

CHEM 346 – Organic Chemistry I (for Majors)

Instructor: Paul J. Bracher

Practice Hour Examination #2Monday, October 14th, 2013
1:10 p.m.

Student Name (Printed)	Solutions
Student Signature	

Please also write your name on the back of the exam

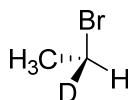
Scoring

Question	Points Earned	Points Available
1		15
2		25
3		25
4		20
5		15
TOTAL		100

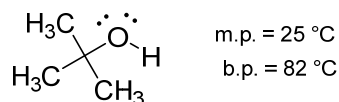
Original Problems, **Required Information in Answers**, and **Supplementary Explanation**

Problem 1. (15 points total, 3 points each) Determine whether the following five statements are true or false. Write out the full word “true” or “false” beside each statement; do not just write “T” or “F”. If any part of the statement is false, the entire statement is false.

- (i) TRUE If the *S* stereoisomer of compound **A** reacts with chloride ion (Cl^-) in an $\text{S}_{\text{N}}2$ reaction, the designation of the stereogenic carbon in the product will be *R*.

**A**

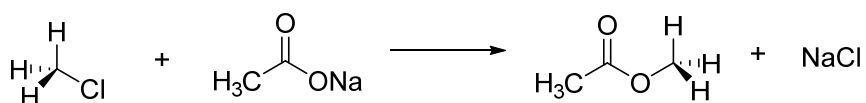
- (ii) TRUE Compound **B**, *tert*-butanol, is a polar, protic molecule that can be used as a solvent for E1 reactions.



m.p. = 25 °C
b.p. = 82 °C

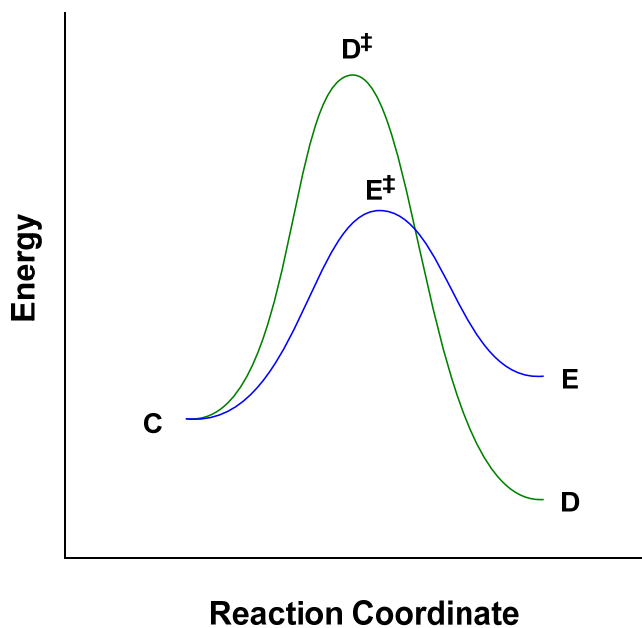
B

- (iii) FALSE Chloromethane and sodium acetate react to produce methyl acetate by an $\text{S}_{\text{N}}1$ mechanism.



The substitution occurs by an $\text{S}_{\text{N}}2$ mechanism.

For questions 1-(iv), 1-(v), and 2-(i), refer to the following figure that plots energy diagrams for the hypothetical competing reactions $C \rightarrow D$ and $C \rightarrow E$.



(iv) TRUE Product **E** is generated faster than product **D** from starting material **C**.

Yes, because the energy of activation (required to reach the transition state) is lower for E^\ddagger than D^\ddagger .

(v) TRUE Compound **E** could be produced from **D** via an intermediate, **C**, in an endothermic process

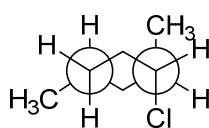
Problem 2. (25 points total, 5 points each) For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided.

(i) E If the system above is allowed to reach equilibrium, what will be the relative concentrations of compounds **C**, **D**, and **E**.

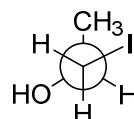
- (a) $[C] < [E] < [D]$
 (b) $[D] < [E] < [C]$
 (c) $[C] < [D] < [E]$
 (d) $[D] < [C] < [E]$
 (e) $[E] < [C] < [D]$

The equilibrium concentrations of stable species are controlled by their relative stabilities.

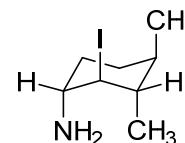
(ii) A Which of the following three-dimensional structures depicts an alkyl halide in a conformation suitable for E2 elimination?



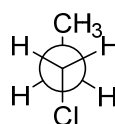
(a)



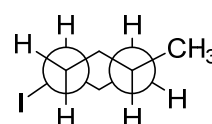
(b)



(c)



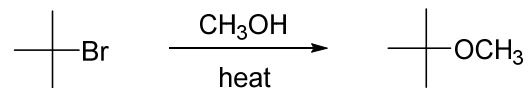
(d)



(e)

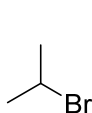
For elimination by an E2 mechanism, the halide leaving group and β -hydrogen should be anti-periplanar. In (a), the chloride is anti-periplanar to an (unlabeled) hydrogen on one of the “middle” methylene ($-\text{CH}_2-$) groups of the ring.

- (iii) D In the S_N1 reaction between methanol and *t*-butyl bromide, the orbital that is attacked by the nucleophile is:

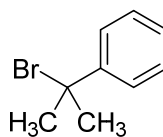


- (a) the backside of the σ bonding orbital of the C–Br bond
 (b) the σ^* antibonding orbital of the C–Br bond
 (c) the σ^* antibonding orbital of the C–H bond
 (d) an unhybridized *p* orbital on carbon
 (e) none of the above

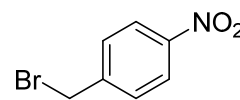
- (iv) B For which of the following compounds would heterolytic cleavage of the carbon–halogen bond be the most facile?



(a)



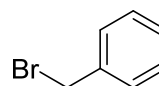
(b)



(c)



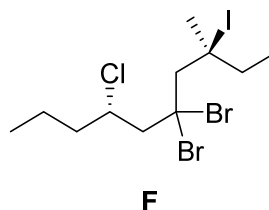
(d)



(e)

This question is equivalent to asking “which compound would generate the most stable carbocation?”

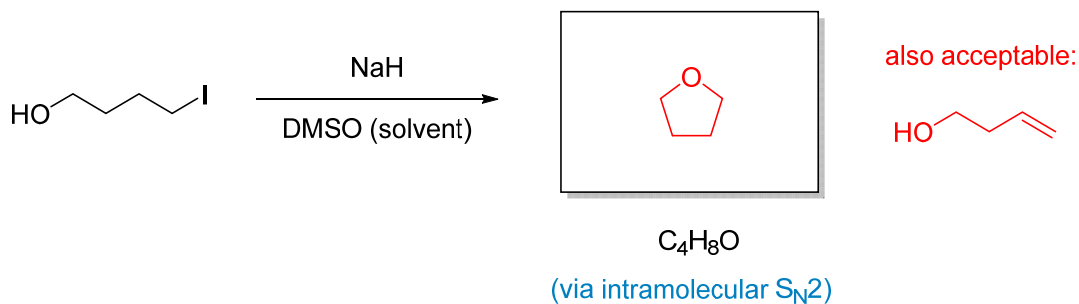
(v) A What is the IUPAC name of compound F.



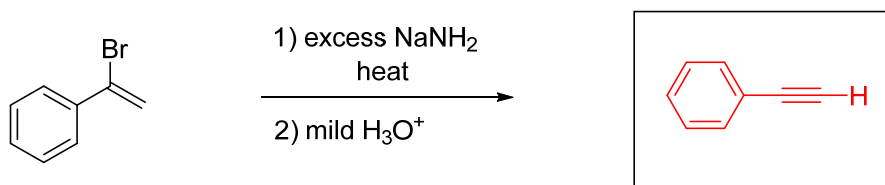
- (a) (3*S*,7*S*)-5,5-dibromo-7-chloro-3-iodo-3-methyldecane
 (b) (3*S*,7*R*)-5,5-dibromo-7-chloro-3-iodo-3-methyldecane
 (c) (4*S*,8*R*)-6,6-dibromo-4-chloro-8-iodo-8-methyldecane
 (d) (4*S*,8*S*)-6,6-dibromo-4-chloro-8-iodo-8-methyldecane
 (e) (4*S*,8*R*)-6,6-dibromo-4-chloro-8-iodo-8-methylundcane

Problem 3. (25 points total, 5 points each) Reactions. The following chemical reactions are missing their starting materials, reagents, or products. Write the missing compounds into the empty boxes below, as appropriate. In some cases, there will be more than one correct answer that will merit full credit.

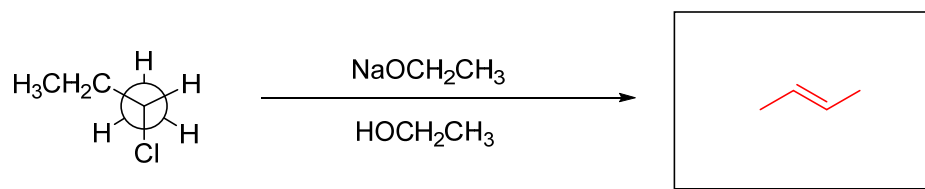
(i) (5 points)



(ii) (5 points)

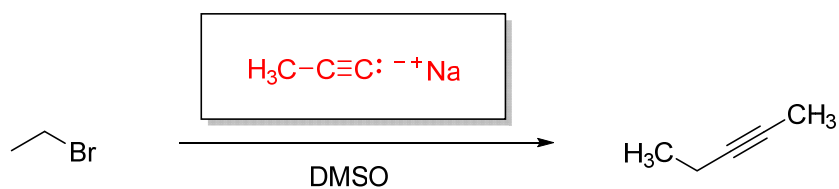


(iii) (5 points)

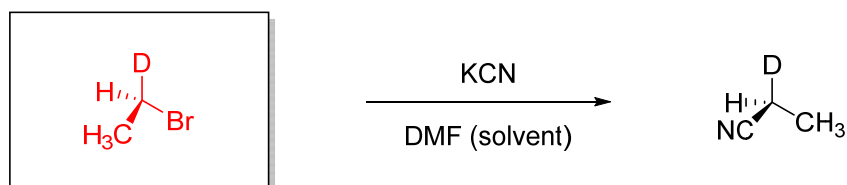


Don't be fooled by how the starting material is drawn! The major product will be produced from E2 elimination involving deprotonation at the methylene ($-\text{CH}_2-$) group to produce the disubstituted, *trans*-alkene.

(iv) (5 points)

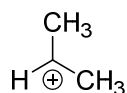


(v) (5 points)

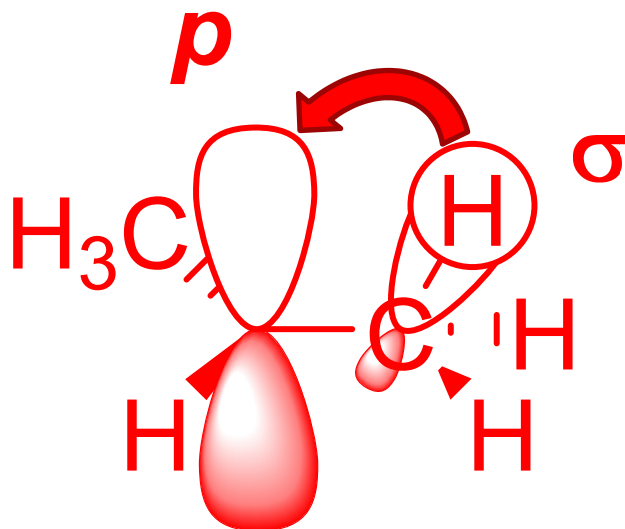


Problem 4. (20 points total) Short answers.

- (i) (10 points) Hyperconjugation is responsible for stabilizing carbocations substituted with alkyl groups. Draw a picture that shows one hyperconjugative interaction for carbocation **G**. Label the identity of the filled orbital and the empty orbital that are interacting in your picture.

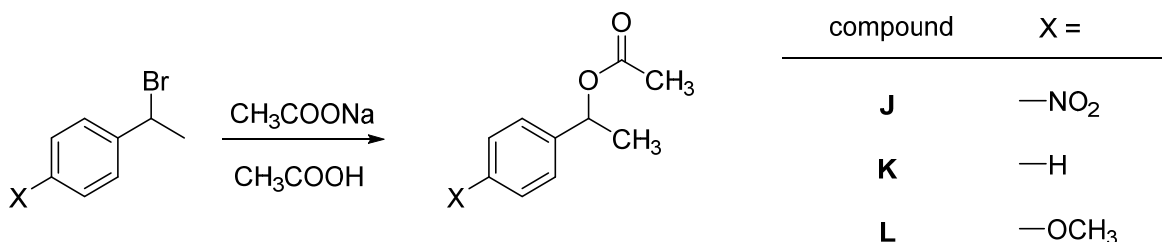


G



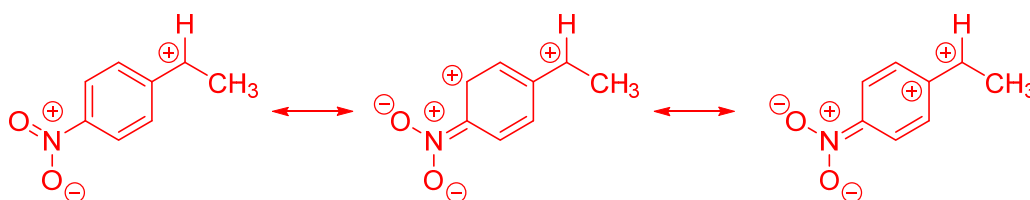
A filled $\sigma_{\text{C-H}}$ bonding orbital overlaps with the empty, unhybridized p orbital on the carbon with the positive formal charge.

(ii) (10 points) Explain why the substitution reaction drawn below is slowest for compound J and fastest for L.

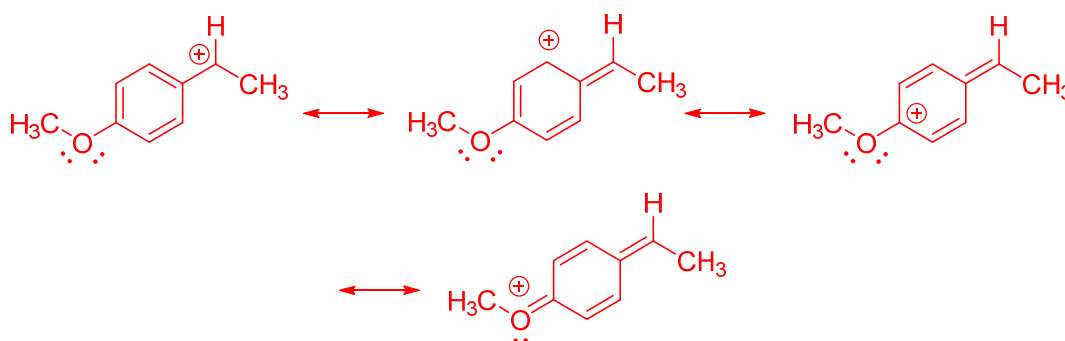


This is a substitution reaction, and the alkyl halide is secondary (2°) and benzylic. This substrate suggests an S_N1 mechanism, as the carbocation would be stabilized by both a resonance effect and hyperconjugation. The generation of the carbocation is the rate-determining step of S_N1 reactions, and the relative rates of the reactions of J, K, and L will depend on the relative stabilities of the carbocations.

Nitro (—NO₂) groups are electron withdrawing by a resonance effect and will destabilize benzylic carbocations:

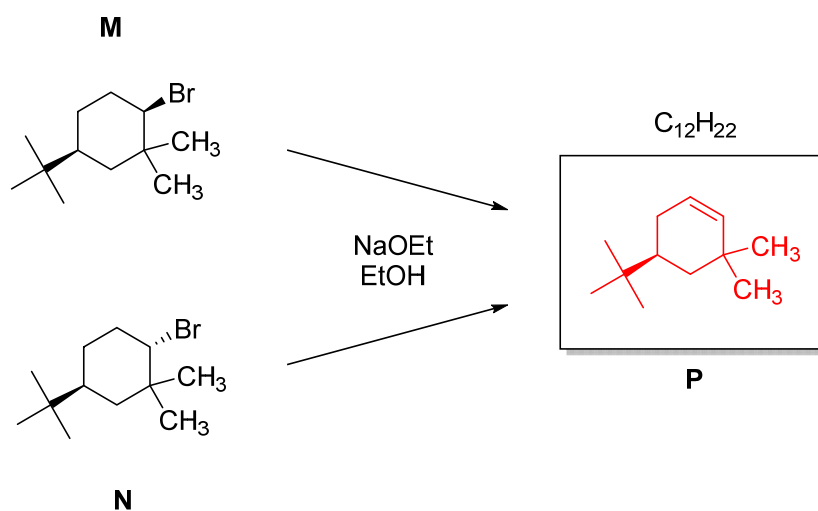


Methoxy (—OCH₃) groups are electron donating by a resonance effect and will stabilize benzylic carbocations:



Problem 5. (15 points total)

Consider the following reactions:

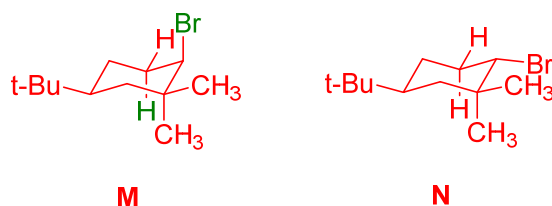


(i) (5 points) Draw the structure of the common product, compound **P**, in the box above.

The molecular formula given, $C_{12}H_{22}$, indicates the loss of HBr . That suggests an elimination reaction, and the only β -hydrogens (relative to the halogen) to eliminate produce the product shown above.

(ii) (10 points) Explain why compound **N** reacts more slowly than compound **M** to produce the same product. You will want to draw things here.

Let's draw 3-D structures for **M** and **N**:



The energetically preferred conformations of **M** and **N** will have the bulky *tert*-butyl groups in equatorial positions. With the *t*-Bu group equatorial in stereoisomer **M**, the bromine will occupy an axial position while in **N**, the bromine will be in an equatorial position. In **M**, the bromine is in an anti-periplanar geometry with a β -hydrogen (shown in green). This is the preferred geometry for $E2$ elimination, which is why it occurs at a relatively high rate. In the structure for **N**, the bromine is not anti to either of the β -hydrogens, so the elimination reaction will proceed very slowly (by $E2$, with an inversion of the chair, first) or by an $E1$ mechanism.