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Chem 30 – Section 7

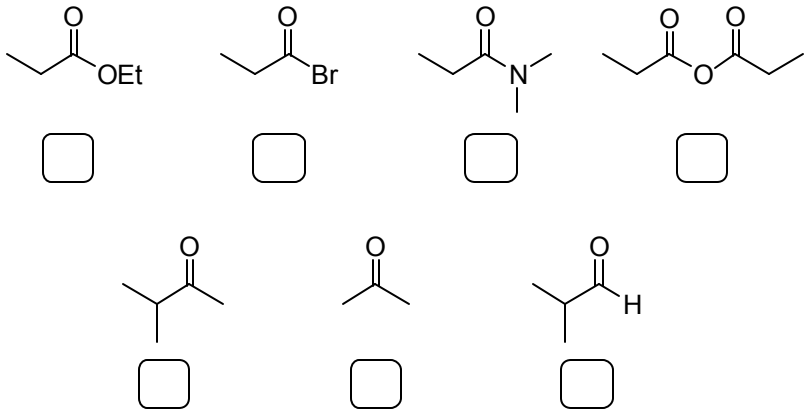
Section Practice Exam II

Whether problems old
Or problems new,
You'd better practice,
Or you'll fail exam II.

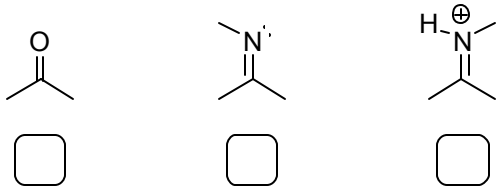
-- Anonymous TF

Problem 1

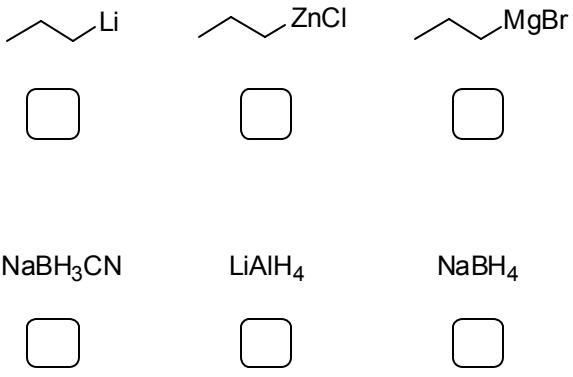
a) Rank the following series of electrophiles in order of decreasing reactivity towards methylmagnesium bromide.



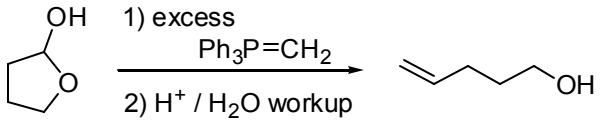
b) Rank this series of electrophiles in order of decreasing reactivity towards sodium borohydride.



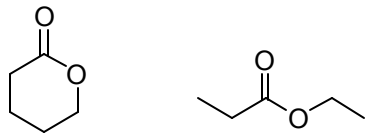
c) Rank this series of nucleophilic reagents in order of decreasing reactivity towards acetone.



Problem 2 (Problem Set #2, 1999). Provide a mechanism for the following reaction.

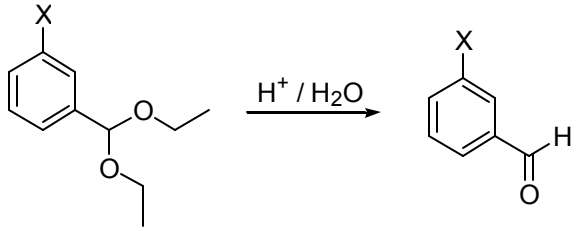


Problem 3 (Problem Set #3, 1999). Compound **A** reacts with methylamine considerably faster than compound **B**. Provide an explanation for this observation.



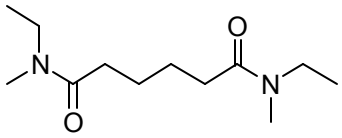
A **B**

Problem 4 (Problem Set #3, 2000). Provide an explanation for the following data concerning the rate of hydrolysis of aryl diethyl acetals.



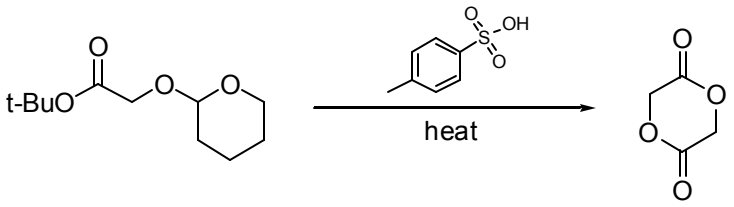
X	log *k*
OMe	2.66
Me	3.07
H	2.86
NO_2	0.39

Problem 5 (based on Problem Set #3, 1999). Provide an efficient synthesis of compound **C** using starting materials containing no more than four carbon atoms.

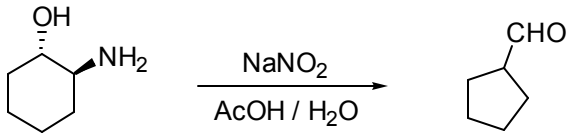


C

Problem 6 Provide a mechanism for the following transformation.



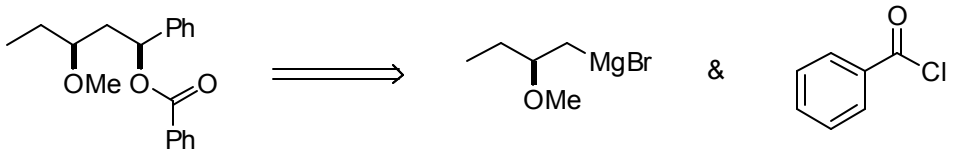
Problem 7 (A section problem repeat originally from the Fall 2003 Chem 30 Exam III Review Session). The amine below undergoes the following reaction when treated with sodium nitrite in the presence of acid.



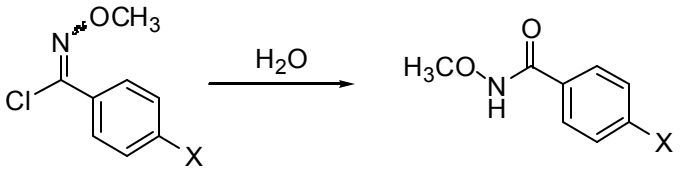
a) Provide an arrow formalism mechanism for this transformation

b) Draw a Newman projection showing the orbitals that interact in the step where the nitrogen atom attached to the ring is lost.

Problem 8 Provide an asymmetric synthesis of the compound below using the two indicated starting materials and any inorganic reagents that meet your fancy.



Problem 9 James Johnson and coworkers at Texas Woman's University recently studied the hydrolysis of O-methylbenzohydroximoyl chlorides.

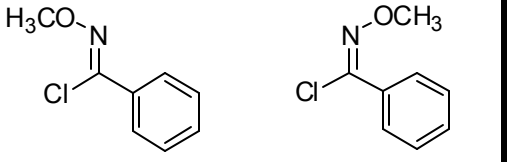


1

Johnson. *J Org. Chem.* **1996**, *61*, 45.

a) The rate of this reaction increases when **X** becomes more electron donating (the slope of the Hammett plot is negative and large). Propose an "arrow pushing" mechanism that is consistent with this observation.

b) The (*Z*)-isomer of **1** is about two orders of magnitude more reactive towards hydrolysis than the (*E*)-isomer. Drawing on your knowledge of molecular orbital theory, provide an explanation for this observation.



(*Z*)-**1** (more reactive)

(*E*)-**1**