

RADICALS FALL 2020 MIDTERM (60+40 = 100pts) Name _____

1) (10pts) Define (or explain) the following scientific terms within the context of this lecture course:

FREE RADICAL

SINGLE BARB FISH HOOK ARROW

INITIATOR

INHIBITOR

CHAIN PROCESS

HOMOLYTIC CLEAVAGE

CARBON CENTERED RADICAL

TERMINATION STEP

S_{RN}1

EXO CYCLIZATION

2) (2+2=4pts) Draw a reasonable Lewis structure (or line angle diagram) for the following species:

A SECONDARY ALKYL RADICAL

A PERSISTENT (LONG LIVED) RADICAL

3) (2pts) What is the historical scientific significance that many of the reactions we have studied this semester have generated products that can be described as “dimers” (products resulting from dimerization)?

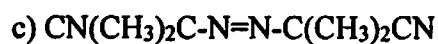
4) (2pts) Write a chemical equation showing a reaction that strongly implies that carbon centered radicals are planar (or quickly inverting shallow pyramidal) structures.

5) (1pt) Name one gas commonly used as an inert atmosphere for radical reactions.

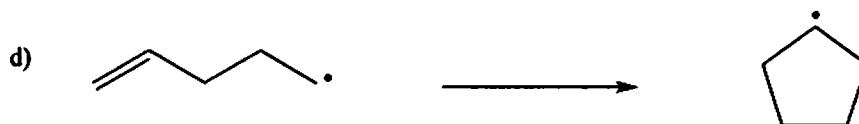
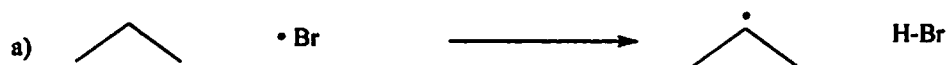
6) (1pts) State one way that you could experimentally distinguish between an S_N1 mechanism and an $S_{RN}1$ mechanism.

7) (1pt) How are the rates of radical reactions impacted by increasing the polarity of the reaction solvent?

8) (4x3=12pts) Draw a correct Lewis structure for the following molecules (INCLUDE ALL LONE PAIRS), and also draw the expected radicals produced when they are heated (arrows not needed).



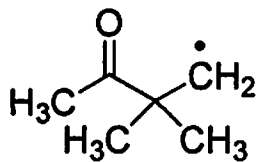
9) (4pts) Label each reaction below as an *Addition*; *Abstraction*; *Dimerization*; *Disproportionation* or *Fragmentation*.



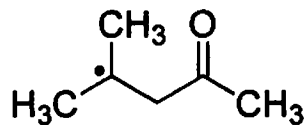
10) (8pts) Write a mechanism for each of the previous four (9a-d) processes.

11) (7pts) Draw a mechanism to show the sequence of interactions when the free radical initiator AIBN reacts with tributyltin hydride and an alkyl halide to ultimately produce an alkyl radical.

12) (1+1+2+4=8pts) For the two below radicals:



(I)



(II)

a) Are they isomeric?

b) Which is more stable?

c) In one sentence, explain your reasoning for part b).

d) Draw a mechanism for this radical rearrangement.

A-E) Attempt all of the following 5 problems,

and I will select your best 4.

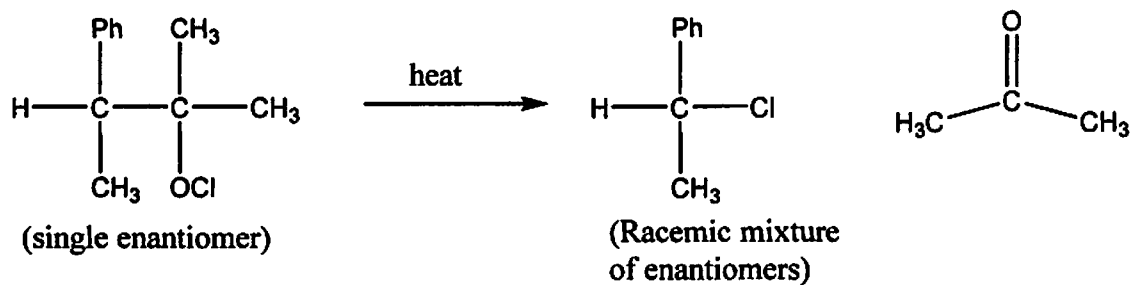
(4 x 10 = 40)

There are also **2 bonus points** available here:

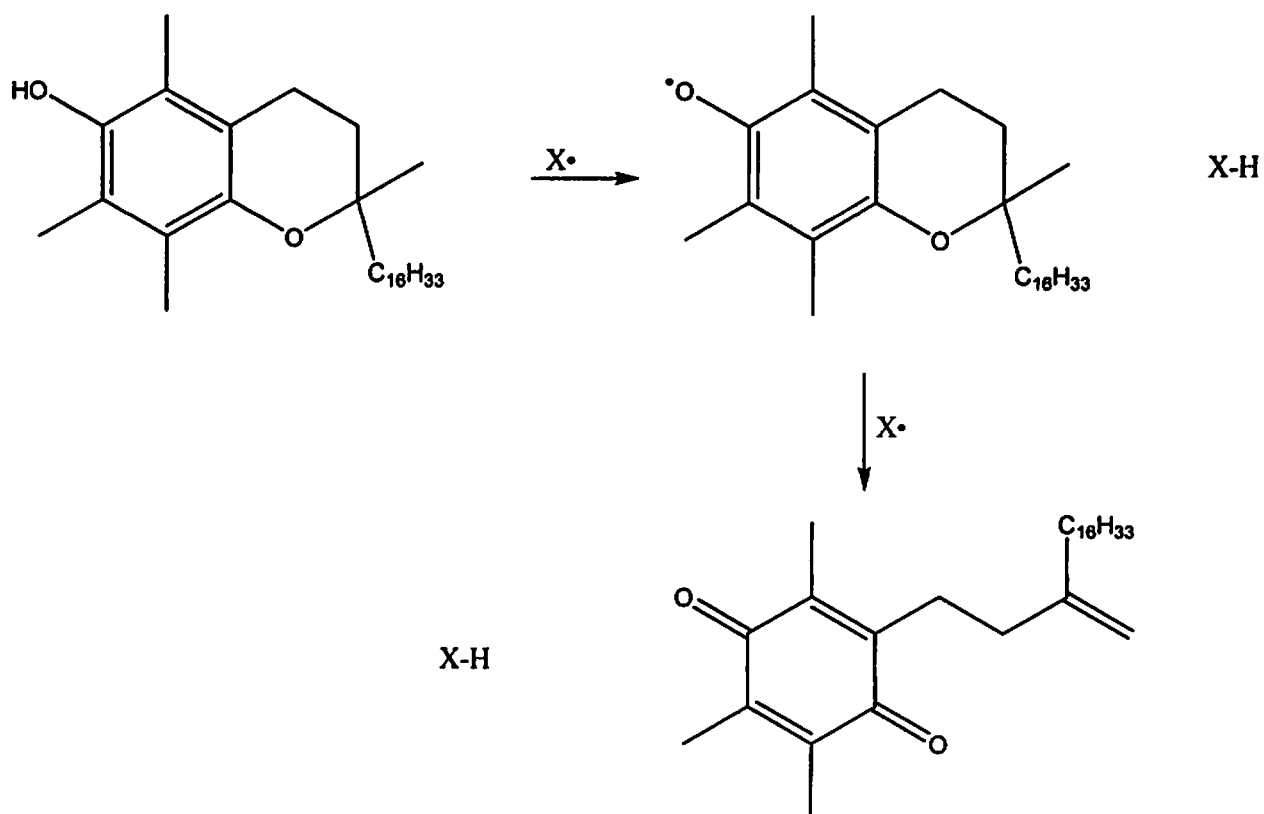
- What is the common name of the bicyclic organic starting material in PROBLEM B?

- What is the functional group in the starting material of PROBLEM E?

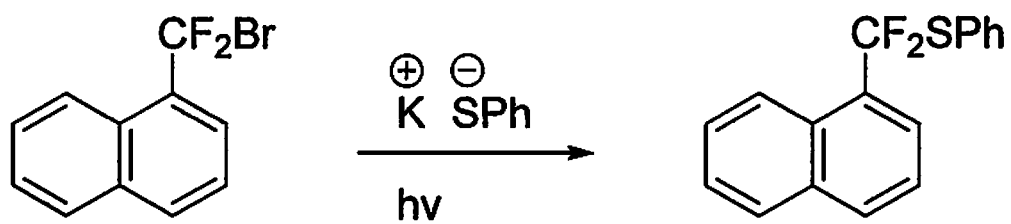
A) Draw a plausible mechanism for the following chain process that is initiated by the thermal homolytic cleavage of the O-Cl bond in the organic hypochlorite. Also make sure that you explain the stereochemical outcome.



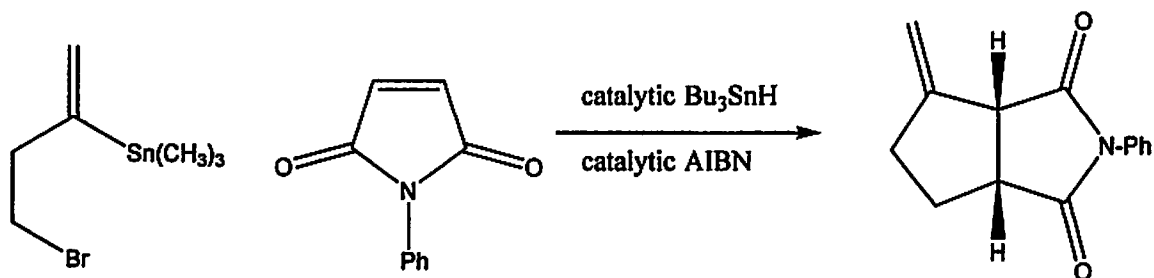
B) The below molecule is a natural fat-soluble antioxidant. In this role, it is capable to act as a radical scavenger, ultimately delivering two Hydrogens to otherwise reactive and damaging free radicals. Draw a mechanism to show this process (and note that the second Hydrogen abstraction is NOT a single step process).



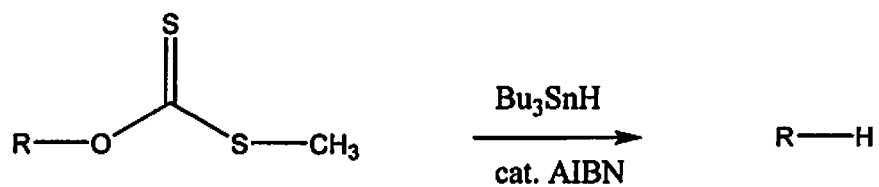
C) Write a plausible mechanism for the following $S_{RN}1$ reaction.



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



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



1) (10pts) Define (or explain) the following scientific terms within the context of this lecture course:

FREE RADICAL A species with (at least) one unpaired valence electron.

SINGLE BARB FISH HOOK ARROW

 means the movement of one electron.

INITIATOR

A species that reacts to produce one or more radicals.

INHIBITOR

A species that reacts with a radical to produce something much more stable so the radical processes slow down or stop.

CHAIN PROCESS

A process where many molecules of product are produced from a single reactive intermediate, in a repeating series of events.

HOMOLYTIC CLEAVAGE

Bond breakage where each connected atom gets one electron.

CARBON CENTERED RADICAL

A radical species where the odd unpaired electron is on carbon.

TERMINATION STEP

A step in a free radical chain process where no radicals are generated.

S_{RN}1

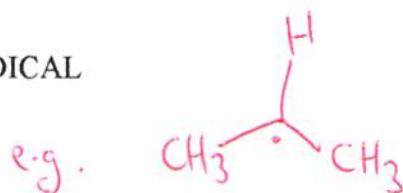
Substitution, radical-nucleophile, unimolecular.

EXO CYCLIZATION

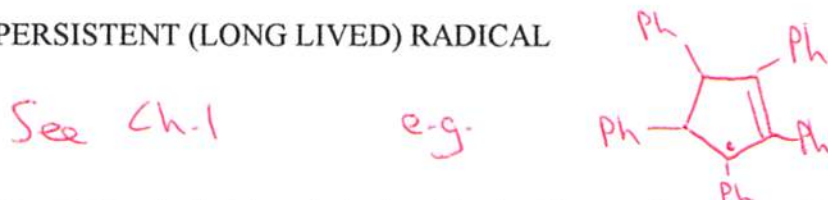
A ring closure where only one of the π bonded atoms is included in the new ring structure; or where the new radical centre is outside of the new ring structure.

2) (2+2=4pts) Draw a reasonable Lewis structure (or line angle diagram) for the following species:

A SECONDARY ALKYL RADICAL



A PERSISTENT (LONG LIVED) RADICAL



3) (2pts) What is the historical scientific significance that many of the reactions we have studied this semester have generated products that can be described as “dimers” (products resulting from dimerization)?

If the intermediates react with themselves, then they are unlikely to be charged (and therefore not cations nor anions).

4) (2pts) Write a chemical equation showing a reaction that strongly implies that carbon centered radicals are planar (or quickly inverting shallow pyramidal) structures.

E.g. Question A later in this exam.

5) (1pt) Name one gas commonly used as an inert atmosphere for radical reactions.

Argon, Nitrogen.

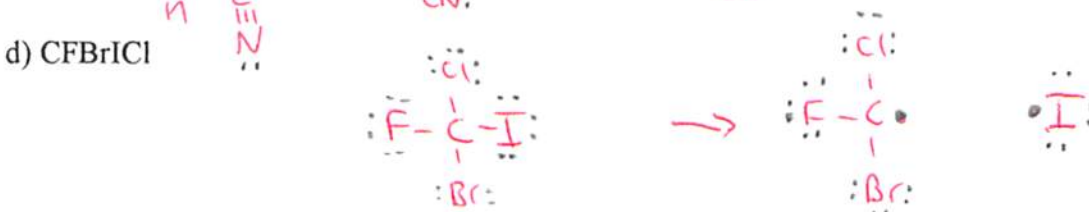
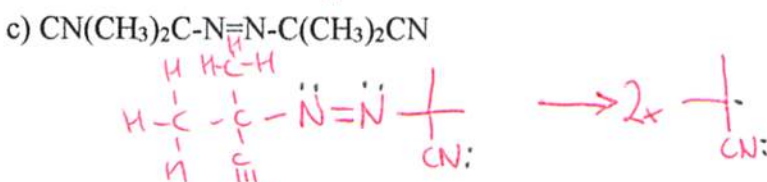
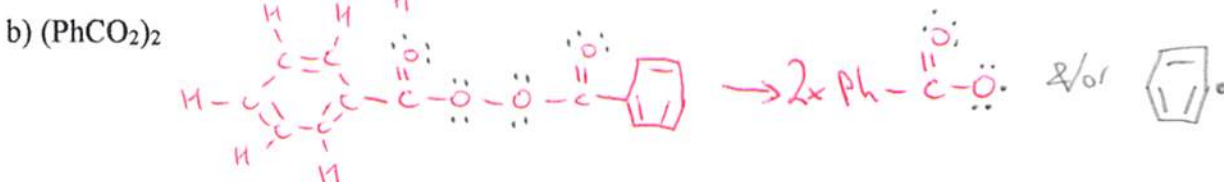
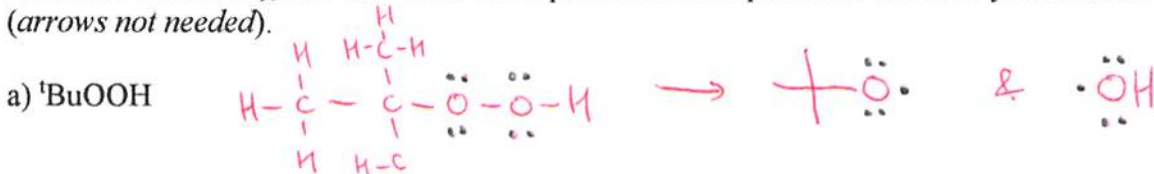
6) (1pts) State one way that you could experimentally distinguish between an S_N1 mechanism and an $S_{RN}1$ mechanism.

See the impact of changing reaction conditions. (Eg add a free radical inhibitor, or no photochemical irradiation). S_N1 & $S_{RN}1$ behave differently.

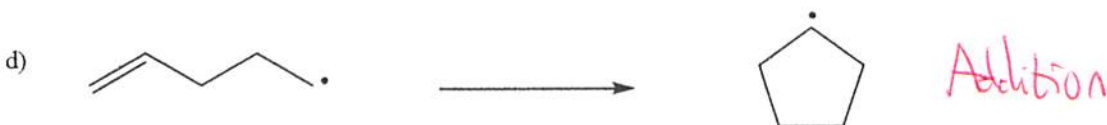
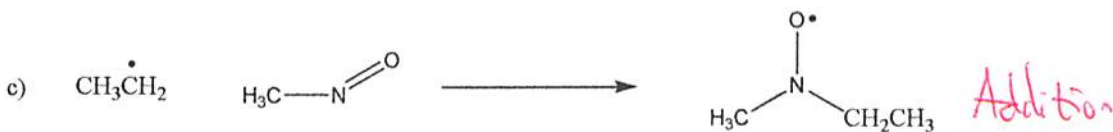
7) (1pt) How are the rates of radical reactions impacted by increasing the polarity of the reaction solvent?

The rates stay (approx.) the same

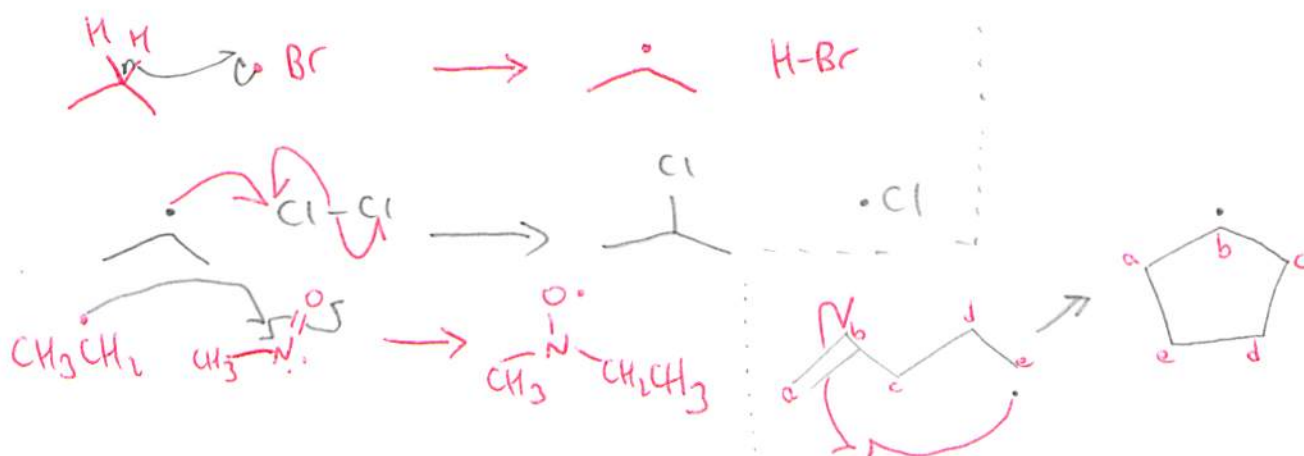
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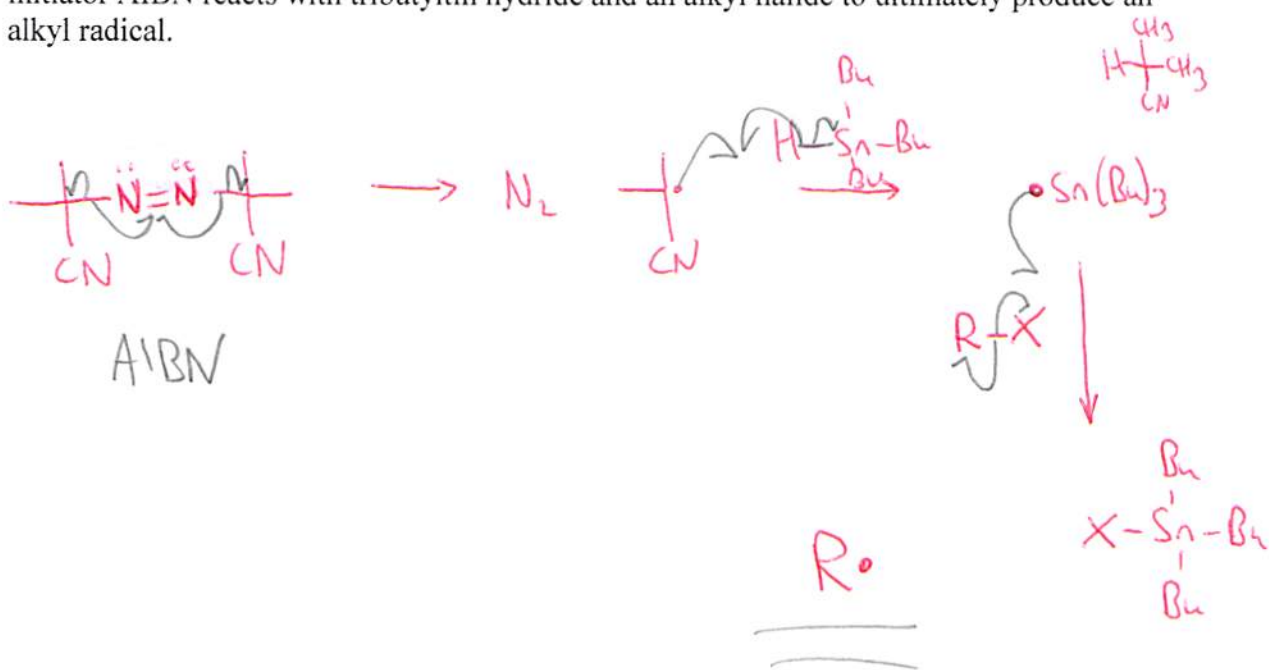
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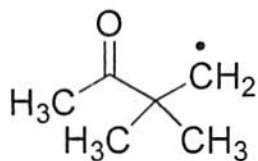
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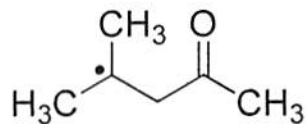
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12) (1+1+2+4=8pts) For the two below radicals:



(I)



(II)

a) Are they isomeric?

Yes.

b) Which is more stable?

(II)

c) In one sentence, explain your reasoning for part b).

(II) is more allyl substituted than (I), and the tertiary radical is better stabilized by the increased inductive and hyperconjugative effects.

d) Draw a mechanism for this radical rearrangement.



A-E) Attempt all of the following 5 problems,

and I will select your best 4.

(4 x 10 = 40)

There are also **2 bonus points** available here:

- What is the common name of the bicyclic organic starting material in PROBLEM B?

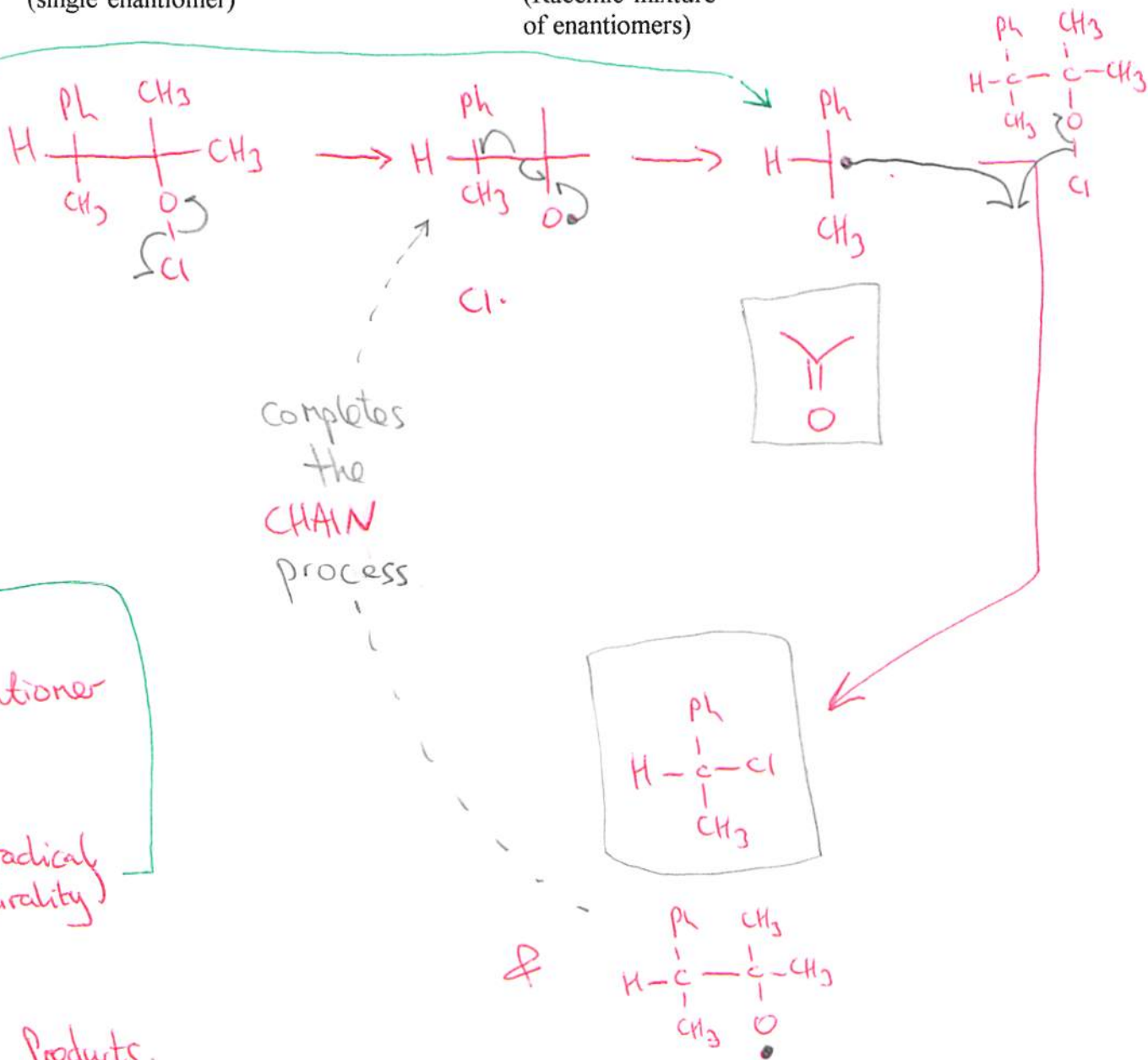
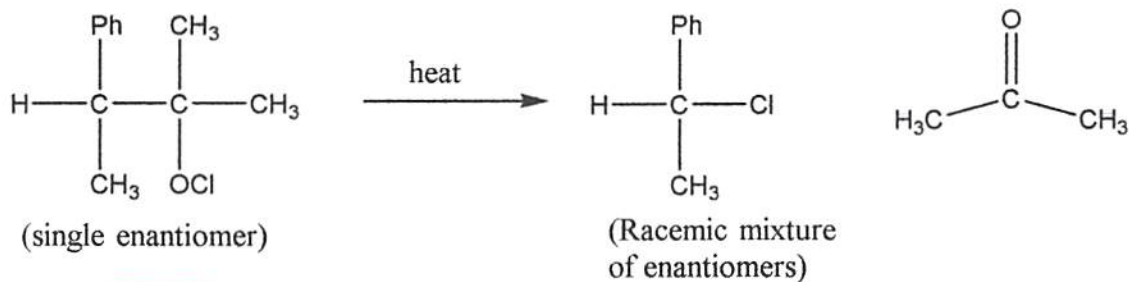
Vitamin E

- What is the functional group in the starting material of PROBLEM E?

Xanthate

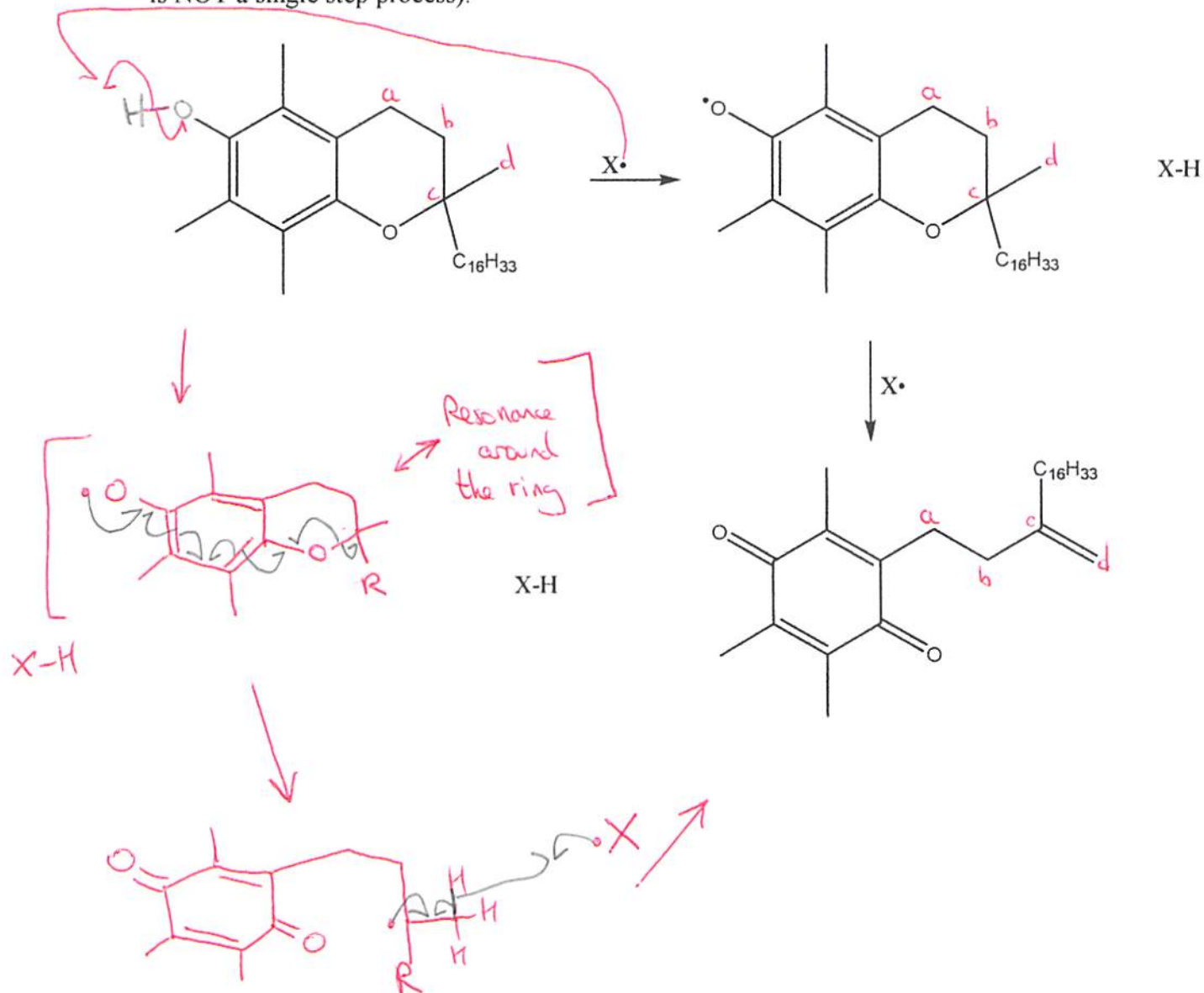


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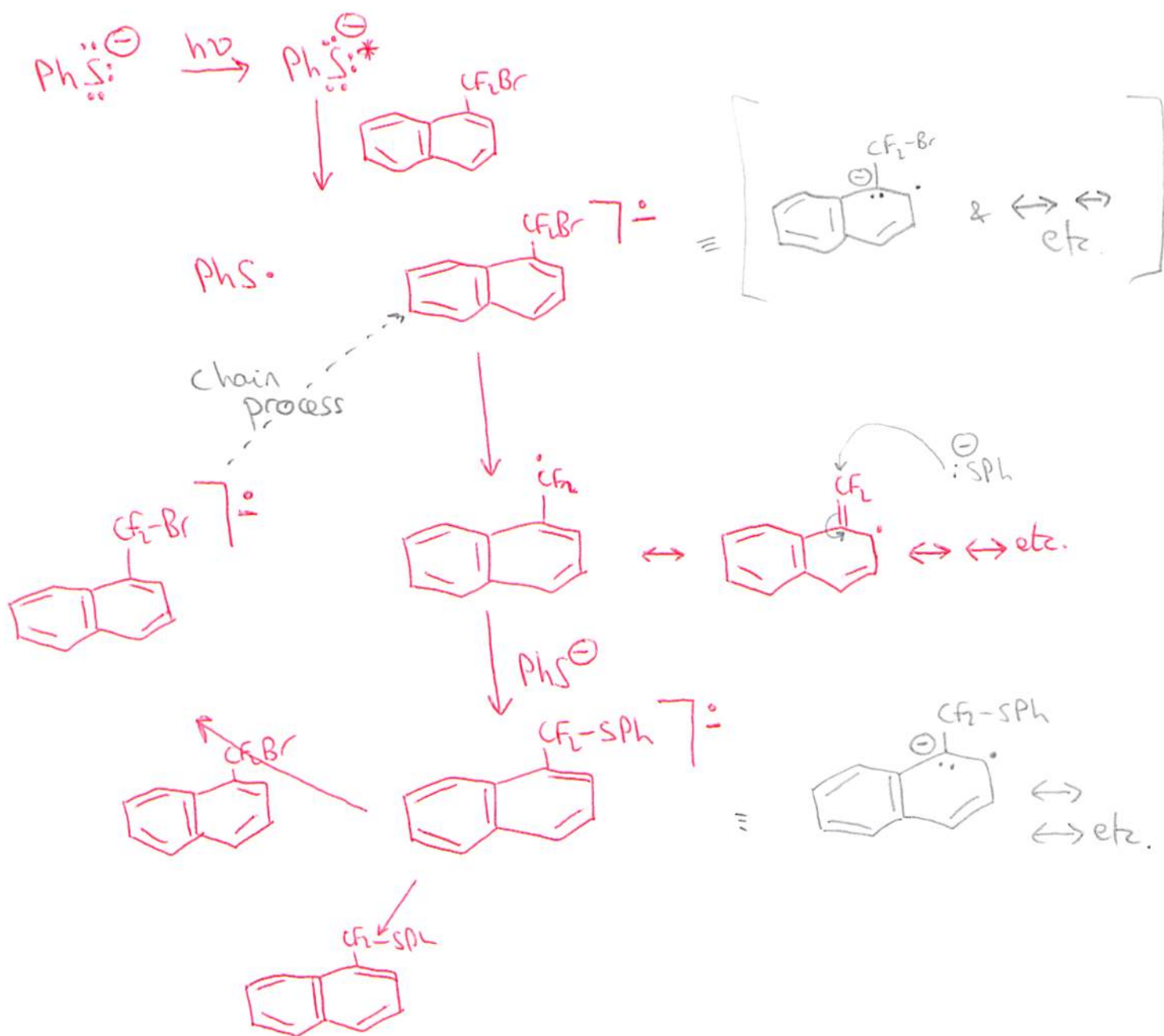
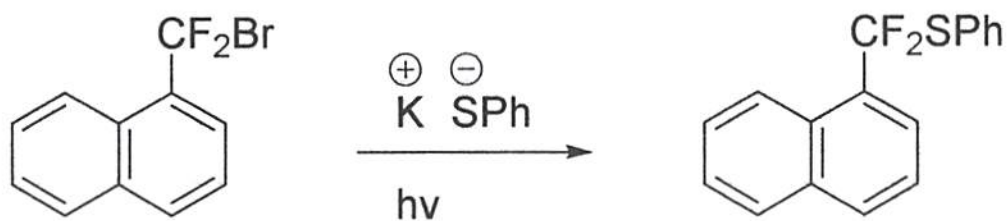


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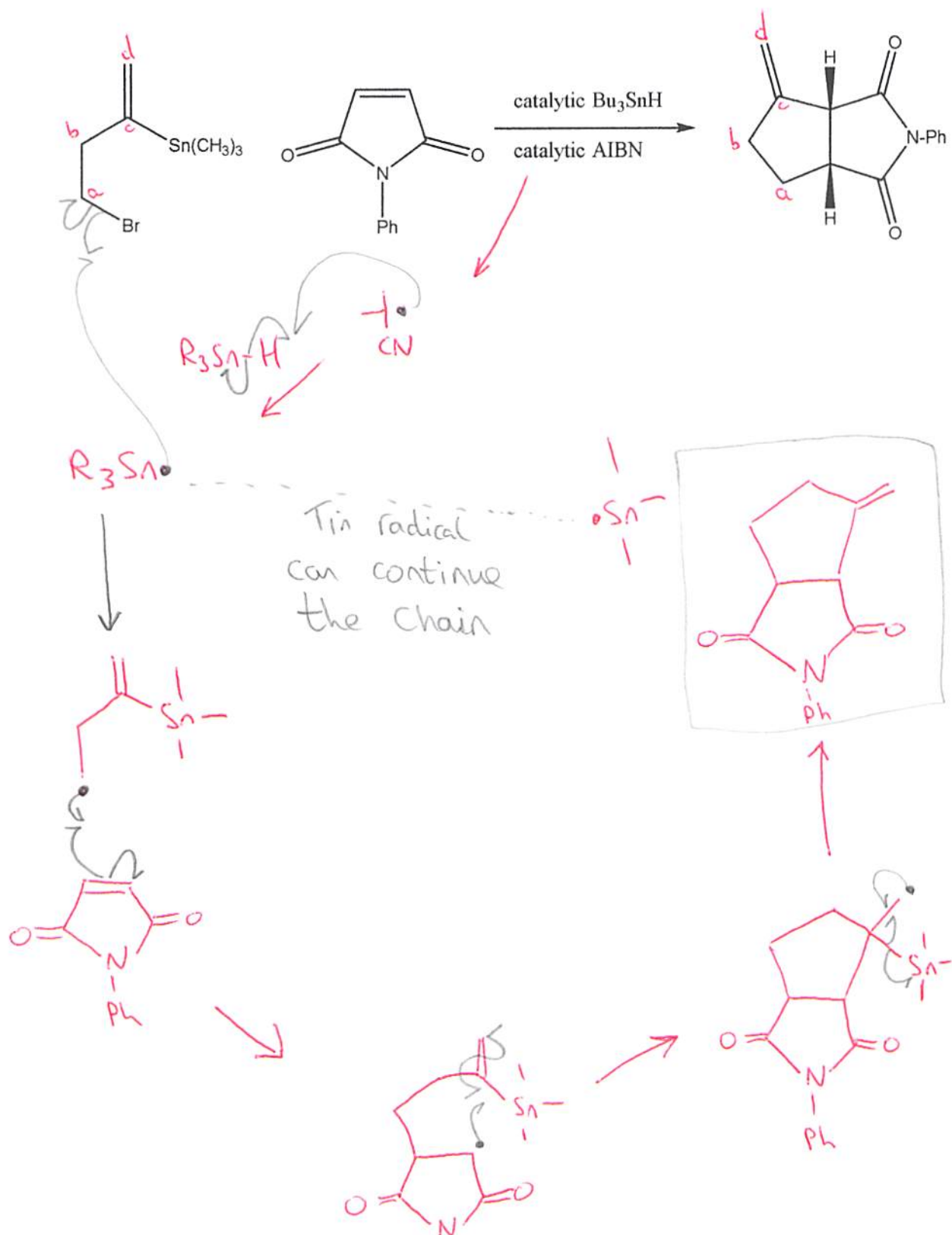
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C) Write a plausible mechanism for the following $S_{RN}1$ reaction.



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



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