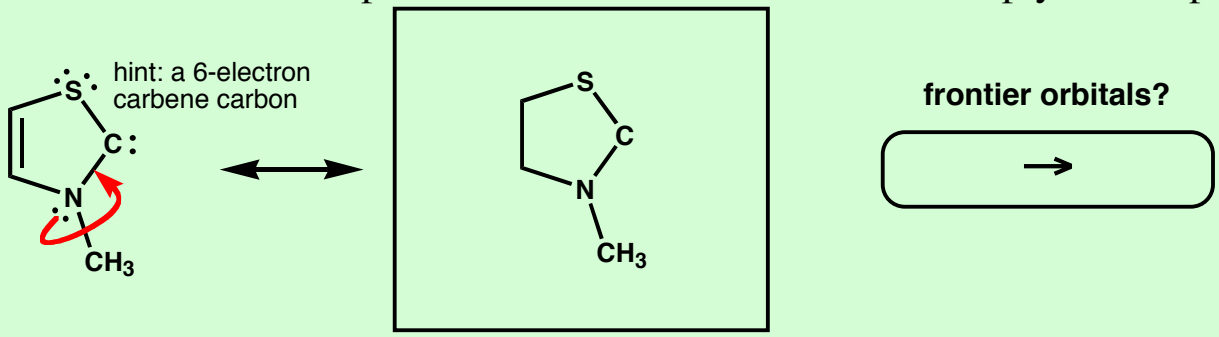


Discussion Problems (resonance)

Draw curved arrows to show the flow of electrons from the one resonance contributor to the next. Indicate the frontier orbitals involved based on the arrows that you draw. Your answers should be one of the nine possible combinations of filled→empty orbital pairs (e.g., π → π*). Indicate the type of frontier orbital interaction (i.e., σ-type or π-type).

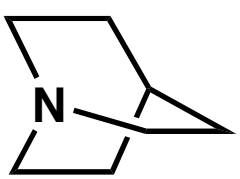


For the diagram below, finish drawing the resonance contributor resulting from the curved arrow notation provided at the left. Show all electron lone pairs and formal charges. In the box at the right, indicate the frontier orbitals involved in the interaction that is represented by the curved arrow notation. Your answer should be one of the nine possible combinations of filled → empty orbital pairs.

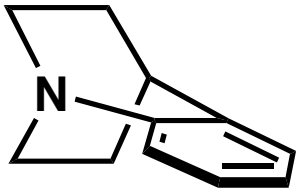


Discussion Problem

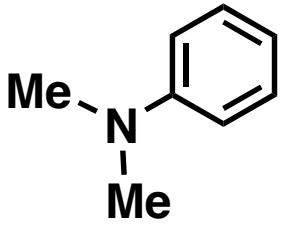
Benzoquinuclidine (**B**) is a significantly weaker base than quinuclidine (**A**) but a significantly stronger base than N,N-dimethylaniline (**C**). Account for these facts. Be prepared to show molecular models to justify your answer.



A



B



C

pKa of conjugate acid: **10.65** **7.79** **5.20**