WILFRID LAURIER UNIVERSITY
Organic Chemistry I (CHEM 202/204)

Mid-term Test 2A
November 7, 2014

Answers

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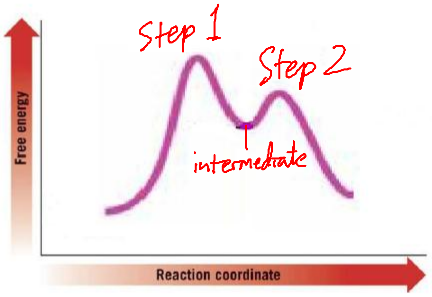
1. The energy diagram below represents which pair of reactions?



[✓ (a) SN1 and E1]
(b) SN2 and E2
(c) SN1 and E2
(d) SN2 and E1

SN1 and E1 have 2 mechanistic steps

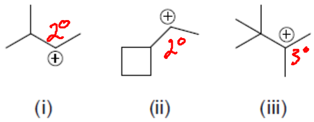
SN2 and E2 have 1 mechanistic step

2. With regard to the energy diagram shown in Question 1, which of the following statements is true?

(a) The 2nd step is the rate-limiting step. — False - 1st step has higher activation energy
(b) The reaction is exergonic. — False - product higher in energy ∴ endergonic
(c) The transition state for the 2nd step is more similar in structure to the final product than to the intermediate. - False - By, Hammond postulate, more similar to intermediate
[✓ (d) The equilibrium constant, K_{eq}, for this reaction is < 1.]

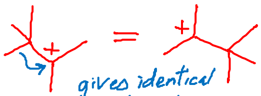
based on $\Delta G = -RT \ln K_{eq}$
→ $K_{eq} < 1$ makes ΔG positive ∴ endergonic

3. Which of the following carbocations are likely to undergo a carbocation rearrangement?

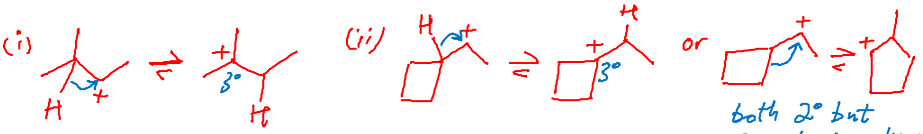


[✓ (a)] i and ii
(b) i and iii
(c) ii and iii
(d) all of these

(iii)

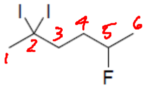


gives identical carbocation



both 2° but ring strain relieved

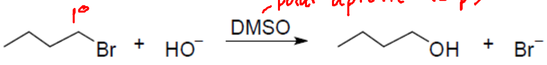
4. What is the IUPAC name of the compound shown below?



(a) 2,2-diiodo-5-fluorohexane
(b) 2-fluoro-5,5-diiodohexane
[✓ (c)] 5-fluoro-2,2-diiodohexane
(d) 5,5-diiodo-2-fluorohexane

- numbered from left so that substituents are at 2,2,5 – not 2,5,5
- substituents listed alphabetically and "di" is not alphabetized.

5. Consider the reaction of butyl bromide with HO⁻ ion.



polar aprotic helps

Which of the following statements is true?

- substrate : 1°
- reagent : not −O^tBu

∴ SN2
–bimolecular
–rate depends on [HO⁻]

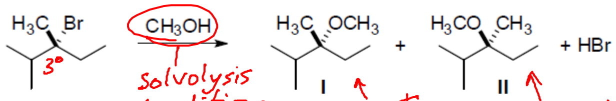
[✓ (a)] If the concentration of hydroxide, HO⁻, is doubled, the rate will double.
(b) If the substrate, bromobutane, was replaced with iodobutane, the reaction would proceed slower.
(c) If the solvent was changed to H_2O, the reaction would proceed faster.
(d) If HS⁻ was used in place of HO⁻, the reaction would proceed faster.

better LG so would be faster

weaker nucleophile in polar aprotic solvent ∴ slower reaction

solvates HO−, reduces its reactivity ∴ slows reaction

6. Consider the following reaction then choose the statement that is correct.



solvolysis conditions

retention

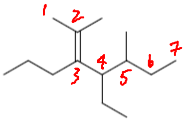
inversion

∴ SN1

(a) **I** would be formed as the only product.
(b) **II** would be formed as the only product.
(c) An equal mixture of **I** and **II** would be formed.
[✓ (d)] An *un*equal mixture of **I** and **II** would be formed. ← ∴

slightly more owing to tight ion pair

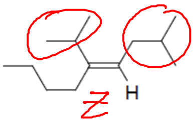
7. What is the IUPAC name of the compound shown below?



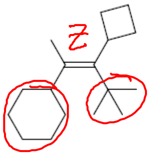
(a) 4-ethyl-3,6-dimethyl-5-propylhept-5-ene
(b) 4-ethyl-3-methyl-5-(propan-2-ylidene)octane
(c) 2,5-dimethyl-4-ethyl-3-propylhept-2-ene
[✓ (d)] 4-ethyl-2,5-dimethyl-3-propylhept-2-ene

- parent chain must include double bond
- numbered from side closer to double bond
- substituents listed alphabetically; "di" not alphabetized

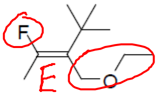
8. Which of the following alkenes possesses an *E* double bond?



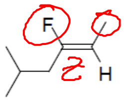
(a)



(b)



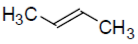
[✓ (c)]



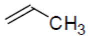
(d)

– higher priority substituents – based on Cahn-Ingold-Prelog rules – are circled.

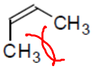
9. Rank the following alkenes from most stable to least stable.



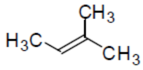
(i)



(ii)



(iii)



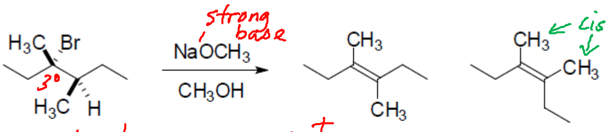
(iv)

[✓ (a)] iv (most stable) > i > iii > ii (least stable)
(b) ii (most stable > iii > i > iv (least stable)
(c) iv (most stable) > iii > i > ii (least stable)
(d) ii (most stable) > i > iii > iv (least stable)

- hyperconjugation makes more substituted double bonds more stable
- cis less stable than trans (steric destabilization)

10. Consider the following reaction then choose the statement that is correct.

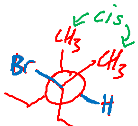
3° + strong base = E2



I II

only product

↑ requires anticoplanar arrangement

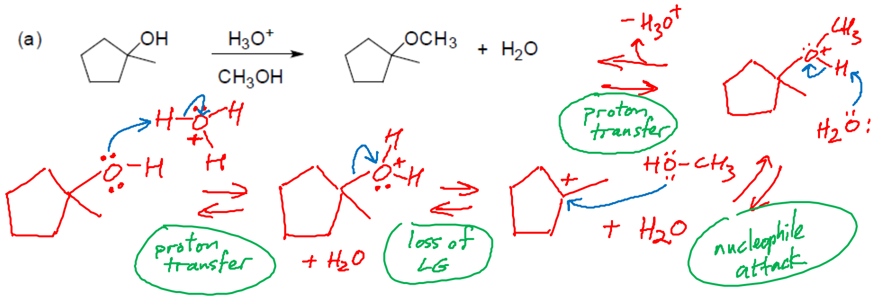


only conformation that allows E2

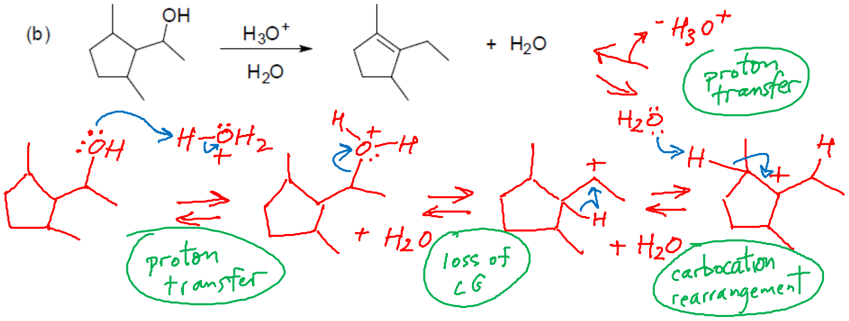
(a) The reaction is stereo*specific* and yields **I** as the *only* product.
[✓ (b)] The reaction is stereo*specific* and yields **II** as the *only* product.
(c) The reaction is stereo*selective* and yields **I** as the *major* product.
(d) The reaction is stereo*selective* and yields **II** as the *major* product.

11. Provide a detailed arrow-pushing mechanism for 1 of the following 2 reactions. For either reaction, your mechanism must account for the fact that H_3O^+ is a catalyst. **(4)**

(a)

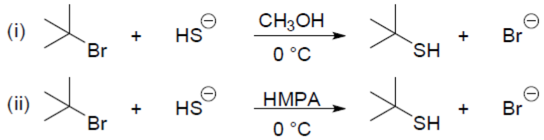


(b)



12. For 3 of the following 4 pairs of reactions, indicate the mechanism taking place (SN1, SN2, E1, E2), state which reaction would occur faster and explain why. Note: For each reaction pair, the same reaction mechanism will occur. **(9)**

(a)

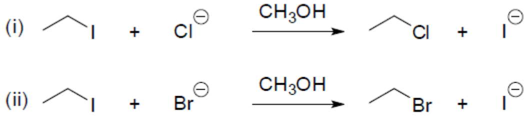


Mech	Faster
SN1	(i)

Explanation:

- 3° substrates with weak base → SN1
- (i) faster because polar protic solvent stabilizes polar transition state

(b)



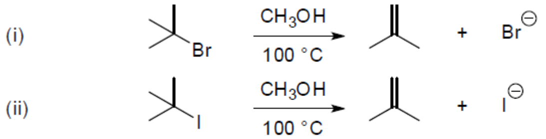
Mech	Faster
SN2	(ii)

Explanation:

- 1° substrates, reagent not ^-OtBu ∴ SN2
- (ii) faster because Br^- larger, less solvated, less stable, more reactive in polar protic solvent

12. For 3 of the following 4 pairs of reactions, indicate the mechanism taking place (SN1, SN2, E1, E2), state which reaction would occur faster and explain why. Note: For each reaction pair, the same reaction mechanism will occur. **(9)**

(c)

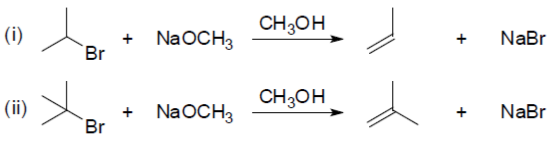


Mech	Faster
E1	(ii)

Explanation:

- 3° substrates, solvolysis conditions ∴ E1
- (ii) faster because I^- is better LG than Br^- (weaker base)

(d)



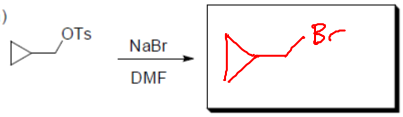
Mech	Faster
E2	(ii)

Explanation:

- 2° and 3° substrate with strong base ∴ E2
- (ii) faster because transition state leading to more highly substituted double bond more stable

13. For 7 of the following 9 reactions, provide the structure of the major organic product, including stereochemistry when required. **(7)**

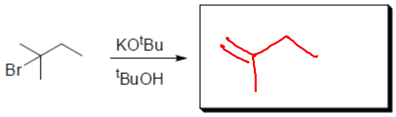
(a)



- substrate 1°
- reagent not $-O^tBu$

∴ SN2

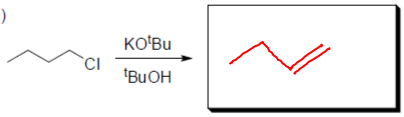
(b)



- substrate 3°
- reagent is $-O^tBu$

∴ E2 yielding Hofmann product

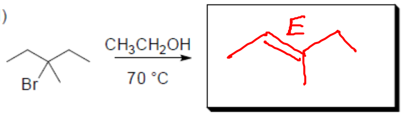
(c)



- substrate 1°
- reagent is $-O^tBu$

∴ E2

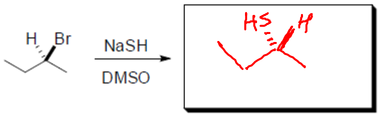
(d)



- substrate 3°
- solvolysis conditions, high temp

∴ E1 yielding Zaitsev product
→ E is major

(e)

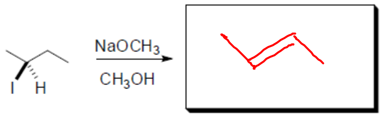


- substrate 2°
- reagent – weak base

∴ SN2 with inversion

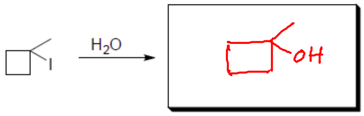
13. For 7 of the following 9 reactions, provide the structure of the major organic product, including stereochemistry when required. **(7)**

(f)



- substrate 2°
- reagent - strong base
- E2, trans major

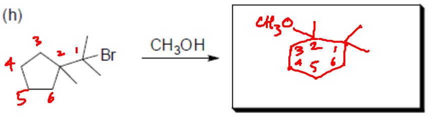
(g)



- substrate 3°
- solvolysis conditions

∴ SN1

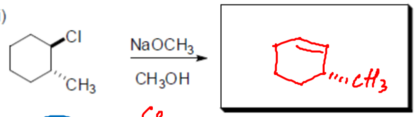
(h)



- substrate 3°
- solvolysis conditions

∴ SN1 ... with rearrangement

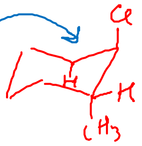
(i)



- substrate 2°
- reagent strong base

∴ E2 ... with Hofmann product

E2 occurs here

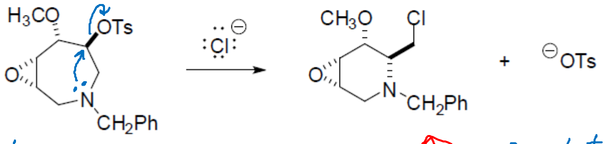


← E2 can't occur here

BONUS QUESTION (1.5)

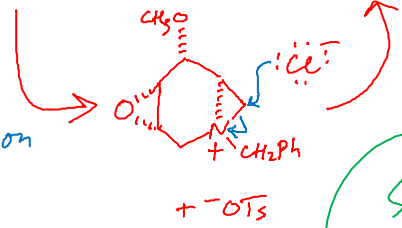
A correct answer to the following question will earn you 1.5 bonus points. No part marks will be awarded.

Provide a detailed arrow-pushing mechanism for the following transformation.



- 2° substrate
- weak base

∴ SN2... with inversion



- 1° substrate
- reagent not OtBu

∴ SN2

See Q 7.81
Klein p339