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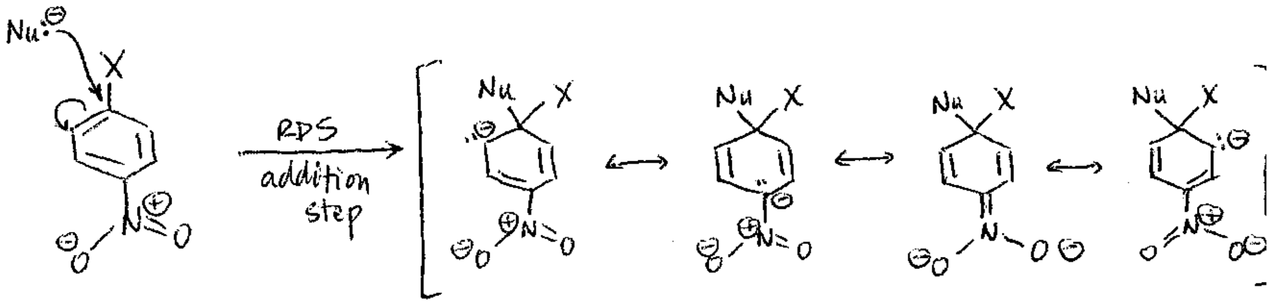
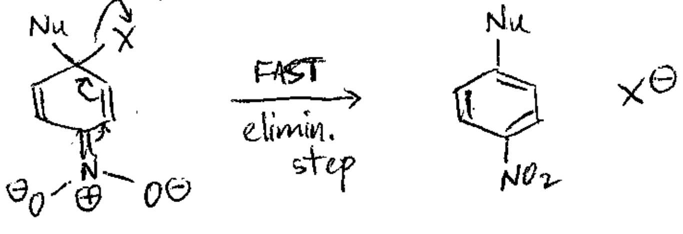
3. Focus on the rate-determining step (RDS) in this nucleophilic aromatic substitution process that goes by addition-elimination here.

RDS is cyclohexadienyl anion formation — this is accelerated by electron withdrawing substituents. To examine the rate of the process, it is the ELECTRONEGATIVITY of X (not its leaving group ability) that is important.

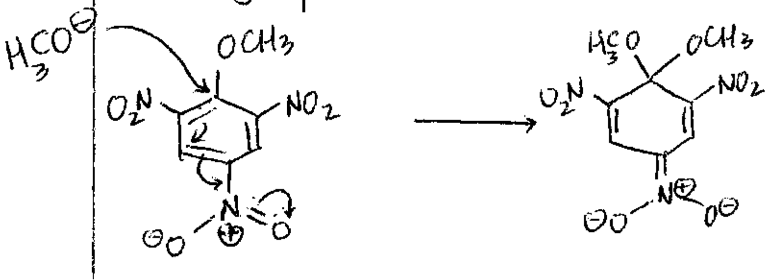


The cyclohexadienyl anion will be inductively stabilized by an ewg (X) here. F is the most ewg here ∴ will stabilize the anion the most.

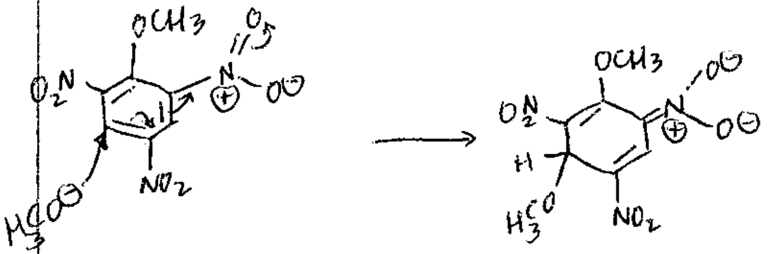
It is important to note that the leaving group is not lost until AFTER the RDS. Therefore, leaving group ability of $X^{\ominus}$ does not impact overall rate of the reaction.



4. There are two ways that the nucleophile can add to get resonance stabilization of the Meisenheimer complex by the $-NO_2$ groups.



This is one of 6 resonance structures for this Meisenheimer complex. Two others have the $\ominus$ on one of the other $-NO_2$ groups. Three res. structures have the $\ominus$ on one of the NO_2-bearing carbons. Be sure you can generate all of these res. structures



There are 5 other res. structures for this Meisenheimer complex. Note that this Meisenheimer complex will not lead to a substitution reaction because methoxide and NEVER hydride ($H:^{\ominus}$ (terrible leaving group) will be the leaving group when aromaticity is restored.

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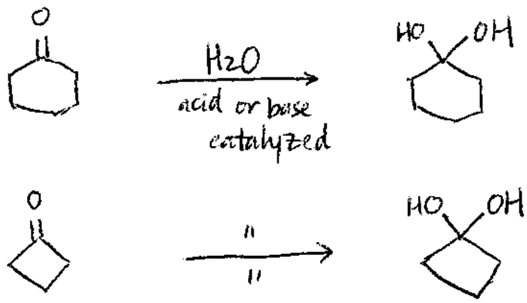
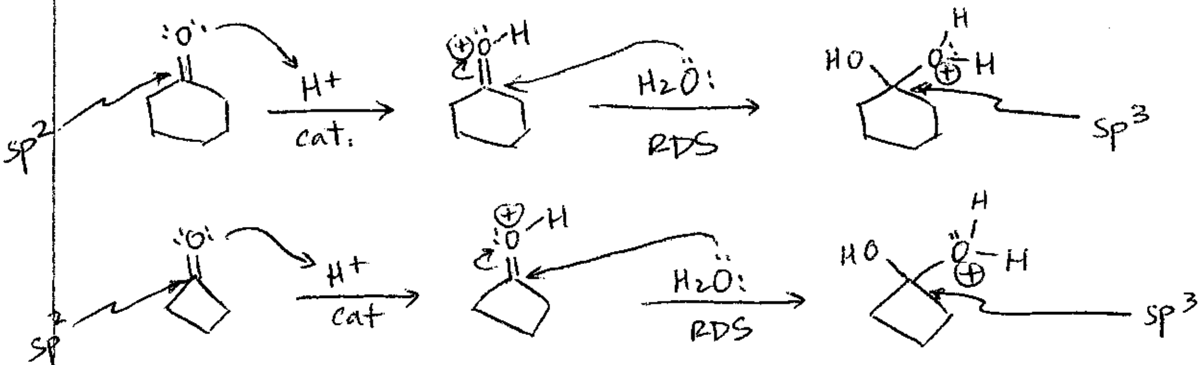
5. Hydration produces the final products:

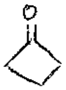
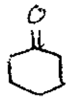


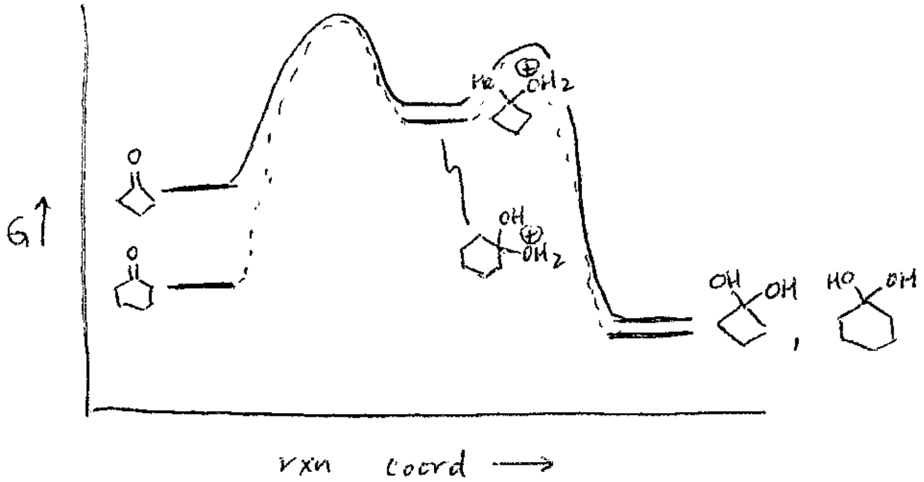
<u>But</u> need to look at the rate determining step to answer this question:

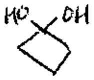
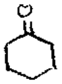
⊛ RDS is addition of H_2O as a nucleophile to form a tetrahedral intermediate



The energies of the two tetrahedral IM's are <u>roughly</u> similar; however, cyclobutanone is appreciably higher in energy than cyclohexanone. This is due to the strain in the smaller ring. The sp^2-hybridized C in the starting ketones wants to (ideally) have 120° bond angles. In cyclobutanone, this is virtually impossible. So the amount of energy released by changing to an sp^3-hybridized C (bond angles ~109°) is much greater for cyclobutanone than cyclohexanone. ⟨OVER⟩

Thus,  is likely to be more hydrated than is .



The overall ΔG_{rxn} for  →  will be more negative than ΔG_{rxn} for  →