

CHE 45: Physical Organic Chemistry

Test 1

January 13, 1995

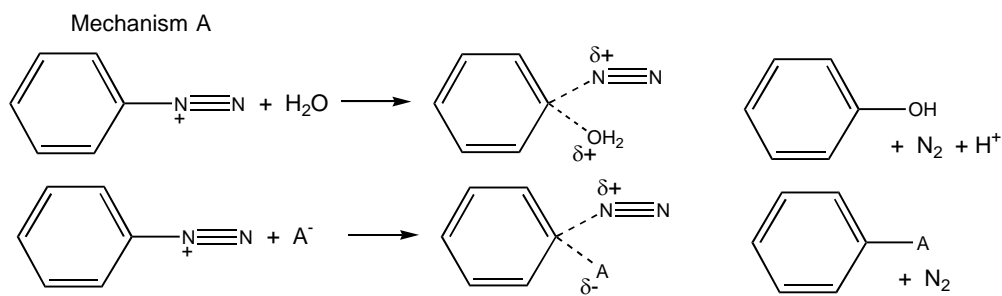
1. Two mechanisms (shown below) are among those that have been postulated for decomposition of aryl diazonium salts in aqueous solution containing nucleophilic anions, A^- . Indicate how each of the following techniques might be applied to distinguish between these mechanisms. (Your answer should explain the expected results for the two mechanisms.) (20 points)

(a) kinetic studies

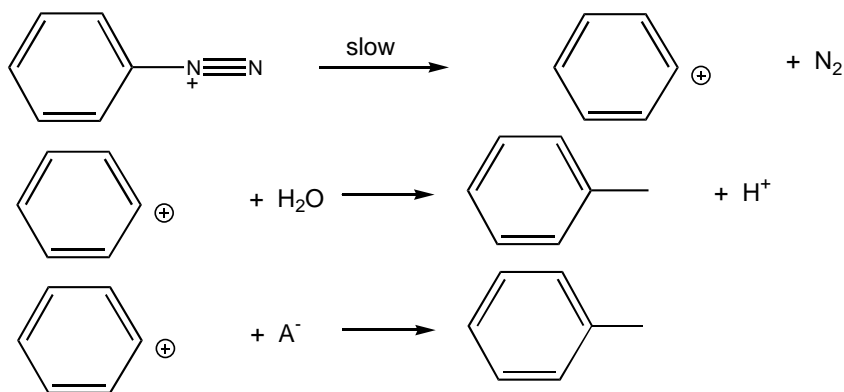
(b) rate and product composition as a function of $[A^-]$

(c) isotope effect resulting from substitution of D for H at ortho positions

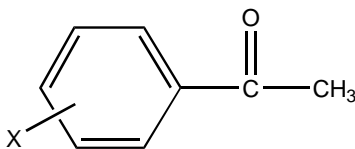
(d) substituent effect studies



Mechanism B

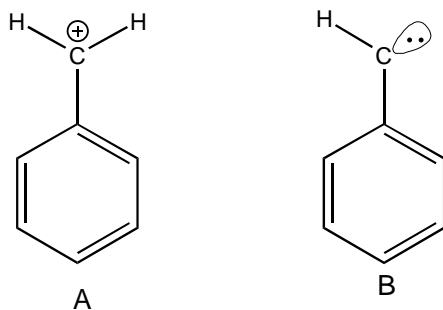


2. The acidity of various substituted acetophenones has been measured in DMSO. Would you expect the ρ value for a Hammett correlation to be positive or negative? Would you expect the best correlation with σ , σ^+ , or σ^- ? Justify your predictions. (15 points)

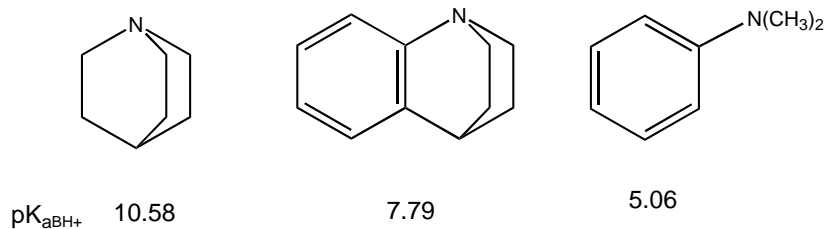


X	pK_{DMSO}
p-(CH ₃) ₂ N	27.48
p-CH ₃	25.70
m-(CH ₃) ₂ N	25.19
p-CH ₃	25.19
m-CH ₃	24.95
p-Ph	24.51
H	24.70
p-F	24.45
m-CH ₃ O	24.52
p-Br	23.81
p-Cl	23.78
m-F	23.45
m-Cl	23.18
m-Br	23.19
m-CF ₃	22.76
p-CF ₃	22.69
p-CN	22.04

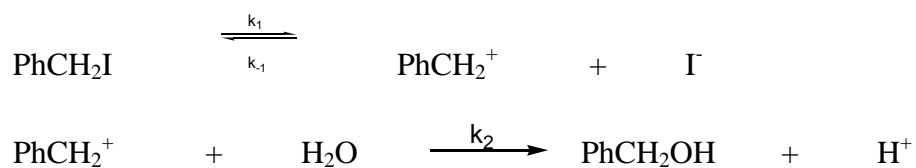
3. Computational comparison of structures of the benzyl cation (A) and singlet phenylcarbene (B) indicates a much greater double bond character for the exocyclic C-C bond in A than in B. Provide a rationalization of this difference. (15 points)



4. What can be concluded from the following pK_a data about the effect of an attached aryl group on the basicity of a nitrogen unshared pair? Explain. (You may find it helpful to include diagrams in your explanation.) (15 points)



5. Derive a complete kinetic expression for the reaction of benzyl iodide to form benzyl alcohol, assuming an S_N1 pathway with a reversible first step. Show your work for full credit. (15 points)



6. In class we discussed how pK_a 's may be determined for the conjugate acids of weak bases (e.g., Bunnett's substituted anilines and the H_0 scale). Devise an experimental process that might be used to study pK_a 's for weak acids (e.g., hydrocarbons). Explain your procedure, describing what type of solvent system (and added base) you would use. (Your thought processes are more important here than whether your method is the best one. Do a good job of explaining!) (20 points)