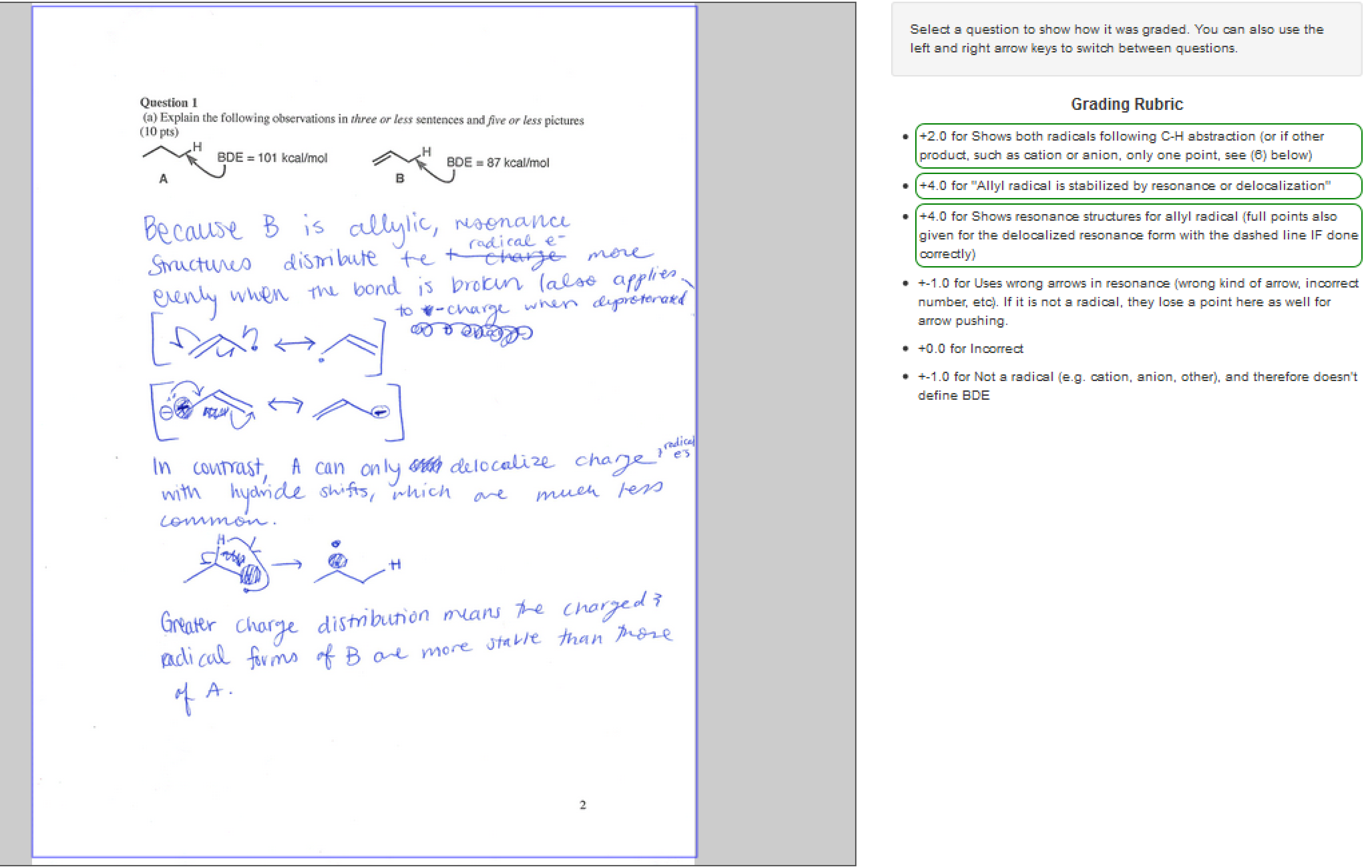


Question 1

(a) Explain the following observations in *three or less* sentences and *five or less* pictures (10 pts)

Because B is allylic, resonance structures distribute the ~~+ charge~~ radical e⁻ more evenly when the bond is broken (also applies to ~~+~~ -charge when deprotonated)

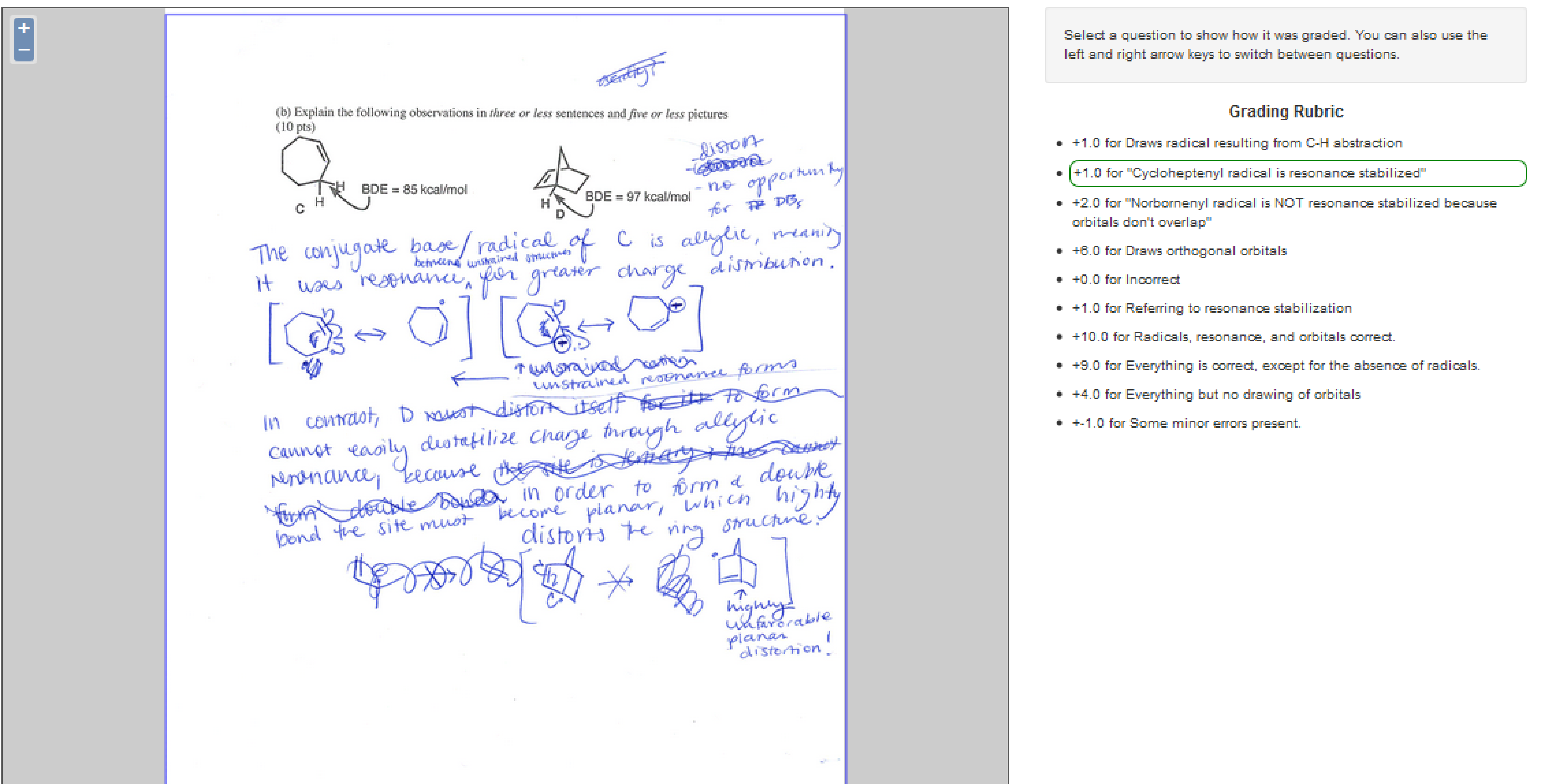
In contrast, A can only ~~[illegible]~~ delocalize charge, radical e⁻s with hydride shifts, which are much less common.

Greater charge distribution means the charged & radical forms of B are more stable than those of A.

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- +2.0 for Shows both radicals following C-H abstraction (or if other product, such as cation or anion, only one point, see (6) below)
- +4.0 for "Allyl radical is stabilized by resonance or delocalization"
- +4.0 for Shows resonance structures for allyl radical (full points also given for the delocalized resonance form with the dashed line IF done correctly)
- +-1.0 for Uses wrong arrows in resonance (wrong kind of arrow, incorrect number, etc). If it is not a radical, they lose a point here as well for arrow pushing.
- +0.0 for Incorrect
- +-1.0 for Not a radical (e.g. cation, anion, other), and therefore doesn't define BDE



~~[illegible]~~

(b) Explain the following observations in *three or less* sentences and *five or less* pictures (10 pts)

- distort
- ~~[illegible]~~
- no opportunity for ~~[illegible]~~ DBs

The conjugate base/radical of C is allylic, meaning it uses resonance between unstrained structures for greater charge distribution.

← ~~unstrained cation~~ unstrained resonance forms

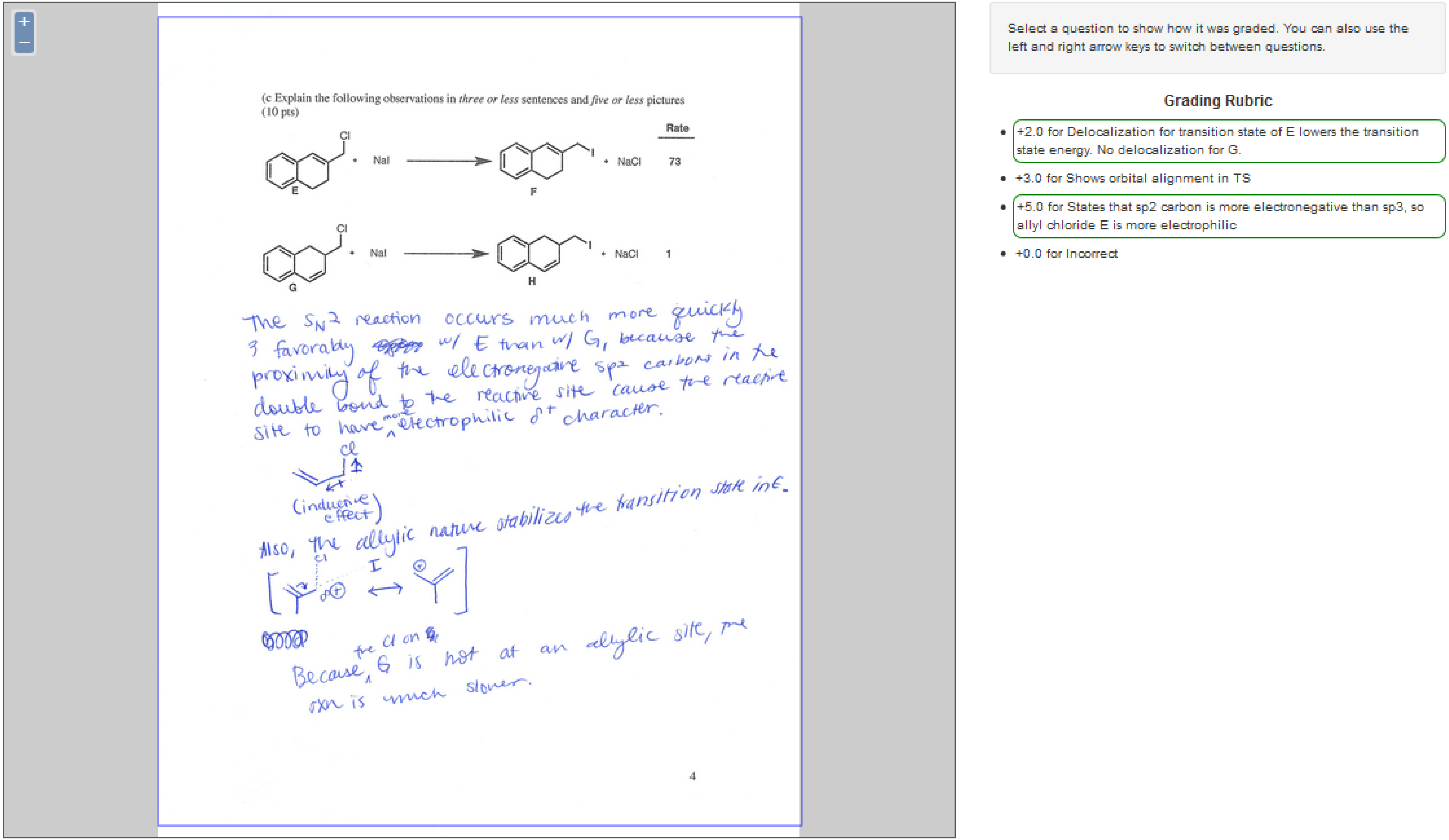
In contrast, D ~~must distort itself for it to form~~ cannot easily destabilize charge through allylic resonance, because ~~the site is tertiary + thus cannot form double bond~~ in order to form a double bond the site must become planar, which highly distorts the ring structure.

highly unfavorable planar distortion!

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- +1.0 for Draws radical resulting from C-H abstraction
- +1.0 for "Cycloheptenyl radical is resonance stabilized"
- +2.0 for "Norbornenyl radical is NOT resonance stabilized because orbitals don't overlap"
- +6.0 for Draws orthogonal orbitals
- +0.0 for Incorrect
- +1.0 for Referring to resonance stabilization
- +10.0 for Radicals, resonance, and orbitals correct.
- +9.0 for Everything is correct, except for the absence of radicals.
- +4.0 for Everything but no drawing of orbitals
- +-1.0 for Some minor errors present.



(c Explain the following observations in *three or less* sentences and *five or less* pictures (10 pts)

The S_N2 reaction occurs much more quickly 3 favorably w/ E than w/ G, because the proximity of the electronegative sp2 carbons in the double bond to the reactive site cause the reactive site to have more electrophilic δ^+ character.

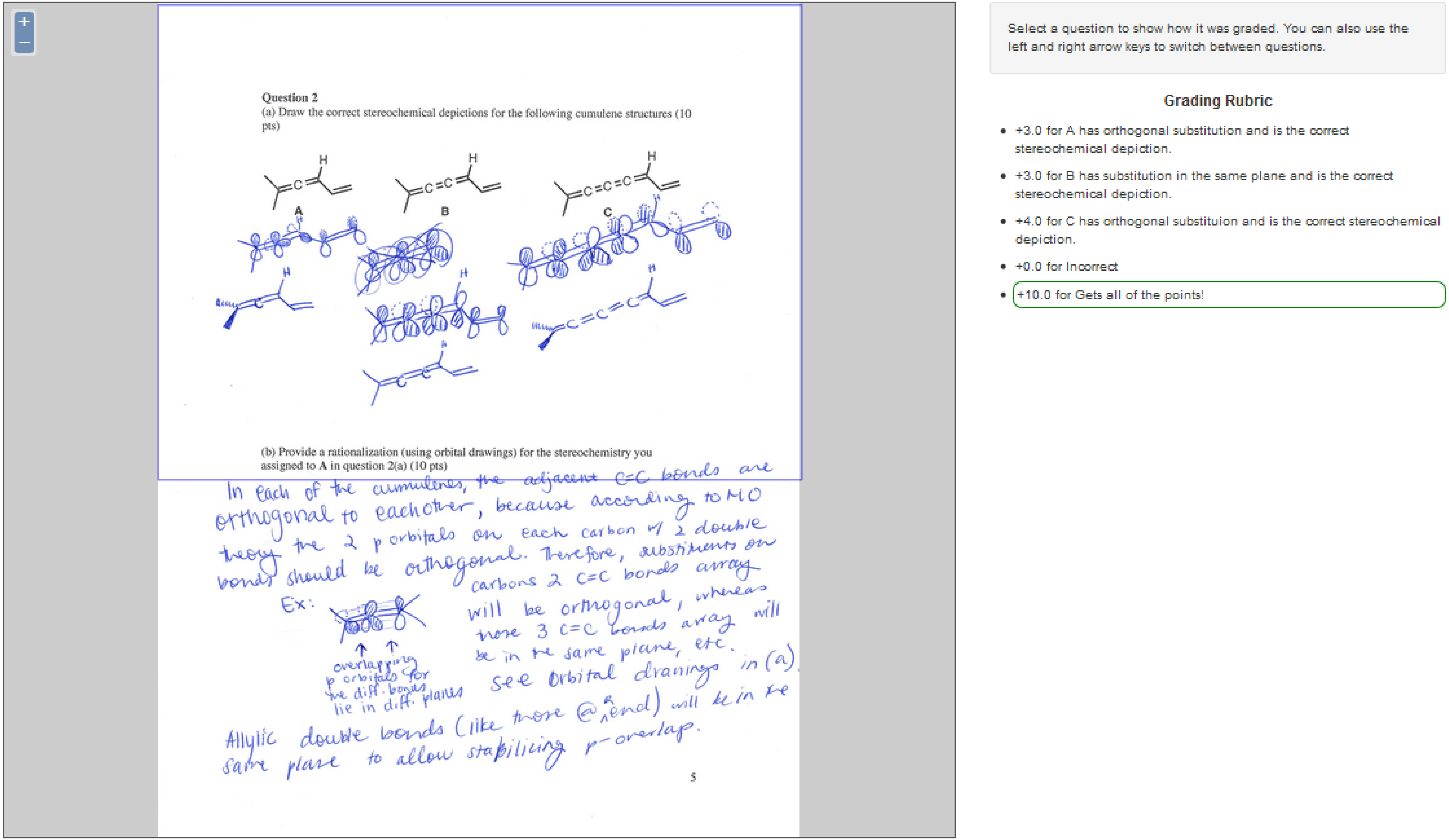
Also, the allylic nature stabilizes the transition state in E.

Because the Cl on G is not at an allylic site, the rxn is much slower.

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- +2.0 for Delocalization for transition state of E lowers the transition state energy. No delocalization for G.
- +3.0 for Shows orbital alignment in TS
- +5.0 for States that sp2 carbon is more electronegative than sp3, so allyl chloride E is more electrophilic
- +0.0 for Incorrect



Question 2

(a) Draw the correct stereochemical depictions for the following cumulene structures (10 pts)

(b) Provide a rationalization (using orbital drawings) for the stereochemistry you assigned to A in question 2(a) (10 pts)

In each of the cumulenes, the adjacent C=C bonds are orthogonal to eachother, because according to MO theory the 2 p orbitals on each carbon w/ 2 double bonds should be orthogonal. Therefore, substituents on carbons 2 C=C bonds away will be orthogonal, whereas those 3 C=C bonds away will be in the same plane, etc.

Ex:

overlapping p orbitals for the diff. bonds lie in diff. planes

See orbital drawings in (a).

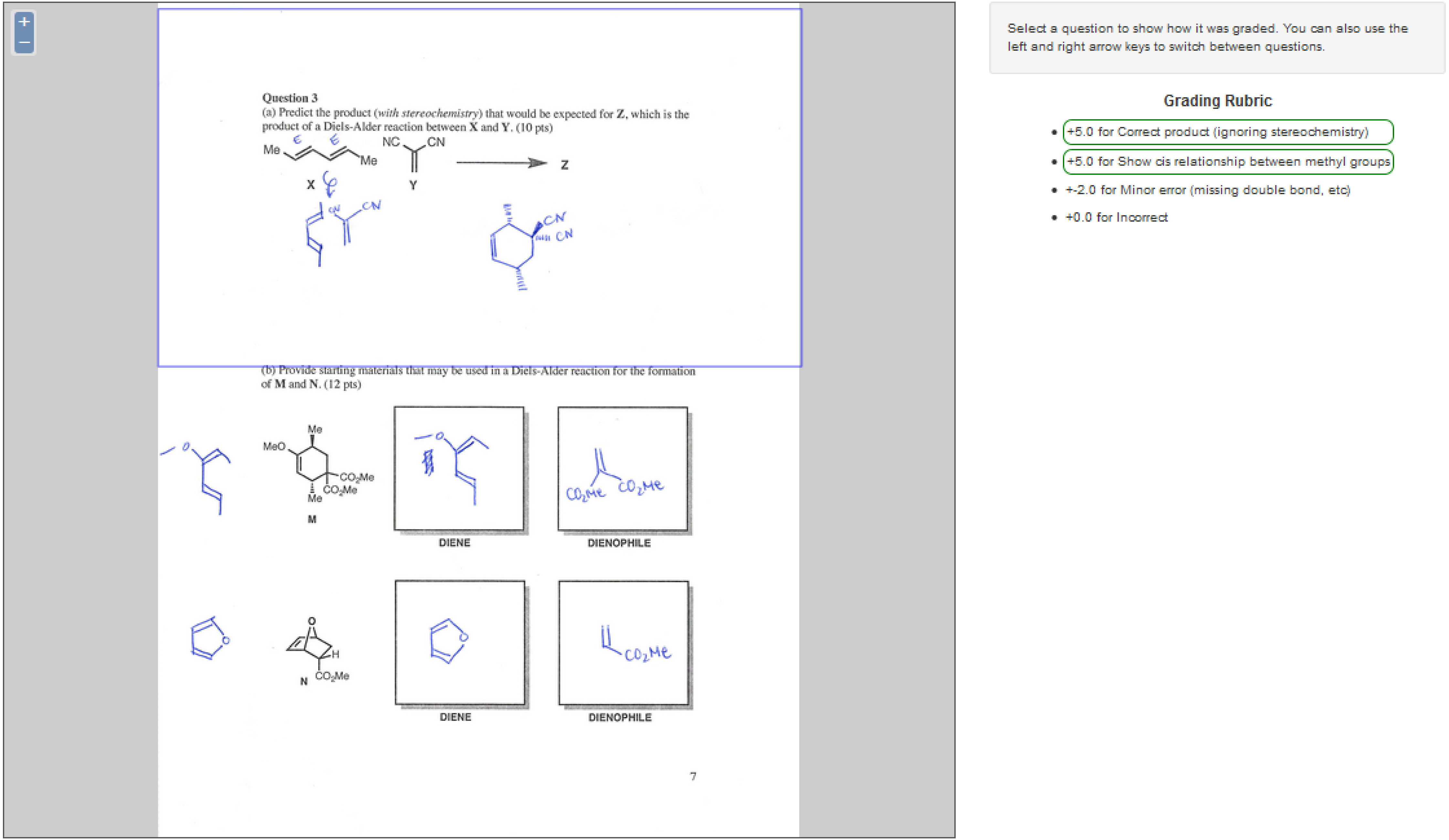
Allylic double bonds (like those @ R end) will be in the same plane to allow stabilicing p-overlap.

5

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- +3.0 for A has orthogonal substitution and is the correct stereochemical depiction.
- +3.0 for B has substitution in the same plane and is the correct stereochemical depiction.
- +4.0 for C has orthogonal substituion and is the correct stereochemical depiction.
- +0.0 for Incorrect
- +10.0 for Gets all of the points!



Question 3

(a) Predict the product (*with stereochemistry*) that would be expected for **Z**, which is the product of a Diels-Alder reaction between **X** and **Y**. (10 pts)

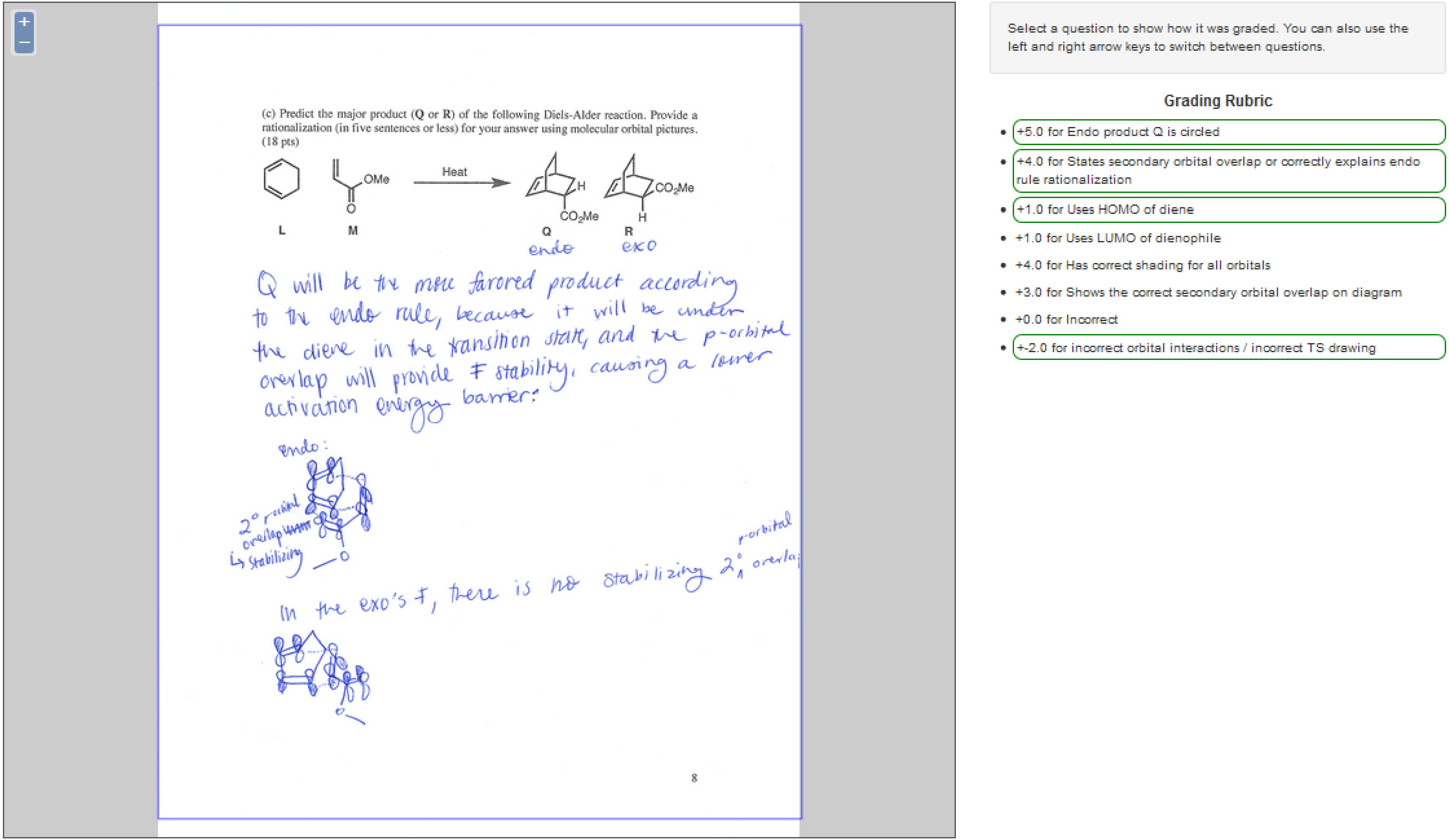
(b) Provide starting materials that may be used in a Diels-Alder reaction for the formation of **M** and **N**. (12 pts)

7

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- +5.0 for Correct product (ignoring stereochemistry)
- +5.0 for Show cis relationship between methyl groups
- +-2.0 for Minor error (missing double bond, etc)
- +0.0 for Incorrect



(c) Predict the major product (Q or R) of the following Diels-Alder reaction. Provide a rationalization (in five sentences or less) for your answer using molecular orbital pictures. (18 pts)

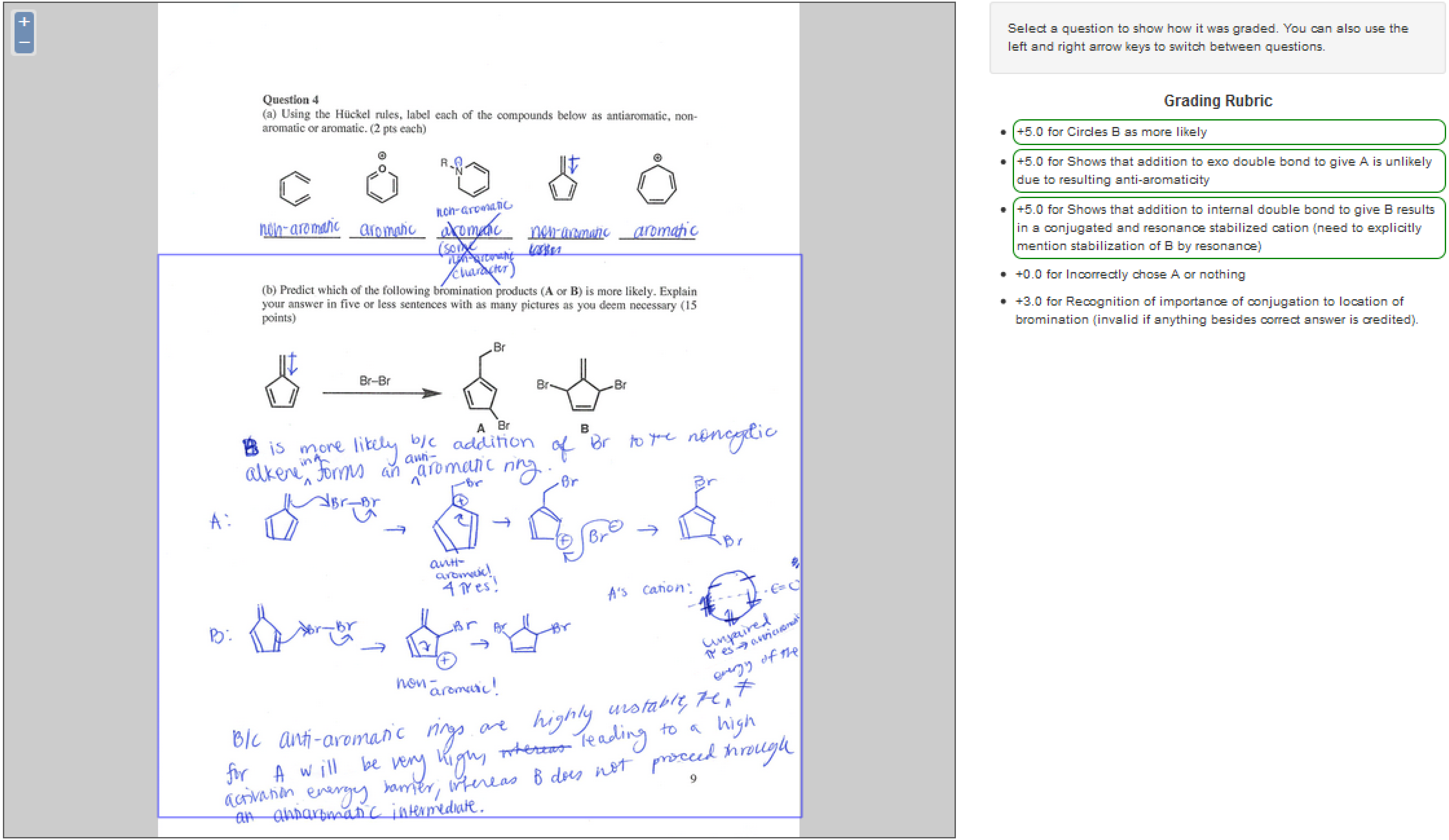
Q will be the more favored product according to the endo rule, because it will be under the diene in the transition state, and the p-orbital overlap will provide ‡ stability, causing a lower activation energy barrier.

In the exo's ‡, there is no stabilizing 2° p-orbital overla

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- +5.0 for Endo product Q is circled
- +4.0 for States secondary orbital overlap or correctly explains endo rule rationalization
- +1.0 for Uses HOMO of diene
- +1.0 for Uses LUMO of dienophile
- +4.0 for Has correct shading for all orbitals
- +3.0 for Shows the correct secondary orbital overlap on diagram
- +0.0 for Incorrect
- +-2.0 for incorrect orbital interactions / incorrect TS drawing



Question 4

(a) Using the Hückel rules, label each of the compounds below as antiaromatic, non-aromatic or aromatic. (2 pts each)

non-aromatic

aromatic

non-aromatic
~~aromatic (some non-aromatic character)~~

non-aromatic
~~[illegible]~~

aromatic

(b) Predict which of the following bromination products (A or B) is more likely. Explain your answer in five or less sentences with as many pictures as you deem necessary (15 points)

B is more likely b/c addition of Br to the noncyclic alkene in forms an anti-aromatic ring.

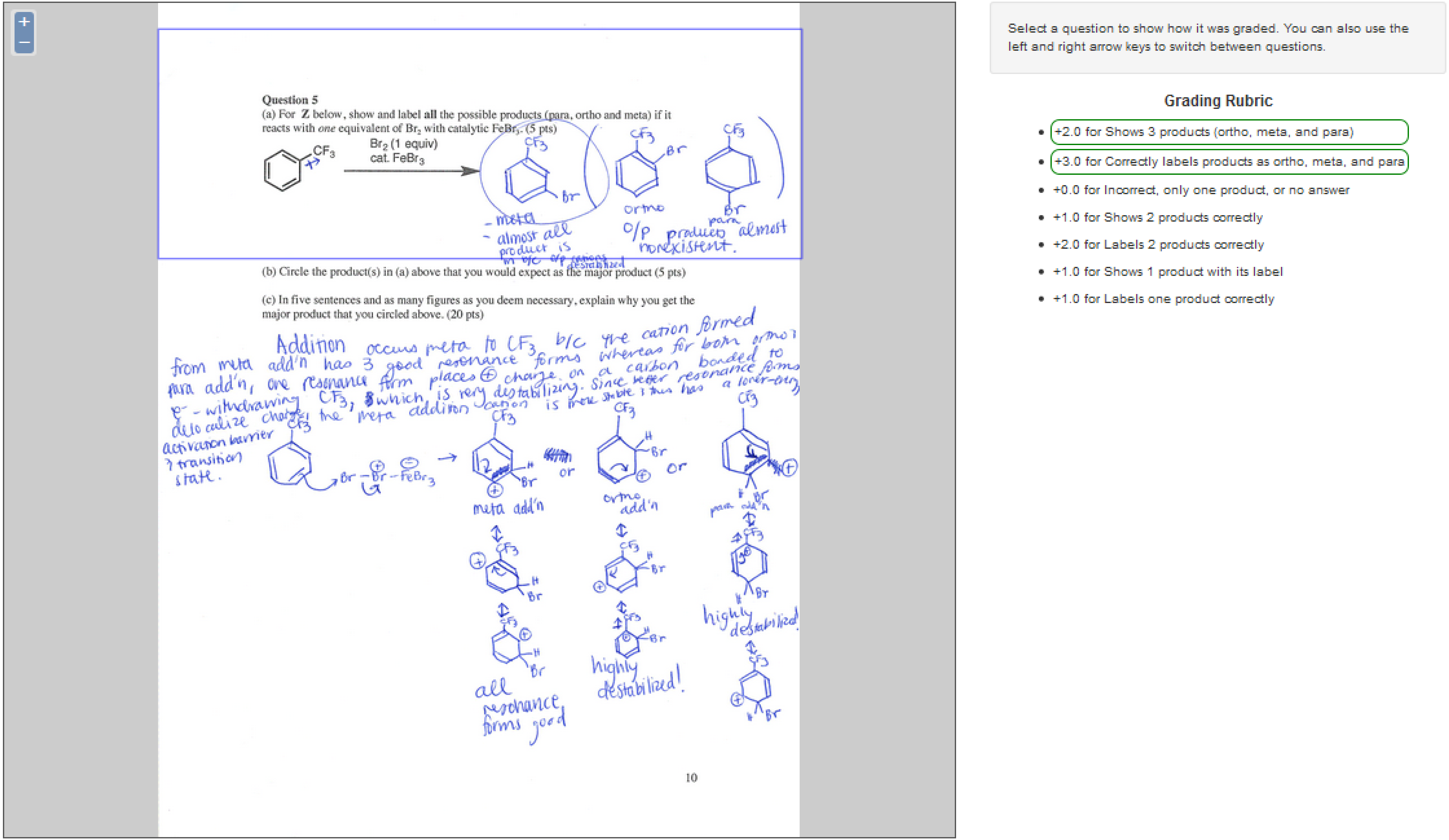
unpaired π es → antiaromatic energy of the

B/c anti-aromatic rings are highly unstable, $E_a^{\ddagger}$ for A will be very high, ~~whereas~~ leading to a high activation energy barrier, whereas B does not proceed through an antiaromatic intermediate.

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- +5.0 for Circles B as more likely
- +5.0 for Shows that addition to exo double bond to give A is unlikely due to resulting anti-aromaticity
- +5.0 for Shows that addition to internal double bond to give B results in a conjugated and resonance stabilized cation (need to explicitly mention stabilization of B by resonance)
- +0.0 for Incorrectly chose A or nothing
- +3.0 for Recognition of importance of conjugation to location of bromination (invalid if anything besides correct answer is credited).



Question 5

(a) For **Z** below, show and label **all** the possible products (para, ortho and meta) if it reacts with *one* equivalent of Br_2 with catalytic $FeBr_3$. (5 pts)

- meta
- almost all product is m b/c o/p cations destabilized

o/p products almost nonexistent.

(b) Circle the product(s) in (a) above that you would expect as the major product (5 pts)

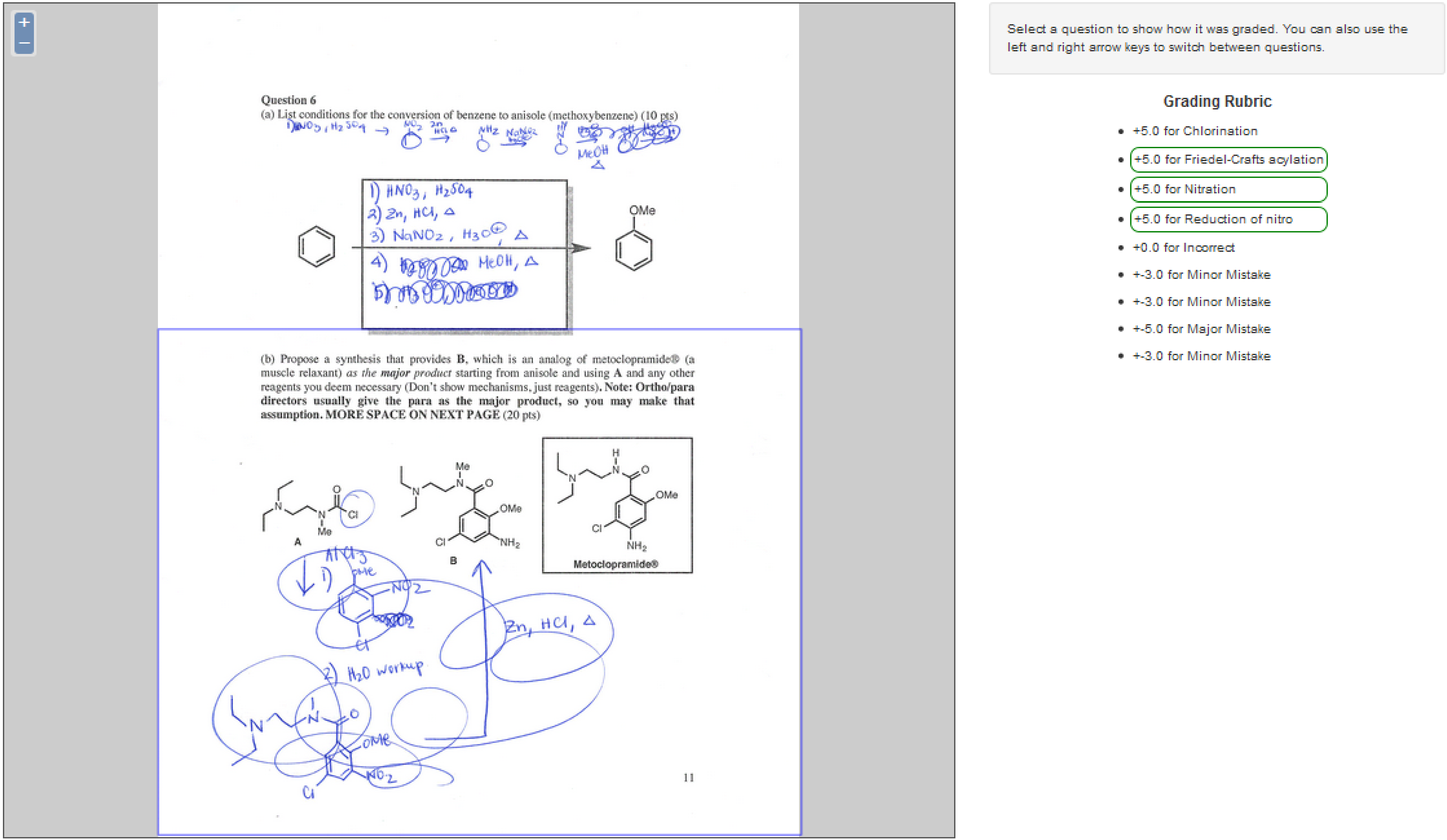
(c) In five sentences and as many figures as you deem necessary, explain why you get the major product that you circled above. (20 pts)

Addition occurs meta to CF_3 b/c the cation formed from meta add'n has 3 good resonance forms whereas for both ortho & para add'n, one resonance form places ⊕ charge on a carbon bonded to e⁻-withdrawing CF_3, which is very destabilizing. Since better resonance forms delocalize charge, the meta addition cation is more stable & thus has a lower-energy activation barrier & transition state.

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- [✓ +2.0 for Shows 3 products (ortho, meta, and para)]
- [✓ +3.0 for Correctly labels products as ortho, meta, and para]
- +0.0 for Incorrect, only one product, or no answer
- +1.0 for Shows 2 products correctly
- +2.0 for Labels 2 products correctly
- +1.0 for Shows 1 product with its label
- +1.0 for Labels one product correctly



Question 6

(a) List conditions for the conversion of benzene to anisole (methoxybenzene) (10 pts)

1) HNO_3, H_2SO_4 → NO_2 Zn HCl △ → NH_2 NaNO2 → MeOH △

1) HNO_3, H_2SO_4
2) Zn, HCl, △
3) $NaNO_2$, $H_3O^{\oplus}$, △
4) MeOH, △
5) [illegible]

(b) Propose a synthesis that provides **B**, which is an analog of metoclopramide® (a muscle relaxant) *as the **major** product* starting from anisole and using **A** and any other reagents you deem necessary (Don't show mechanisms, just reagents). **Note: Ortho/para directors usually give the para as the major product, so you may make that assumption. MORE SPACE ON NEXT PAGE** (20 pts)

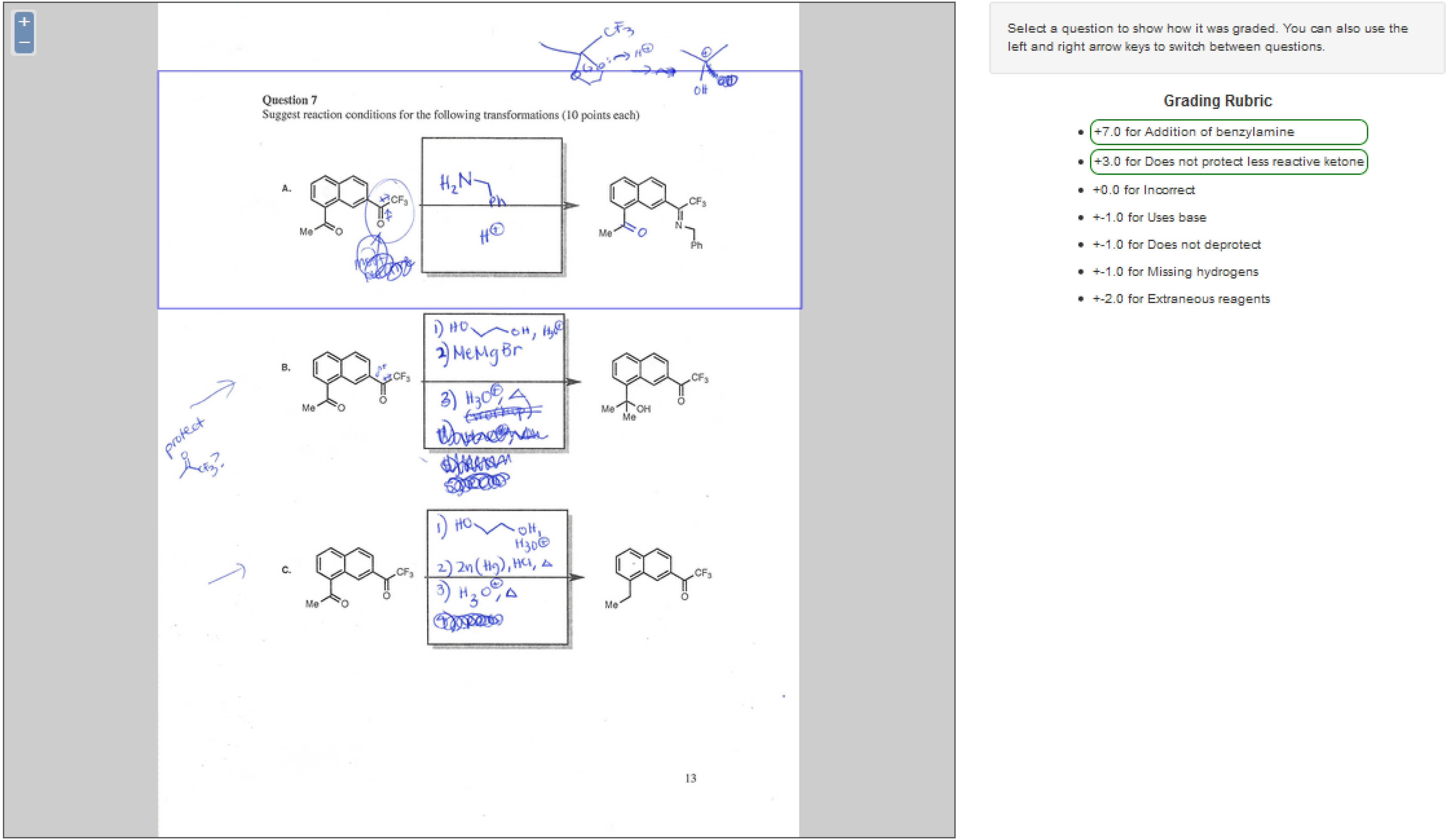
1) $AlCl_3$
2) H_2O workup
Zn, HCl, △

11

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- +5.0 for Chlorination
- [✓ +5.0 for Friedel-Crafts acylation]
- [✓ +5.0 for Nitration]
- [✓ +5.0 for Reduction of nitro]
- +0.0 for Incorrect
- +-3.0 for Minor Mistake
- +-3.0 for Minor Mistake
- +-5.0 for Major Mistake
- +-3.0 for Minor Mistake



Question 7

Suggest reaction conditions for the following transformations (10 points each)

A. H_2N–CH_2Ph

$H^{\oplus}$

B. 1) HO∕∕∕OH, $H_3O^{\oplus}$

2) MeMgBr

3) $H_3O^{\oplus}$, △

C. 1) HO∕∕∕OH, $H_3O^{\oplus}$

2) Zn(Hg), HCl, △

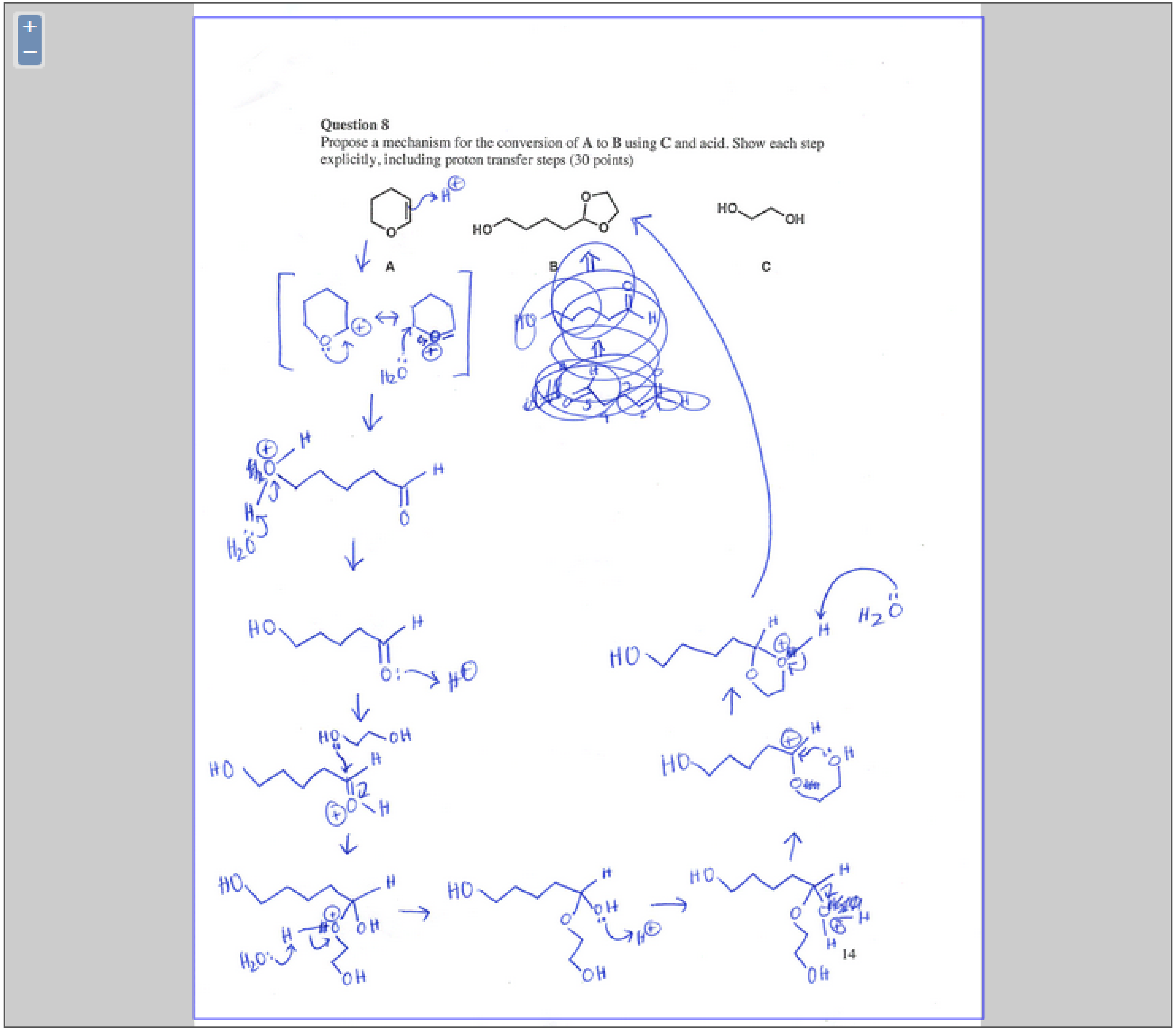
3) $H_3O^{\oplus}$, △

13

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- +7.0 for Addition of benzylamine
- +3.0 for Does not protect less reactive ketone
- +0.0 for Incorrect
- +-1.0 for Uses base
- +-1.0 for Does not deprotect
- +-1.0 for Missing hydrogens
- +-2.0 for Extraneous reagents



Question 8

Propose a mechanism for the conversion of **A** to **B** using **C** and acid. Show each step explicitly, including proton transfer steps (30 points)

Select a question to show how it was graded. You can also use the left and right arrow keys to switch between questions.

Grading Rubric

- [✓ +5.0 for Protonation of alkene to form oxocarbenium ion]
- [✓ +5.0 for Attack of ethylene glycol]
- [✓ +5.0 for Shows proton transfer step]
- +5.0 for Collapse of hemiacetal, ring opening
- [✓ +5.0 for Formation of acetal]
- [✓ +5.0 for Loss of proton]
- +0.0 for Incorrect

Comments

OK