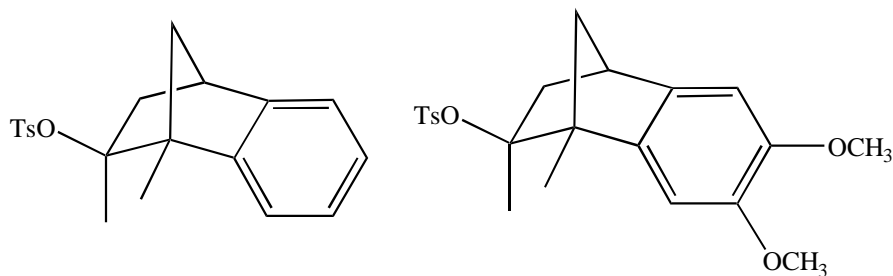
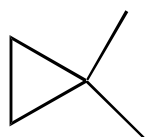


CHE 45: Physical Organic Chemistry
 Test 2b
 January 31, 1995

1. Of each of the following pairs of compounds, which would you expect to solvolyze more rapidly? Why? (8 points each part)

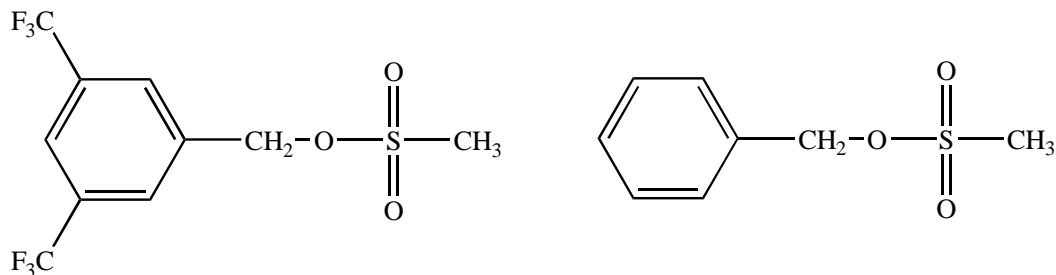


(a)

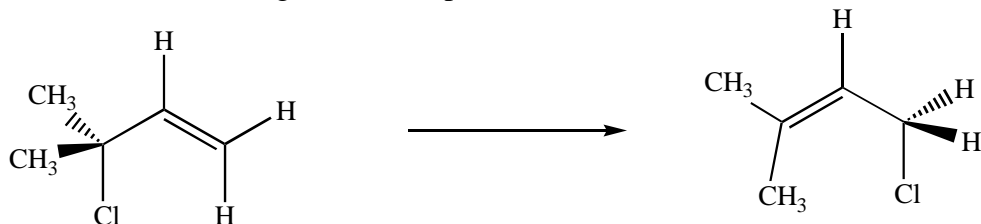


(b)

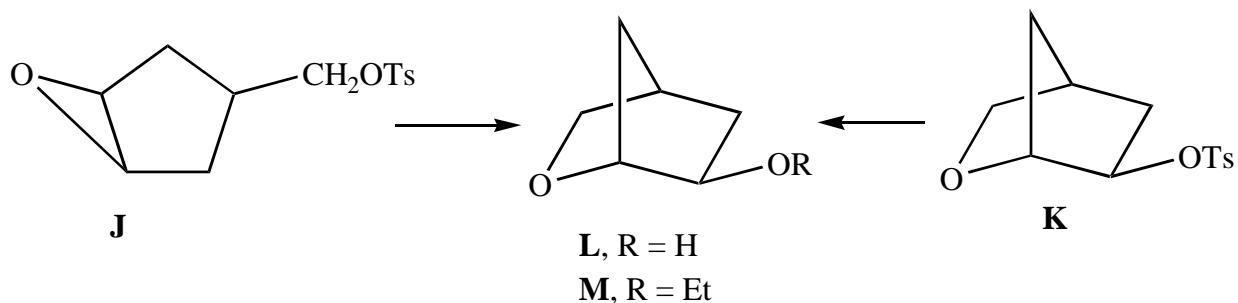
(c)



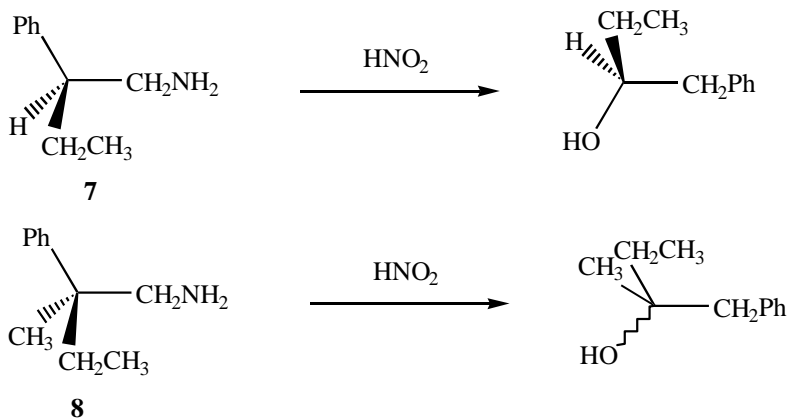
2. Acetolysis of γ,γ -dimethylallyl chloride gives some rearranged starting material as shown in the equation below. The rate of reaction is unaffected by added chloride ion. Propose a mechanism for this rearrangement. (15 points)



3. Offer a mechanistic interpretation of each of the following phenomena. The isomeric tosylates **J** and **K** give an identical product mixture consisting of the alcohol **L** and ether **M** when solvolized in aqueous ethanol. (15 points)



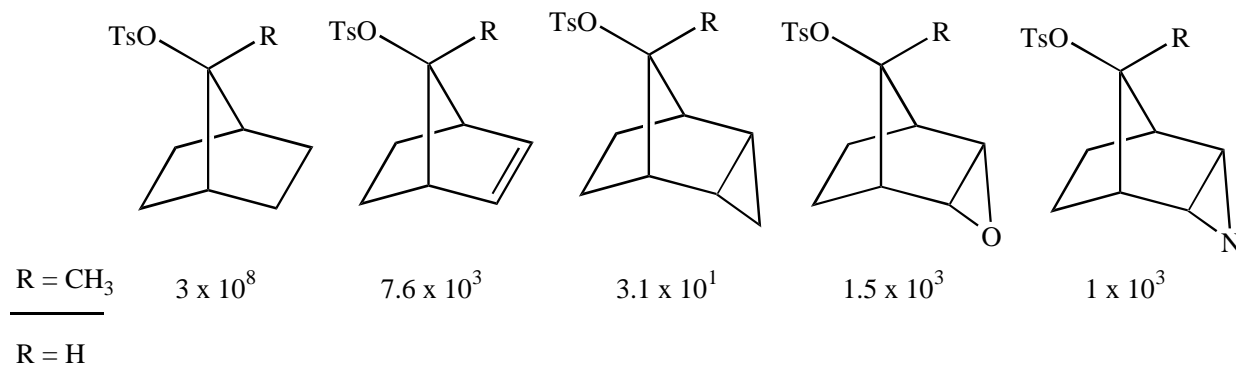
4. Deamination of **7** proceeds with phenyl migration to give 97 percent inversion of configuration at the migration origin, while **8** undergoes the analogous reaction with only 54 percent inversion of configuration. Propose a mechanistic explanation for these observations. (15 points)



5. Consider the relative solvolysis rates of compounds shown below. (16 points)

(a) What does this series tell us about the ability of a methyl group to stabilize a positive charge in the presence of neighboring group participation relative to its ability in the absence of such participation?

(b) What does this series tell us about the relative abilities of the groups shown at C2 and C3 in the bicyclic system to participate in ionization of the leaving group at C7?



6. When 37 is solvolyzed in trifluoroacetic acid, approximately equimolar amounts of 38 and 39 are obtained. Only 4 percent 40 is formed. Is this evidence for or against bridging by hydrogen? Explain. (15 points)

