Organic Cumulative Exam

April 19,1997

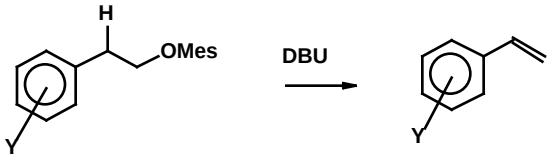
I. The Hammett Equation:

$$\log(k/k_0) = \sigma\rho$$

Is often the most used of all linear free energy relationships.

1. (10) Suppose that you needed to determine a σ value for a new substituent, lets say the nitrosamine group, -N(NO)CH_3. Indicate in detail how you would do this.

2. (10) You are investigating the mechanism of DBU (diazabicycloundecane) catalyzed elimination of methanesulfonates shown below. Describe in detail how you would go determining the value of ρ for this reaction.



3. (14) Indicate the sign of σ for each of the following substituents: p-NH_2, p-NO_2, p-CH_3O, m-CH_3O, m-NH_2, m-H, m-CO_2H.

4. (16) The magnitudes of σ for the following substituents are:

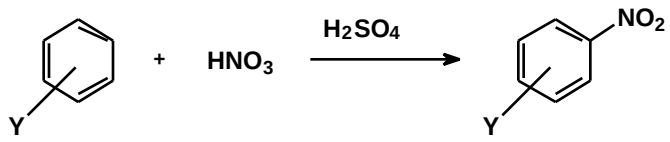
Subst.	σ-meta	σ-para
F	+0.34	+0.06
Cl	+0.37	+0.23

Explain why σ-para for F is so much smaller than: (a) σ-meta and (b) σ-para for Cl.

5. (10) What are σ_+ and σ_- constants and under what circumstances are they employed?

6. (28) For each of the following familiar transformations, show the transition state structure for the rate determining step and predict the sign of ρ and its approximate magnitude.

1.



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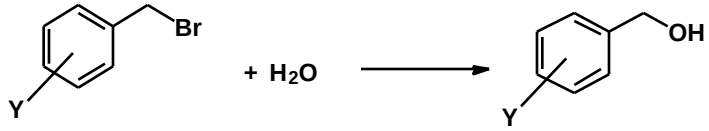

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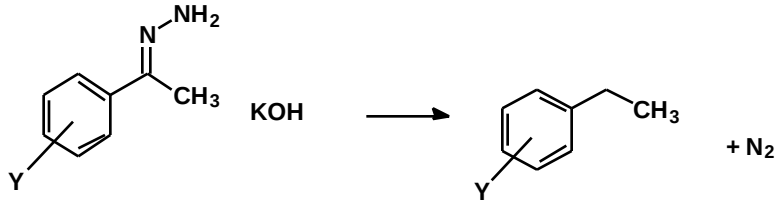

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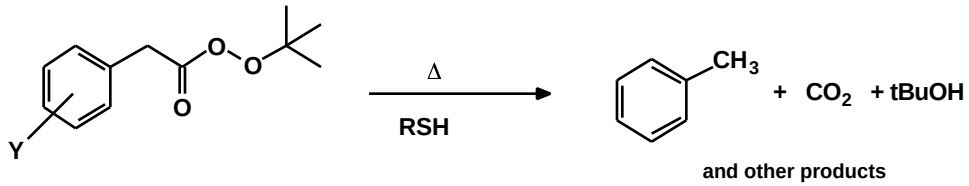

7. (10) The base catalyzed reaction of aryl nitriles with H_2S to give thioamides exhibits a ρ value of +2.14. Give a mechanism for this transformation. Indicate which step is likely to be rate determining and draw a transition state which is consistent with the ρ value.

II. (6) Another useful linear free energy relationship involves the effect of solvent. The Grunwald-Winstein (G-W) equation is

$$\log\left(\frac{k}{k_0}\right) = mY$$

The solvolysis of ethyl bromide exhibits an m of 0.34. What does this mean?

III. (6) Is the Diels-Alder reaction of butadiene with substituted styrenes expected to have large Hammett ρ values and large G-W m values? Explain.