RADICALS FALL 2016 MIDTERM (50+50 = 100pts) **Name**_____

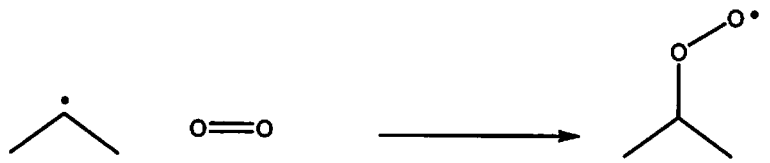
1) (3pts) Define these three terms:

-FREE RADICAL

-FREE RADICAL INITIATOR

-FREE RADICAL INHIBITOR

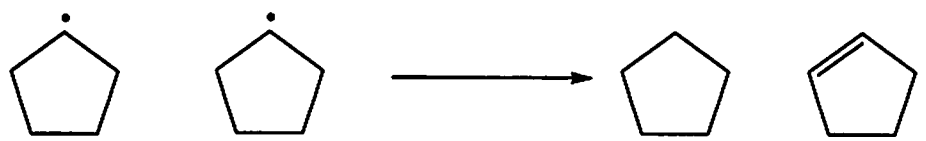
2) (6pts) Label each reaction below as an *Addition*; *Abstraction*; *Dimerization*; *Disproportionation* or *Fragmentation.*

a) 

b) 

c) 

d) Ph• I_2 Ph-I I•

e) 

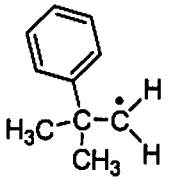
f) 

3) (12pts) Write a mechanism for each of the previous six (2a-f) processes.

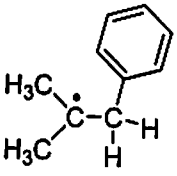
4) (2+6 = 8pts) Radicals can undergo intramolecular addition reactions, which we call cyclizations.
There are two fundamental types (or modes) of cyclization.
-Name these two types of ring closure.

-Briefly explain (with examples) how you classify or identify these two different processes.

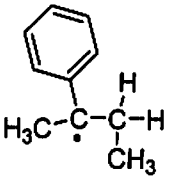
5) (2+2+4+2 = 10pts) For the below three isomeric radicals:



(I)



(II)



(III)

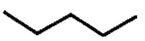
Briefly explain why radical (II) is more stable than radical (I).

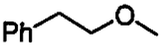
Briefly explain why radical (III) is more stable than radical (II).

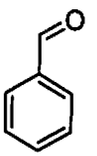
Radical (I) will rearrange into radical (II) – draw a mechanism for this rearrangement.

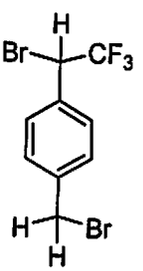
Even though radical (III) is more stable than both radical (I) and radical (II), radical (I) does not rearrange into radical (III). Briefly explain why not.

6) (5+1 = 6pts) Indicate which electron would most **easily** be removed by Electron Ionization for each molecule (producing a radical cation).









For one of them, draw a Lewis structure to indicate where the radical and cation are located.

7) (2pts) Write a chemical equation showing a reaction that strongly implies that carbon centered radicals are planar (or quickly inverting shallow pyramidal) structures.

8) (1pts) Why are special measures taken to remove air from almost all radical reactions?

9) (1pts) Name one gas commonly used as an inert atmosphere for radical reactions.

10) (1pts) State one way that you could experimentally distinguish between an S_N1 mechanism and an $S_{RN}1$ mechanism.

A-C) Attempt 2 of the following 3 (easier, guided) questions.

(2 x 15 = 30)

Note that partial credit will be awarded for:

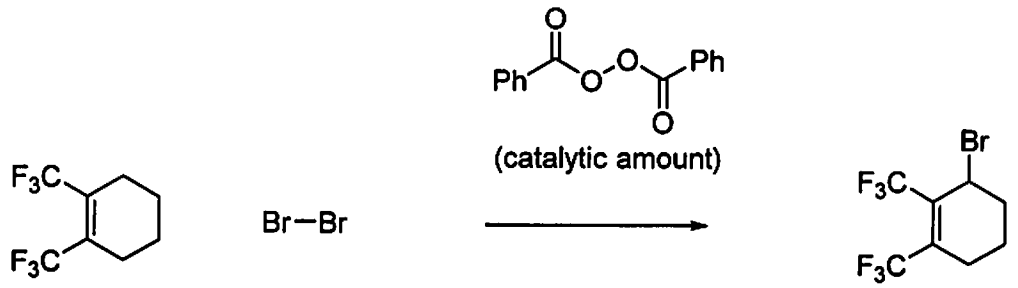
i) correct labeling of atoms in the starting materials and products

ii) correct initiation steps (where applicable)

ii) correct progress within a plausible mechanism.

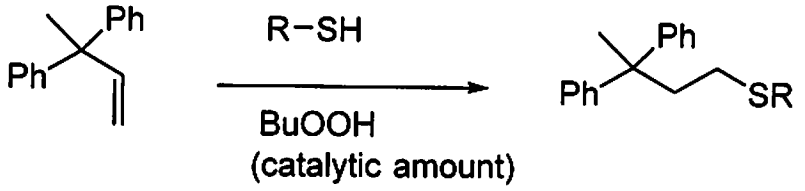
A) Write a plausible mechanism (INITIATION and PROPAGATION steps) for the following *chain* reaction.

(The diacylperoxide initiator homolytically produces radicals which fragment, and then abstract a weakly bound hydrogen. This stabilized carbon centered radical then abstracts a bromine atom to generate the product, and the chain carrying radical).



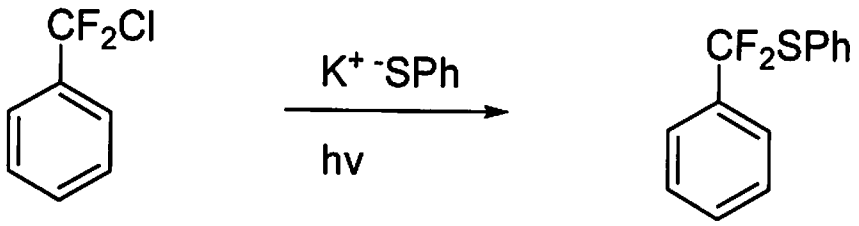
B) Write a plausible mechanism (INITIATION and PROPAGATION steps) for the following *chain* reaction.

(The hydroperoxide homolytically cleaves producing two oxygen centered radicals. The butoxyl radical abstracts a hydrogen from the thiol, and the sulfur centered radical adds to the alkene. This carbon centered radical then abstracts a hydrogen from another molecule of thiol, yielding the product and the chain carrying sulfur centered radical).



C) Write a plausible mechanism for the following $S_{RN}1$ reaction.

(The sulfur based nucleophile is photochemically excited, and transfers an electron to the aromatic trihalide, generating a radical anion. The radical anion expels the leaving group to produce a carbon centered radical that reacts with a new nucleophile, resulting in another radical anion. This new radical anion then yields the product by transferring an electron to another molecule of aromatic trihalide).



X-Z) Attempt 2 of the following 3 questions.

(2 x 10 = 20)

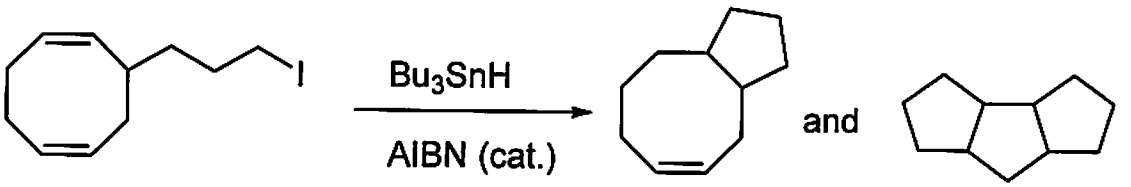
Note that partial credit will be awarded for:

i) correct labeling of atoms in the starting materials and products

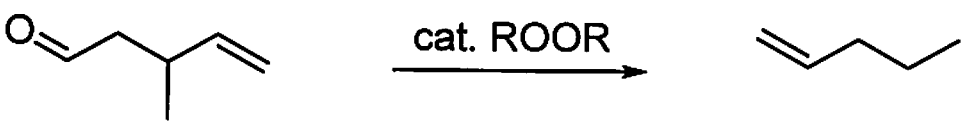
ii) correct initiation steps (where applicable)

ii) correct progress within a plausible mechanism.

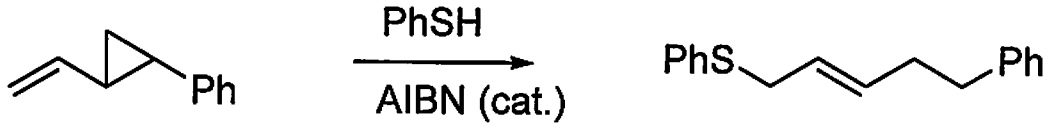
X) Write a plausible mechanism for the following chain reaction.



Y) Provide a plausible mechanism for the formation of the following rearranged product.



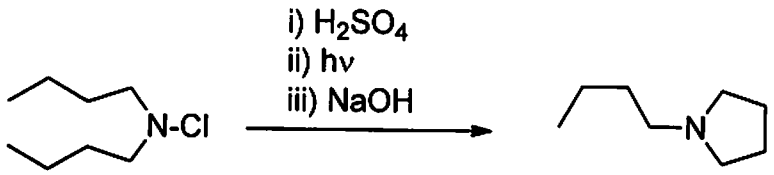
Z) Write a plausible mechanism for the following chain reaction.



*******UP TO 5 bonus points*******

Provide a mechanism for the following reaction, using the following guide:

*Protonation on the Nitrogen (giving intermediate **A**), is followed by homolytic (photochemical) cleavage of the N-Cl bond.*
*This produces a (positively charged) Nitrogen centered radical (intermediate **B**), which abstracts a (convenient) Hydrogen atom intramolecularly, producing a Carbon centered radical.*
*Then, this radical abstracts a Chlorine atom from another equivalent of intermediate **A**, to generate another equivalent of intermediate **B** (it's a chain process), but also more importantly, it generates the protonated form of a secondary amine which has a Chloroalkyl substituent (intermediate **C**).*
*When the base is added, the protonated amine (intermediate **C**) is deprotonated, and the thus generated neutral Nitrogen is now nucleophilic. It performs an intramolecular S_N2 attack (Chloride is the leaving group).*
This cyclization makes the Nitrogen positive, and another equivalent of base deprotonates the Nitrogen, yielding the final product.



RADICALS FALL 2016 MIDTERM (50+50 = 100pts) **Name** MIDTERM

1) (3pts) Define these three terms:

-FREE RADICAL A species with an odd number of electrons (resulting in an unpaired electron).

-FREE RADICAL INITIATOR

A species that reacts to produce radicals.

-FREE RADICAL INHIBITOR

A species that reacts with free radicals, and prevents them from undergoing further productive radical reactions.

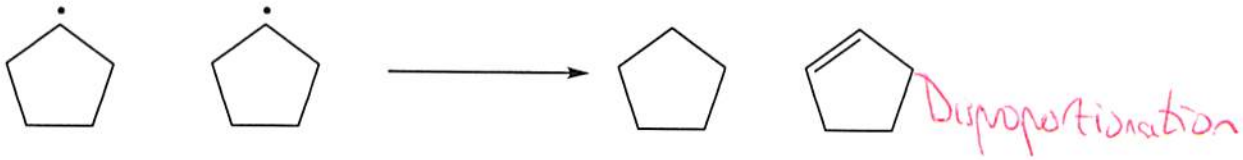
2) (6pts) Label each reaction below as an *Addition*; *Abstraction*; *Dimerization*; *Disproportionation* or *Fragmentation*.

a)  Addition

b)  Dimerization

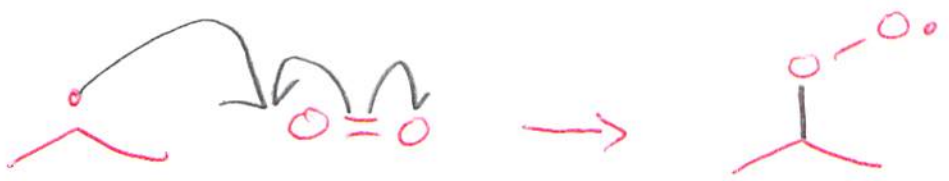
c)  CO_2 Fragmentation

d) Ph• I_2 ⟶ Ph-I I• Abstraction

e)  Disproportionation

f)  H-Cl Abstraction

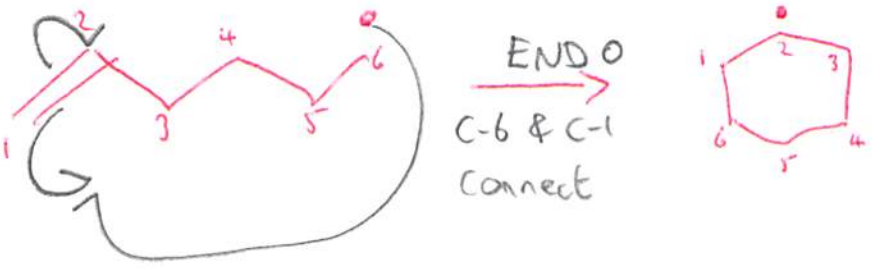
3) (12pts) Write a mechanism for each of the previous six (2a-f) processes.



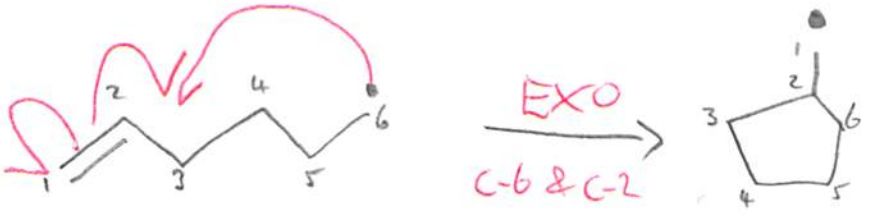
4) (2+6 = 8pts) Radicals can undergo intramolecular addition reactions, which we call cyclizations.
There are two fundamental types (or modes) of cyclization.
-Name these two types of ring closure.

EXO & ENDO cyclizations.

-Briefly explain (with examples) how you classify or identify these two different processes.

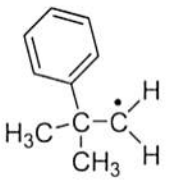


Both atoms of the π system are part of the new ring system.
(or, the radical is in the ring).

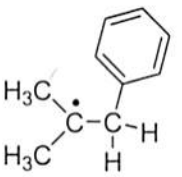


Only one of the atoms of the π bond is in the new ring system.
(or, the radical is outside of the new ring).

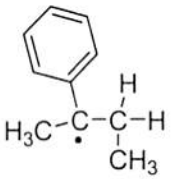
5) (2+2+4+2 = 10pts) For the below three isomeric radicals:



(I)



(II)



(III)

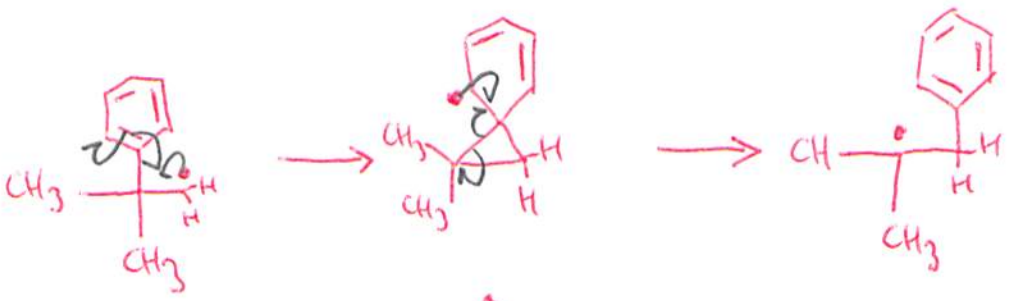
Briefly explain why radical (II) is more stable than radical (I).

(II) has more alkyl substitution (tertiary versus primary), and the increase in hyperconjugation and inductive electron donation stabilizes the electron deficient radical center.

Briefly explain why radical (III) is more stable than radical (II).

(III) has resonance stabilization due to the conjugated aromatic ring, and this delocalization stabilizes the radical.

Radical (I) will rearrange into radical (II) – draw a mechanism for this rearrangement.

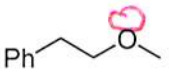


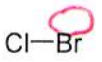
Resonance Structures around the ring

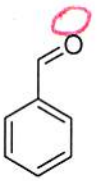
Even though radical (III) is more stable than both radical (I) and radical (II), radical (I) does not rearrange into radical (III). Briefly explain why not.

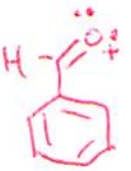
Radical rearrangements are not 1 step processes, they are addition/elimination processes. So only atoms/groups that can accommodate extra electrons in a π bonds, or expand their valence shell, are able to radical migrate. The phenyl can migrate, but the methyl group cannot.

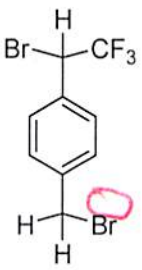
6) (5+1 = 6pts) Indicate which electron would most **easily** be removed by Electron Ionization for each molecule (producing a radical cation).

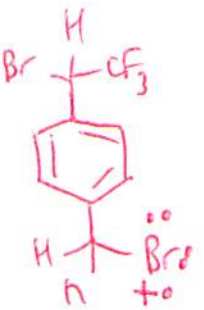










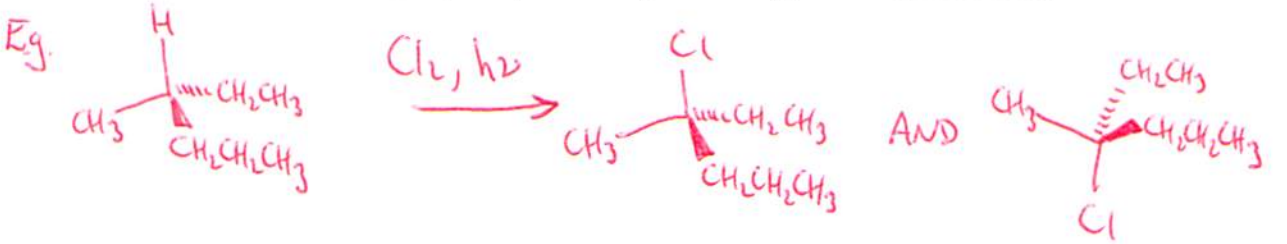


For one of them, draw a Lewis structure to indicate where the radical and cation are located.

Above

7) (2pts) Write a chemical equation showing a reaction that strongly implies that carbon centered radicals are planar (or quickly inverting shallow pyramidal) structures.

Eg.



Basically Single Enantiomer ⟶ Racemic Products

8) (1pts) Why are special measures taken to remove air from almost all radical reactions?

The O_2 in the air can act as a free radical inhibitor.

9) (1pts) Name one gas commonly used as an inert atmosphere for radical reactions.

Nitrogen, Argon.

10) (1pts) State one way that you could experimentally distinguish between an S_N1 mechanism and an $S_{RN}1$ mechanism.

- The requirement of (electrochemical / photochemical) initiation (for $S_{RN}1$).

- The impact of free radical inhibitors on the reaction rate (Slows or stops for $S_{RN}1$).

- Only works for good S.E.T. nucleophiles (for $S_{RN}1$).

A-C) Attempt 2 of the following 3 (easier, guided) questions.

(2 x 15 = 30)

Note that partial credit will be awarded for:

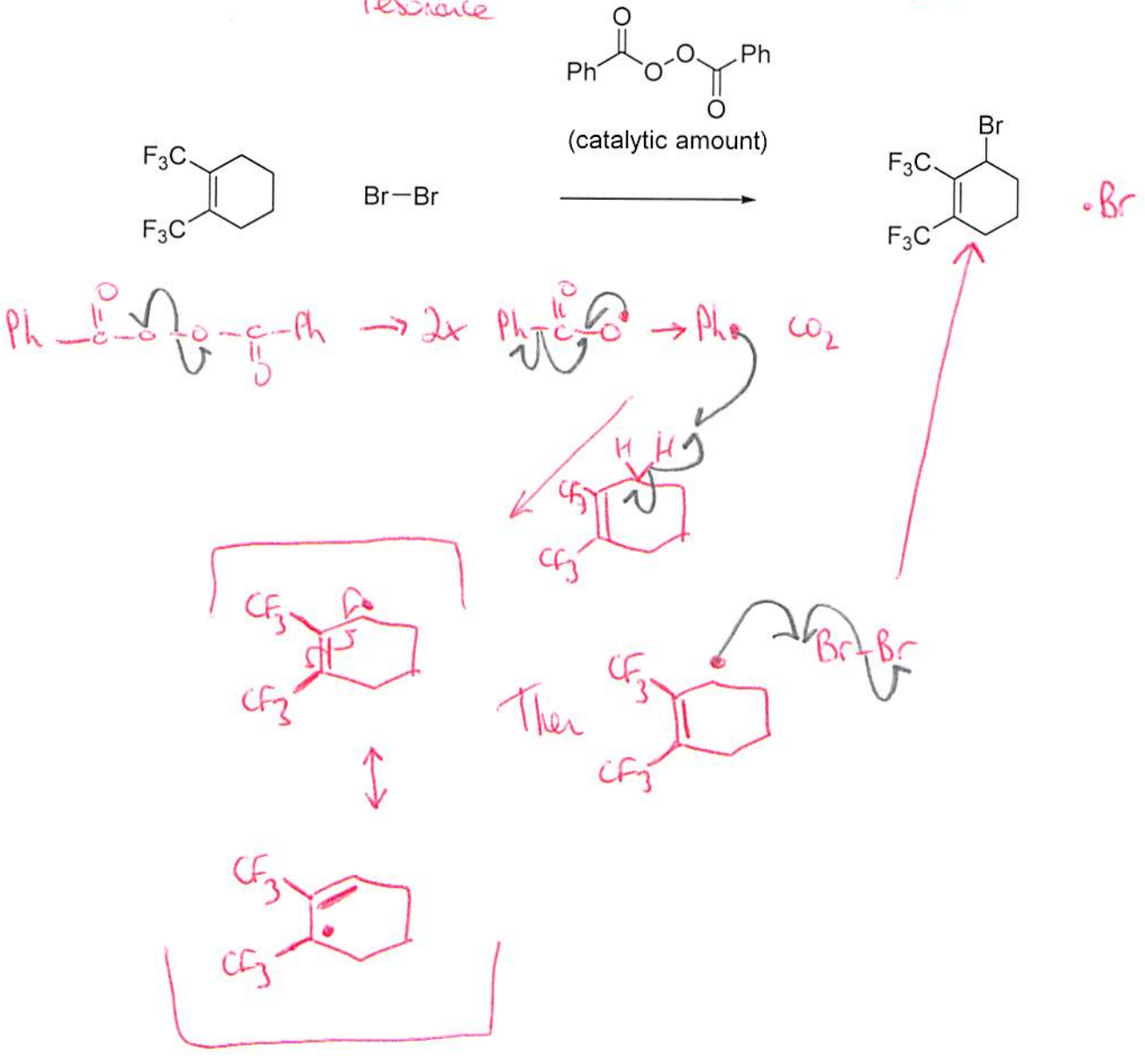
i) correct labeling of atoms in the starting materials and products

ii) correct initiation steps (where applicable)

ii) correct progress within a plausible mechanism.

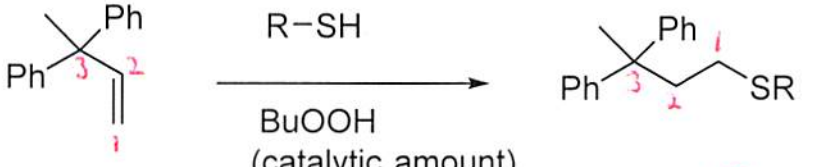
A) Write a plausible mechanism (INITIATION and PROPAGATION steps) for the following *chain* reaction.

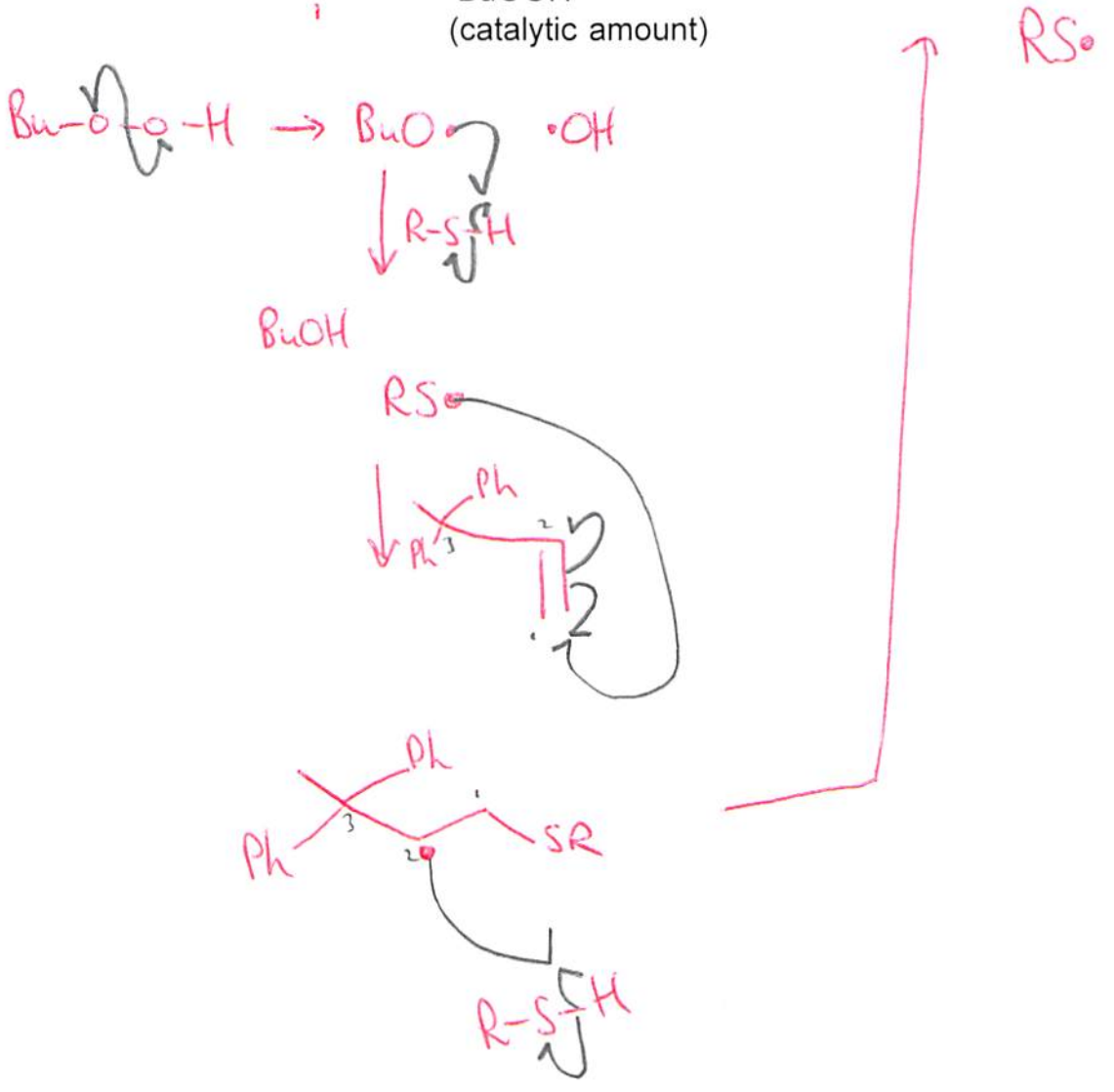
(The diacylperoxide initiator homolytically produces radicals which fragment, and then abstract a weakly bound hydrogen. This stabilized carbon centered radical then abstracts a bromine atom to generate the product, and the chain carrying radical).



B) Write a plausible mechanism (INITIATION and PROPAGATION steps) for the following *chain* reaction.

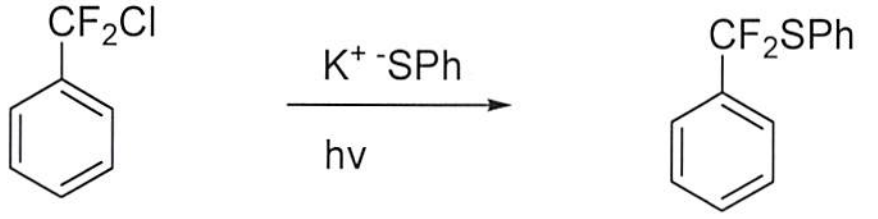
(The hydroperoxide homolytically cleaves producing two oxygen centered radicals. The butoxyl radical abstracts a hydrogen from the thiol, and the sulfur centered radical adds to the alkene. This carbon centered radical then abstracts a hydrogen from another molecule of thiol, yielding the product and the chain carrying sulfur centered radical).

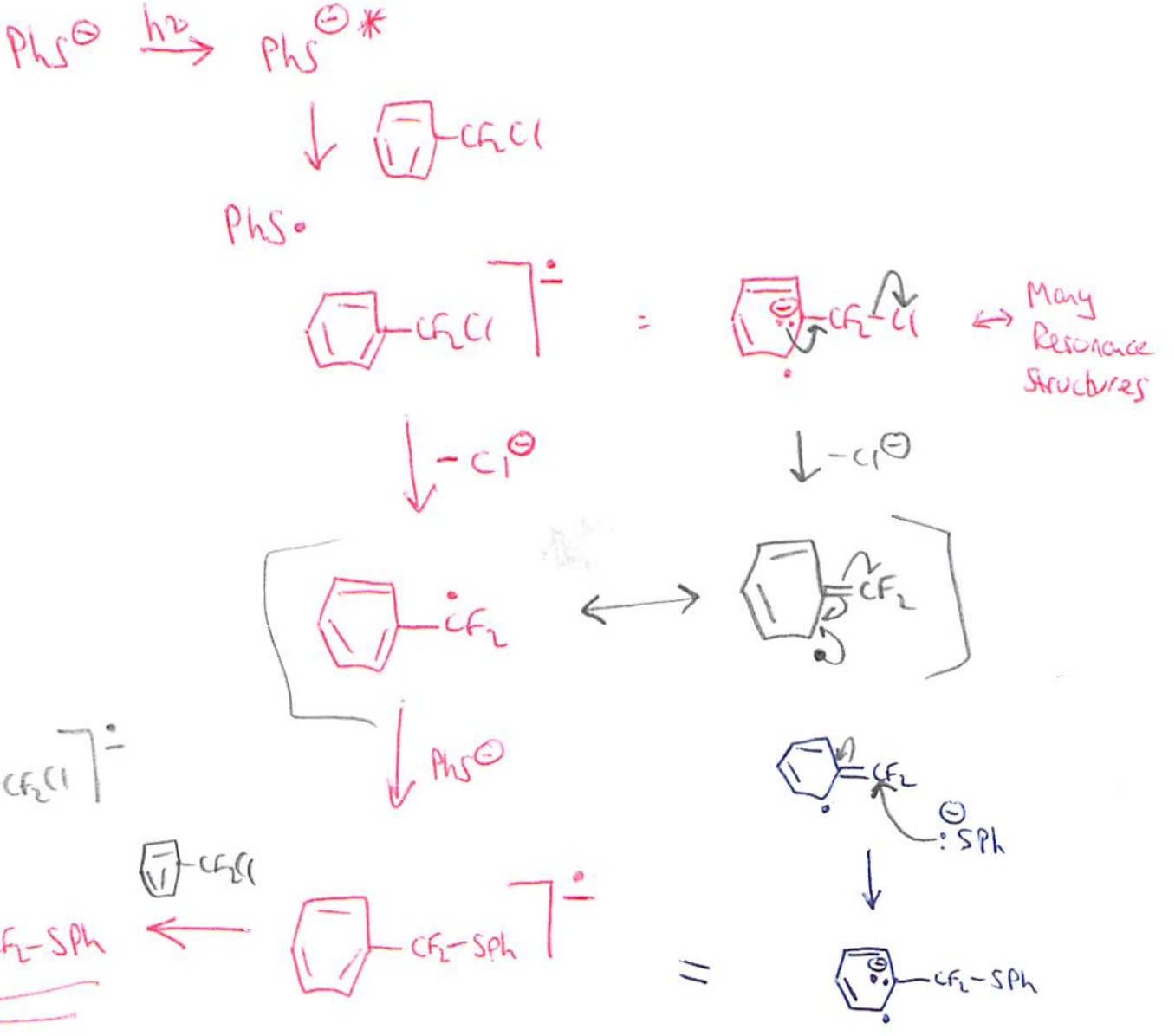




C) Write a plausible mechanism for the following $S_{RN}1$ reaction.

(The sulfur based nucleophile is photochemically excited, and transfers an electron to the aromatic trihalide, generating a radical anion. The radical anion expels the leaving group to produce a carbon centered radical that reacts with a new nucleophile, resulting in another radical anion. This new radical anion then yields the product by transferring an electron to another molecule of aromatic trihalide).





X-Z) Attempt 2 of the following 3 questions.

(2 x 10 = 20)

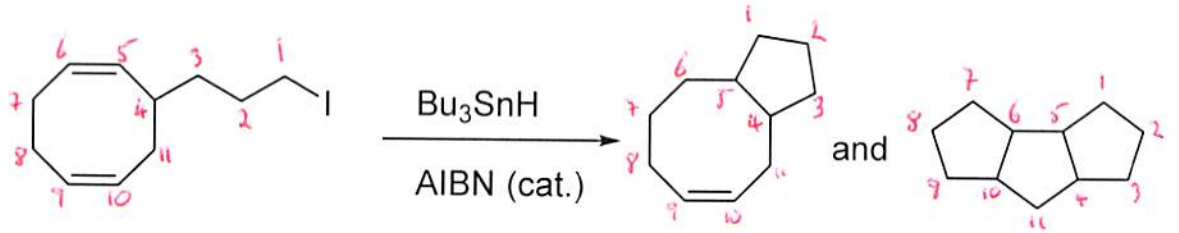
Note that partial credit will be awarded for:

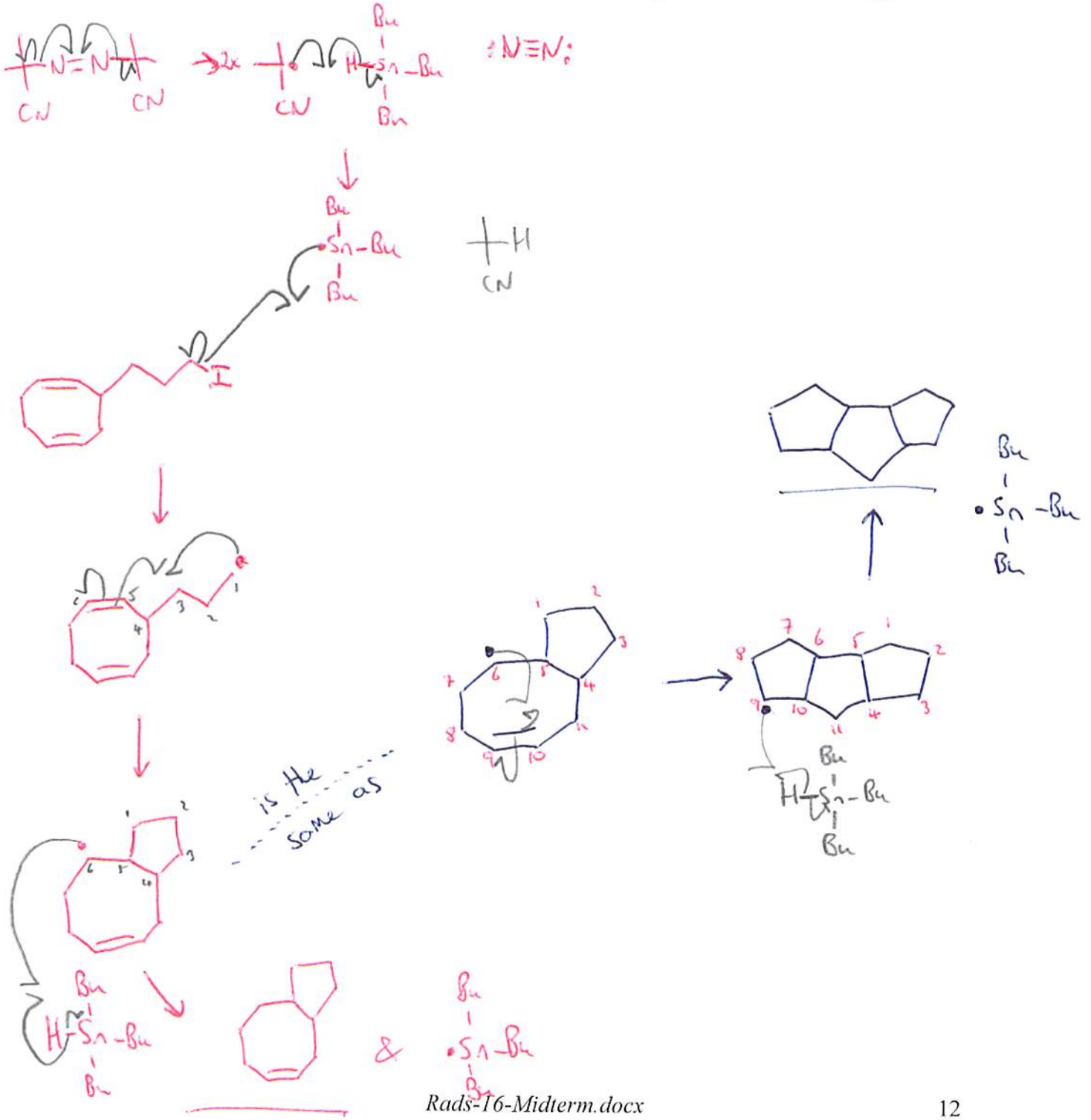
i) correct labeling of atoms in the starting materials and products

ii) correct initiation steps (where applicable)

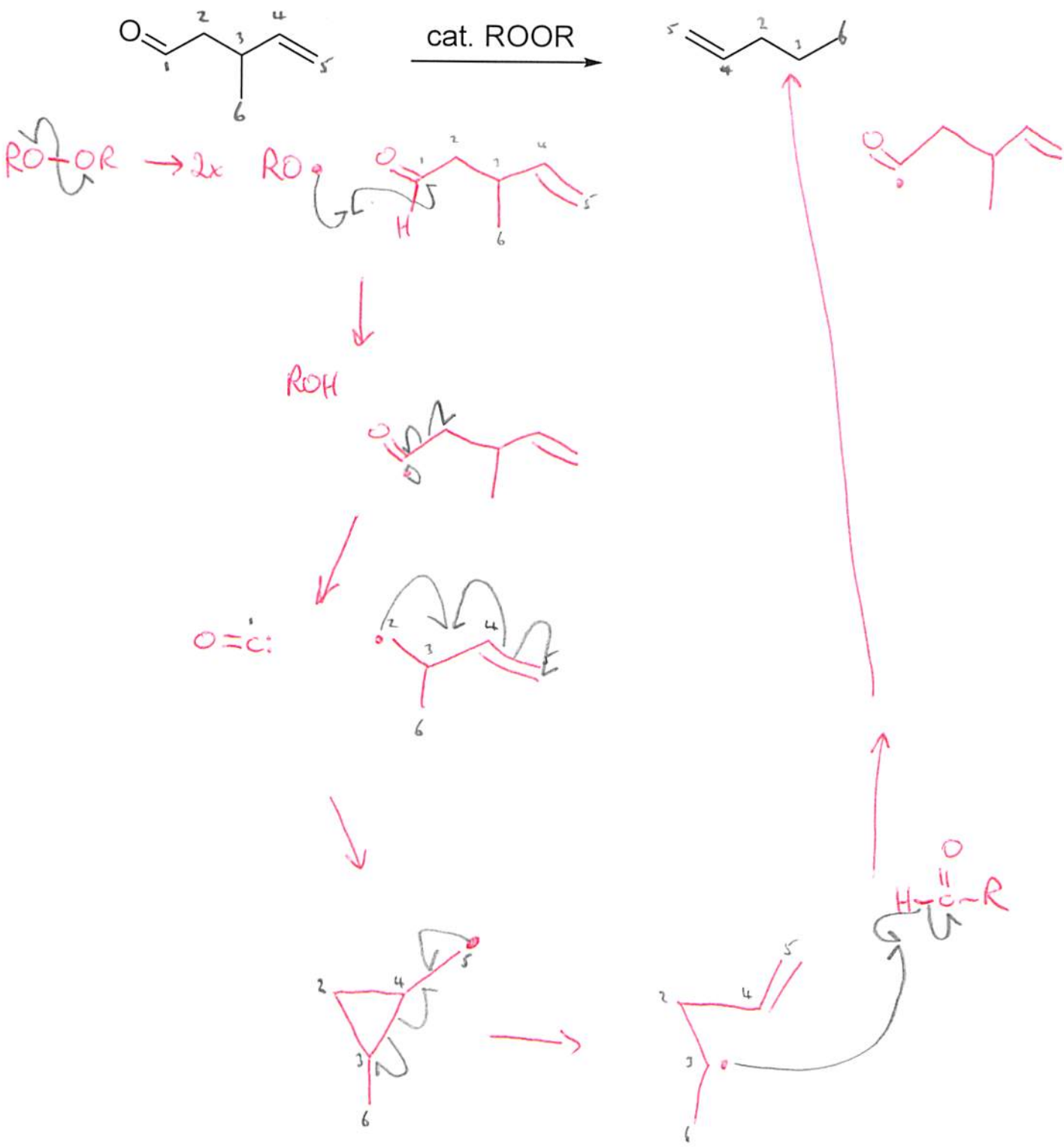
ii) correct progress within a plausible mechanism.

X) Write a plausible mechanism for the following chain reaction.

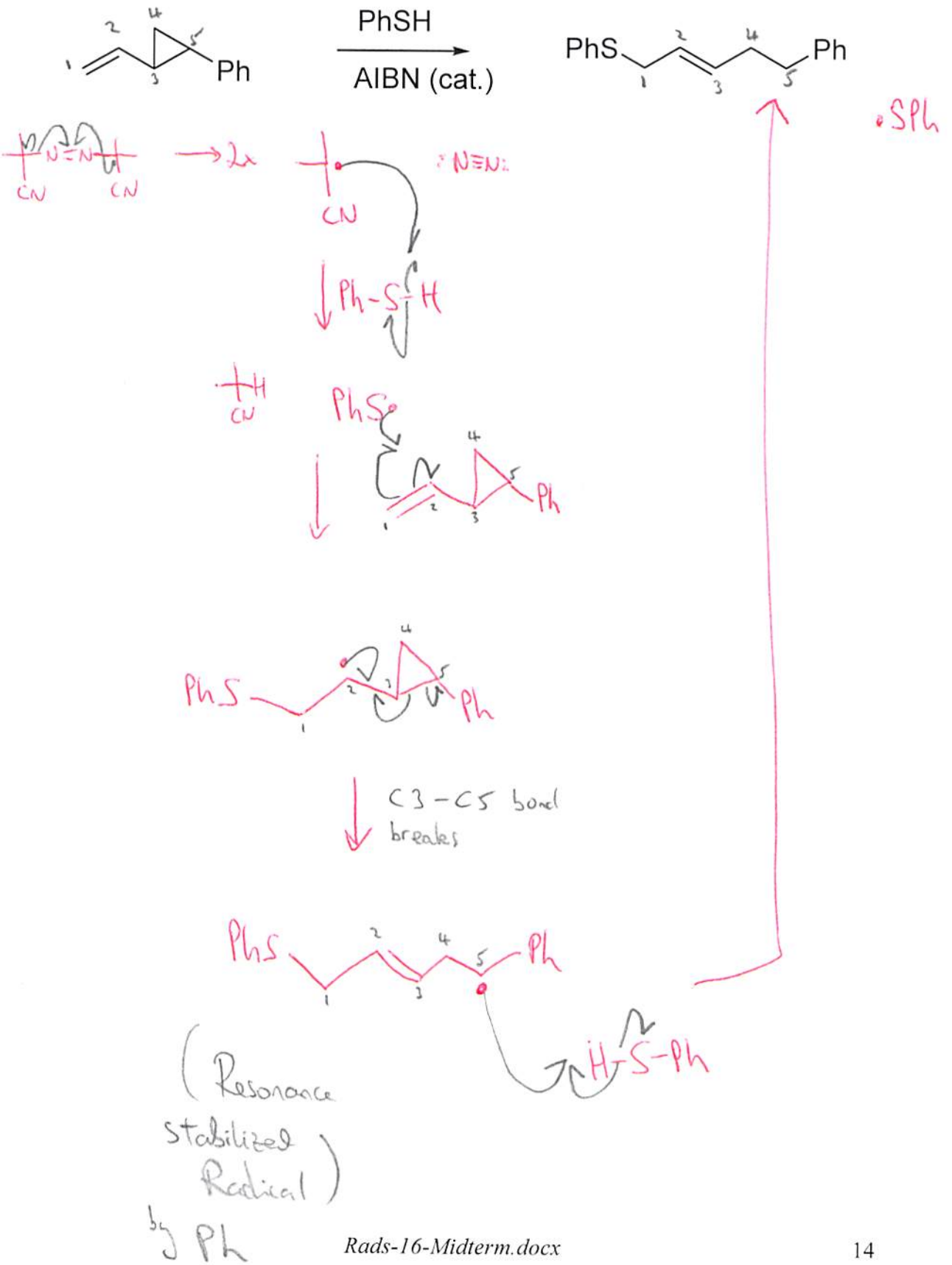




Y) Provide a plausible mechanism for the formation of the following rearranged product.



Z) Write a plausible mechanism for the following chain reaction.



*******UP TO 5 bonus points*******

Provide a mechanism for the following reaction, using the following guide:

*Protonation on the Nitrogen (giving intermediate **A**), is followed by homolytic (photochemical) cleavage of the N-Cl bond.*
*This produces a (positively charged) Nitrogen centered radical (intermediate **B**), which abstracts a (convenient) Hydrogen atom intramolecularly, producing a Carbon centered radical.*
*Then, this radical abstracts a Chlorine atom from another equivalent of intermediate **A**, to generate another equivalent of intermediate **B** (it's a chain process), but also more importantly, it generates the protonated form of a secondary amine which has a Chloroalkyl substituent (intermediate **C**).*
*When the base is added, the protonated amine (intermediate **C**) is deprotonated, and the thus generated neutral Nitrogen is now nucleophilic. It performs an intramolecular S_N2 attack (Chloride is the leaving group).*
This cyclization makes the Nitrogen positive, and another equivalent of base deprotonates the Nitrogen, yielding the final product.