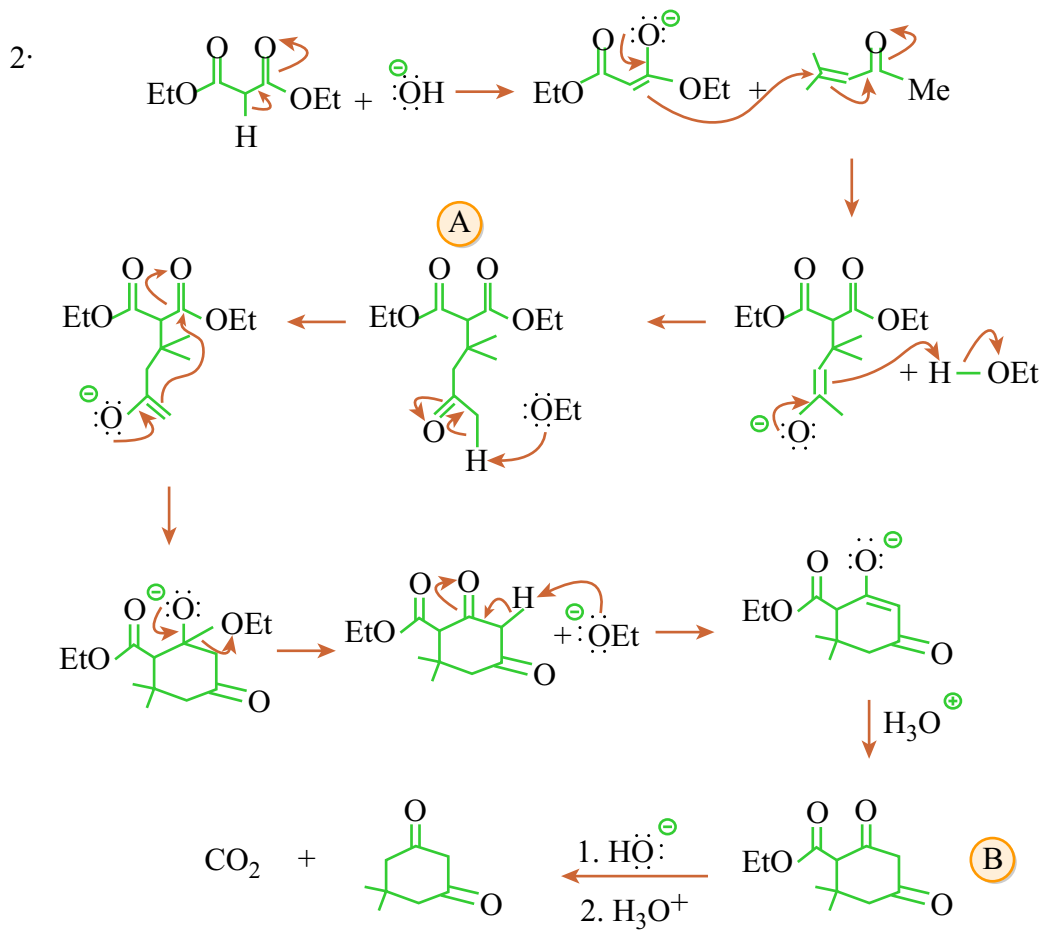
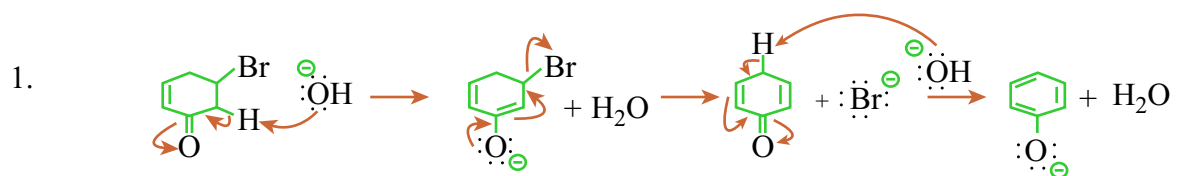
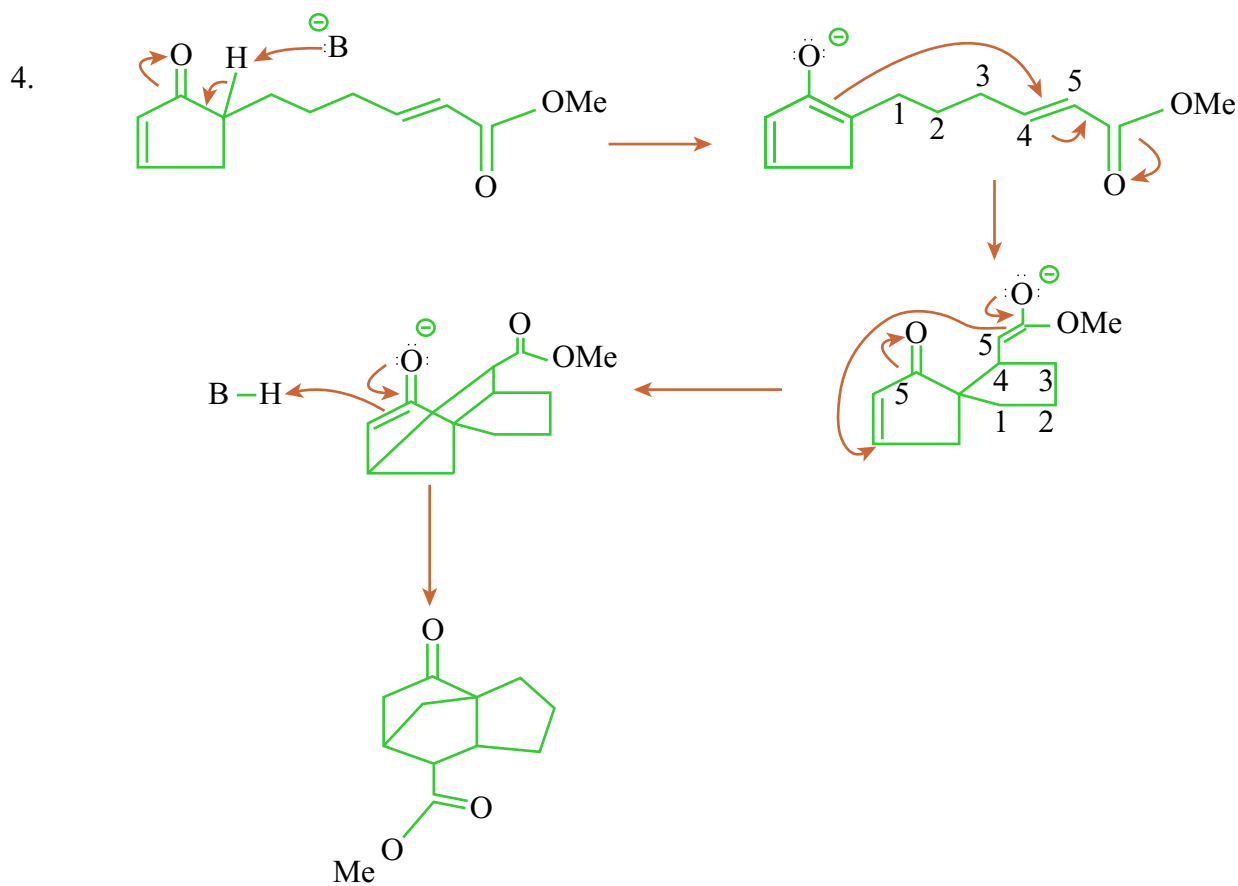
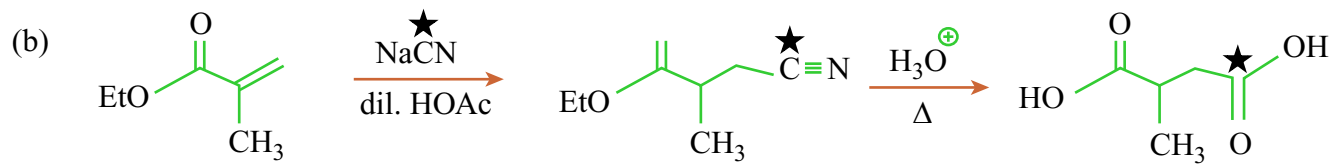
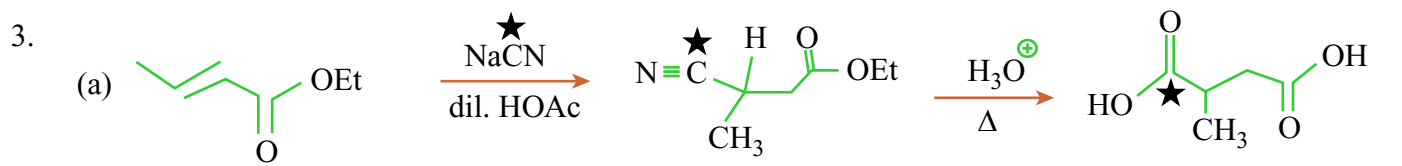


## Exam 4 - Extra Problems - Key



Figures by MIT OCW.

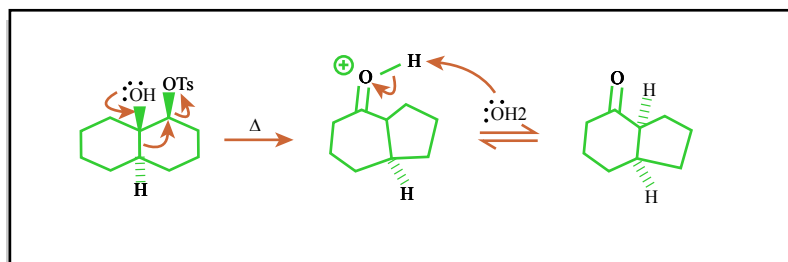


Figures by MIT OCW.

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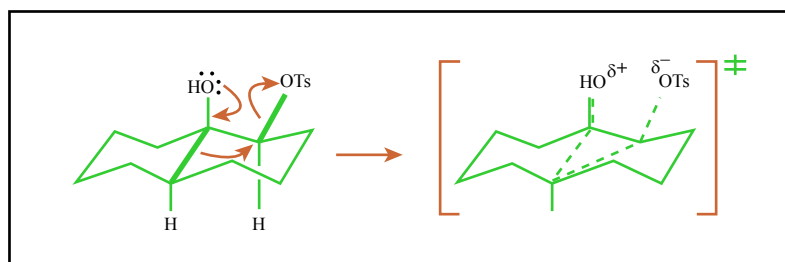
## 5.13: Organic Chemistry II

5.



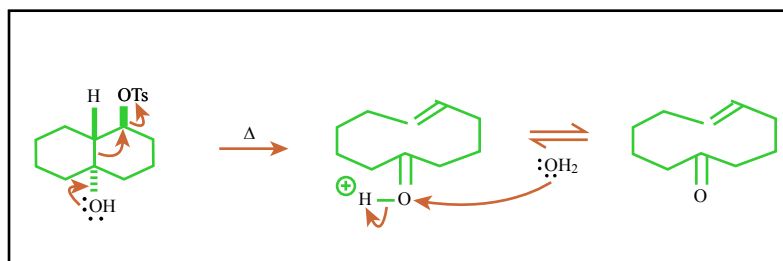
Figures by MIT OCW.

In this "Pinacol- like" concerted process, the migrating bond must be antiperiplanar to the LG so that the oxygen can stabilize the developing charge in the TS.



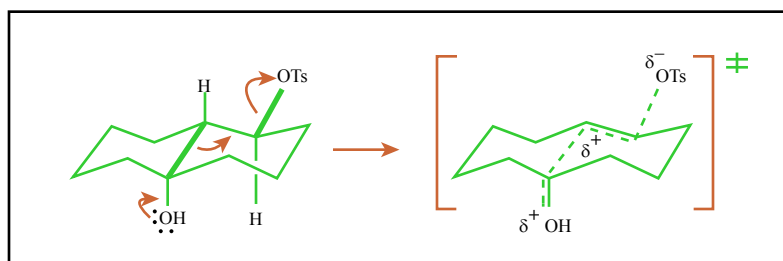
Figures by MIT OCW.

Only the ring fusion bond is a.p.p. to the LG.



Figures by MIT OCW.

This Grob fragmentation is also concerted, so the bond that is cleared must be antiperiplanar to the LG.(only the fusion bond is a.p.p.)



Figures by MIT OCW.

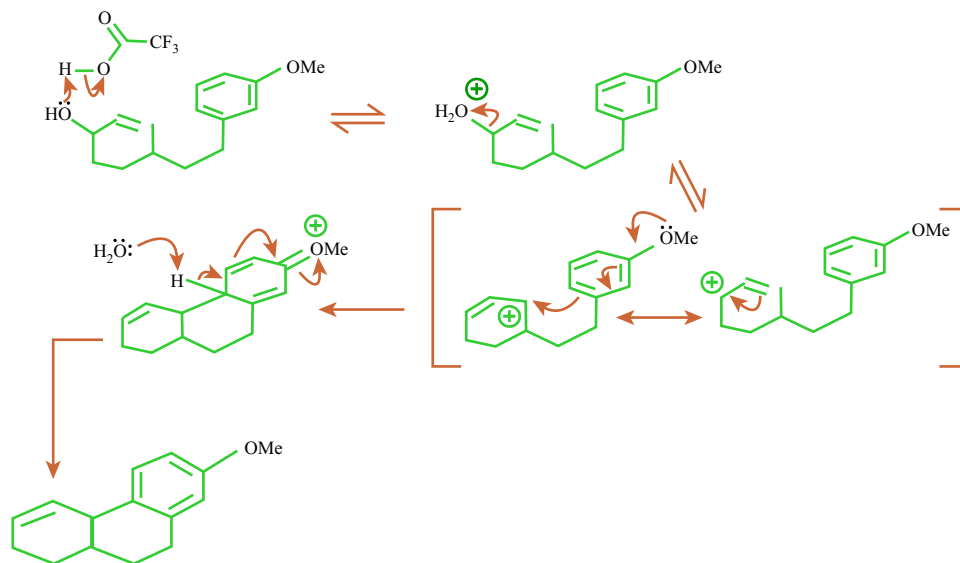
Only the bond a.p.p. to the LG is involved in these processes. The position of the oxygen determines which product will be formed.

Figures by MIT OCW.

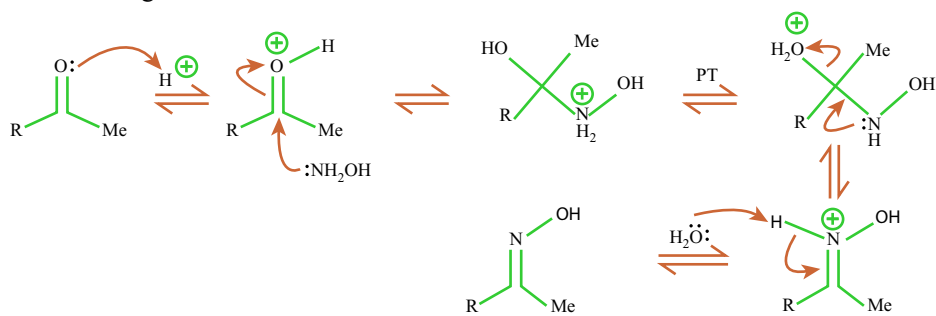
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## 5.13: Organic Chemistry II

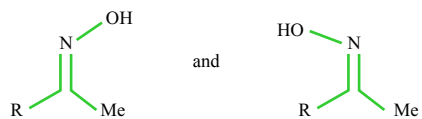
6.



7. Each of these mechanisms proceeds through an oxime.



Would likely form mixture of



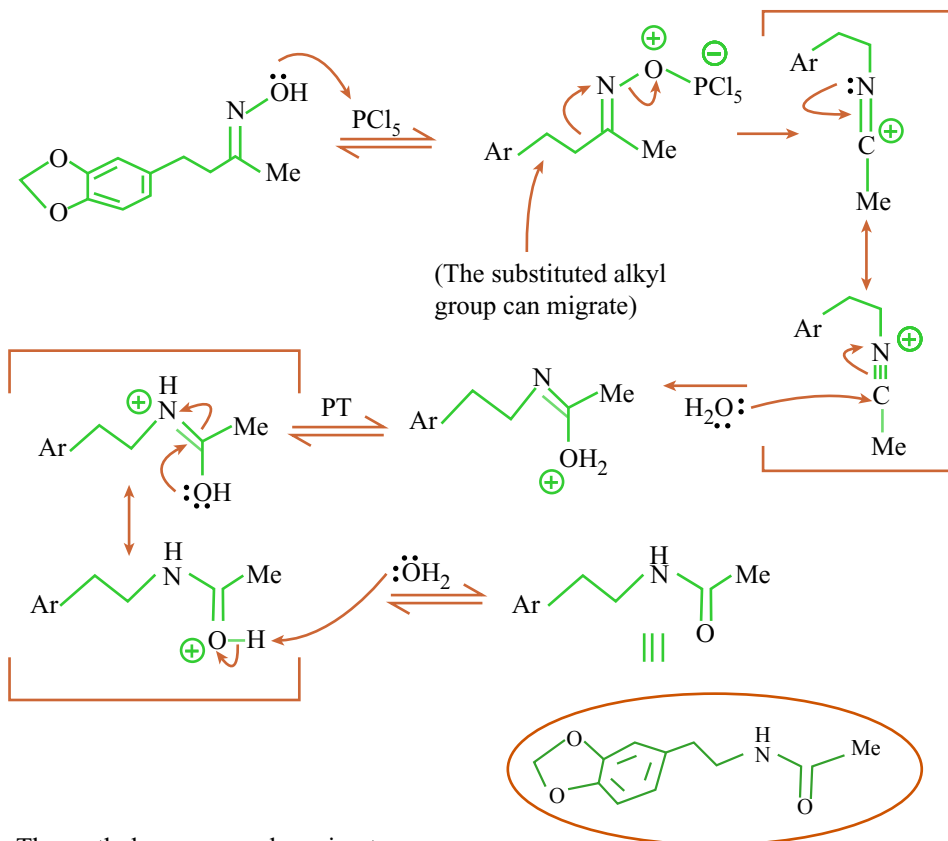
(Cont.)

Figures by MIT OCW.

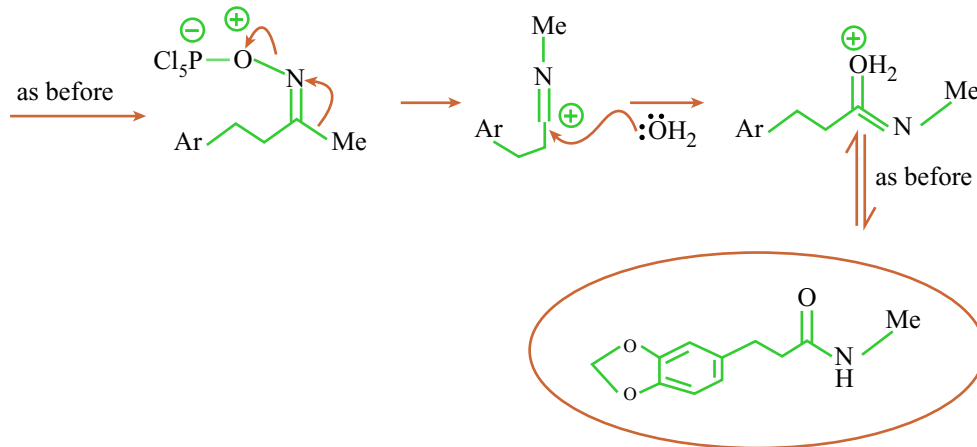
# Massachusetts Institute of Technology

## 5.13: Organic Chemistry II

7. Cont.....



... The methyl group can also migrate.

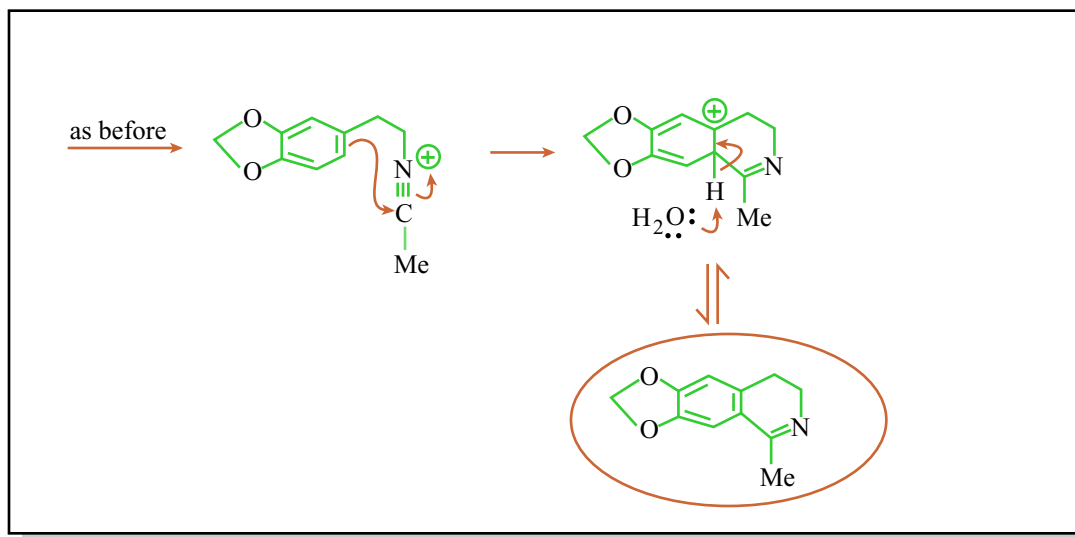


Figures by MIT OCW.

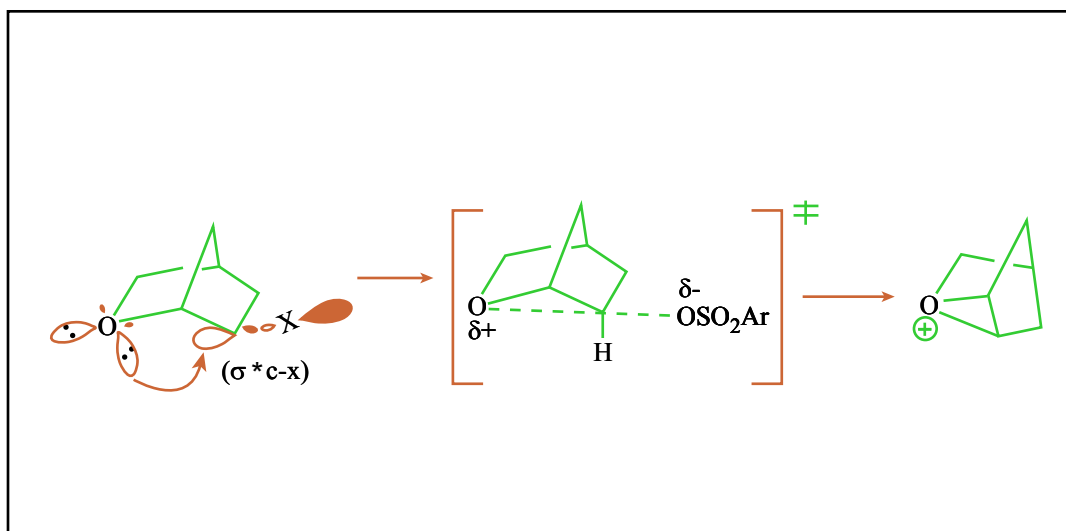
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## 5.13: Organic Chemistry II

7. Continued. The nitrilium ion formed after migration is very electrophilic. the aryl group is electron-rich --> electrophilic aromatic substitution.



8.a) Both of the substitution reactions must go through a cationic species. Formation of this intermediate is the RDS. In the first reaction, the oxygen can facilitate ionization by donating its lone pair into the C-LG antibonding orbital. This speeds up the reaction . (NGP!)

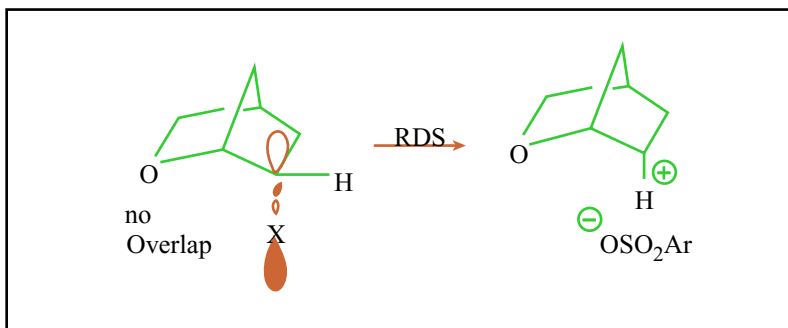


Figures by MIT OCW.

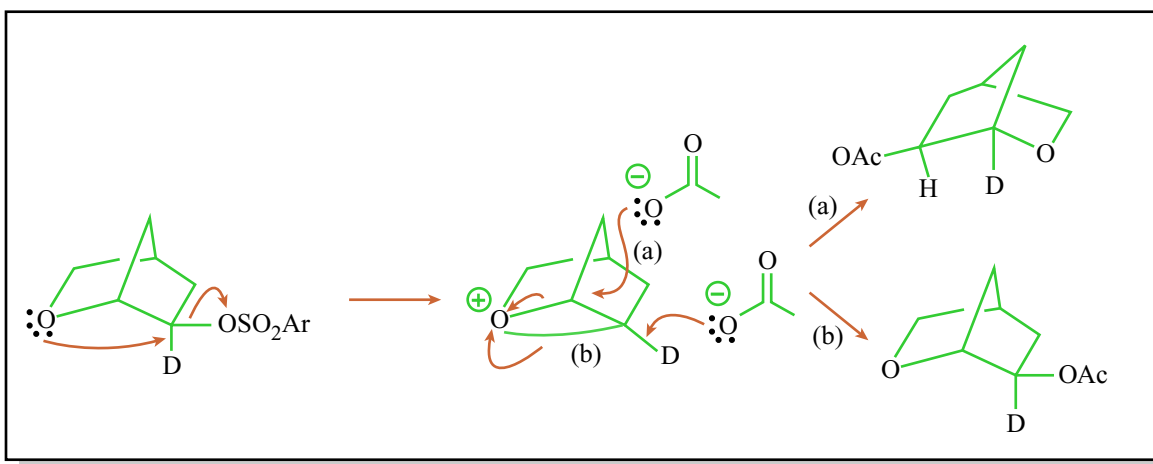
# Massachusetts Institute of Technology

## 5.13: Organic Chemistry II

In the second reaction neighbouring group participation is not possible because there is no overlap between the oxygen lone pair  $\sigma^*_{CX}$ . The ionization step is slower.



b) Both rxns proceed through the following intermediate A. the acetate ion can attack two possible sites to give the two observed products.

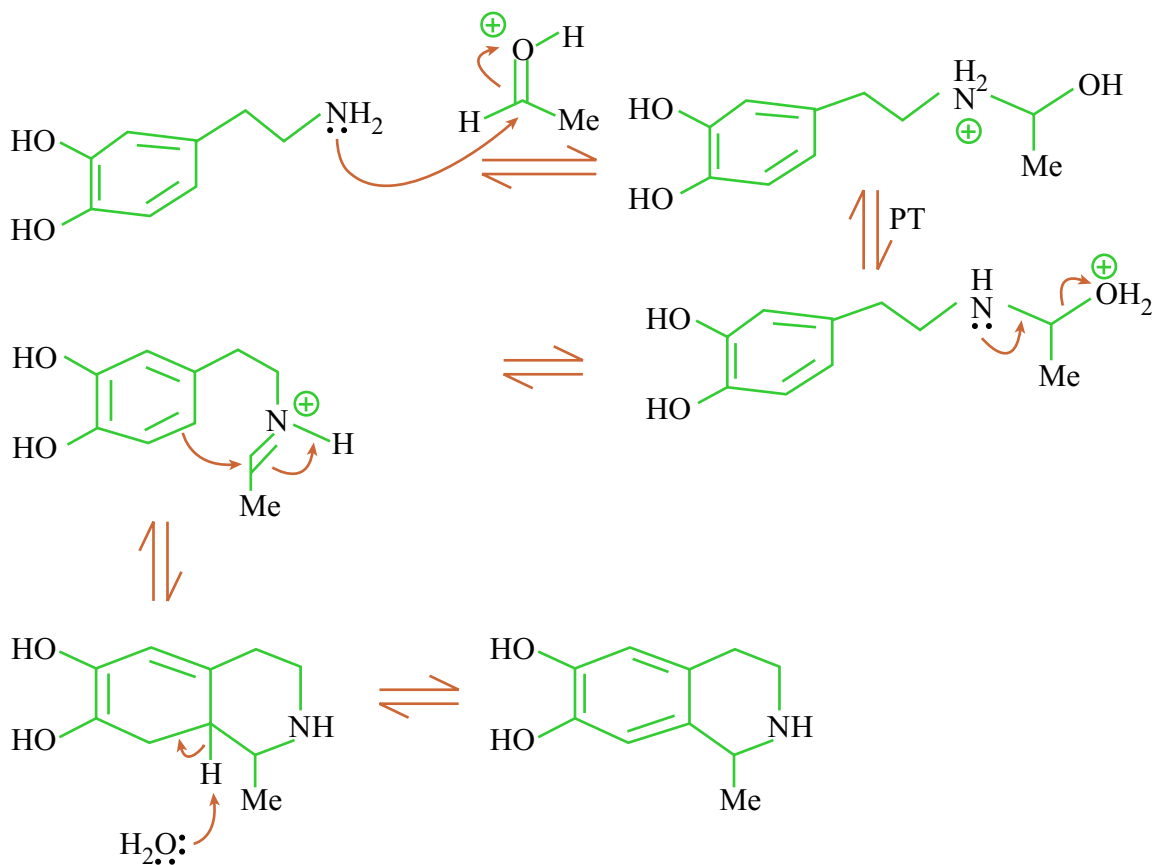


The rxns essentially proceed through an "S<sub>N</sub>2 - like" pathway because of the NGP.  
--> No other stereoisomers are formed.

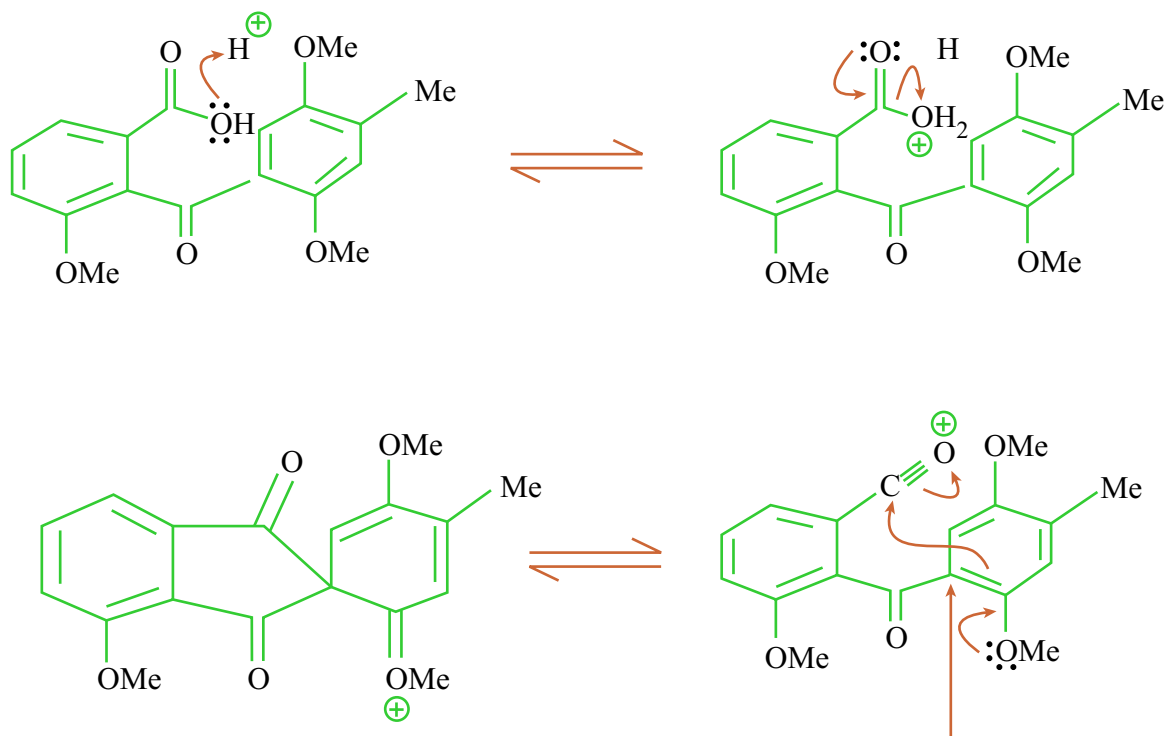
Figures by MIT OCW.

5.13: Organic Chemistry II

9.



10.



This carbon more nucleophilic because cation formed stabilized by OMe & Me & not destabilized by orthoacyl group.

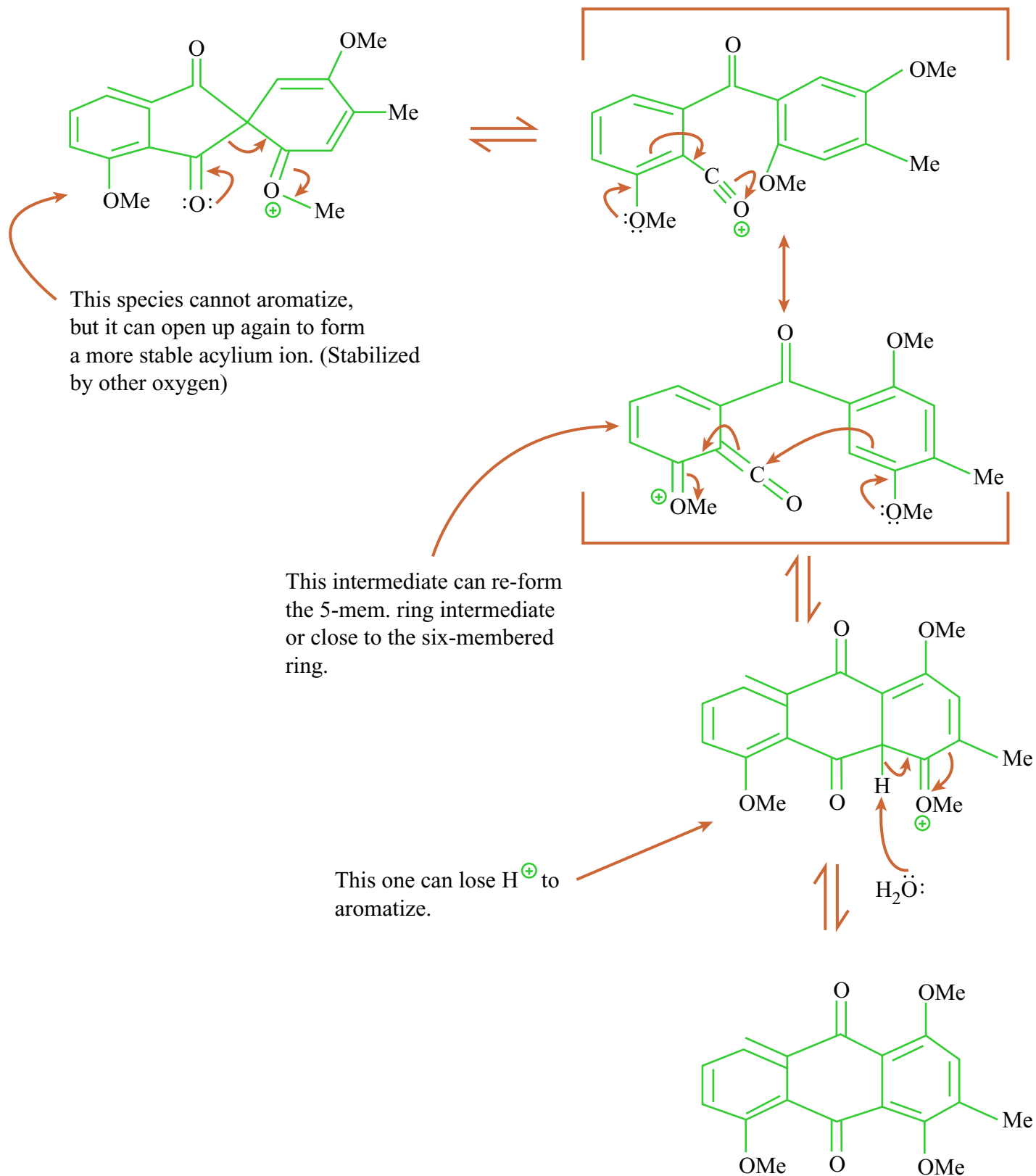
(cont. on next page)

Figures by MIT OCW.



5.13: Organic Chemistry II

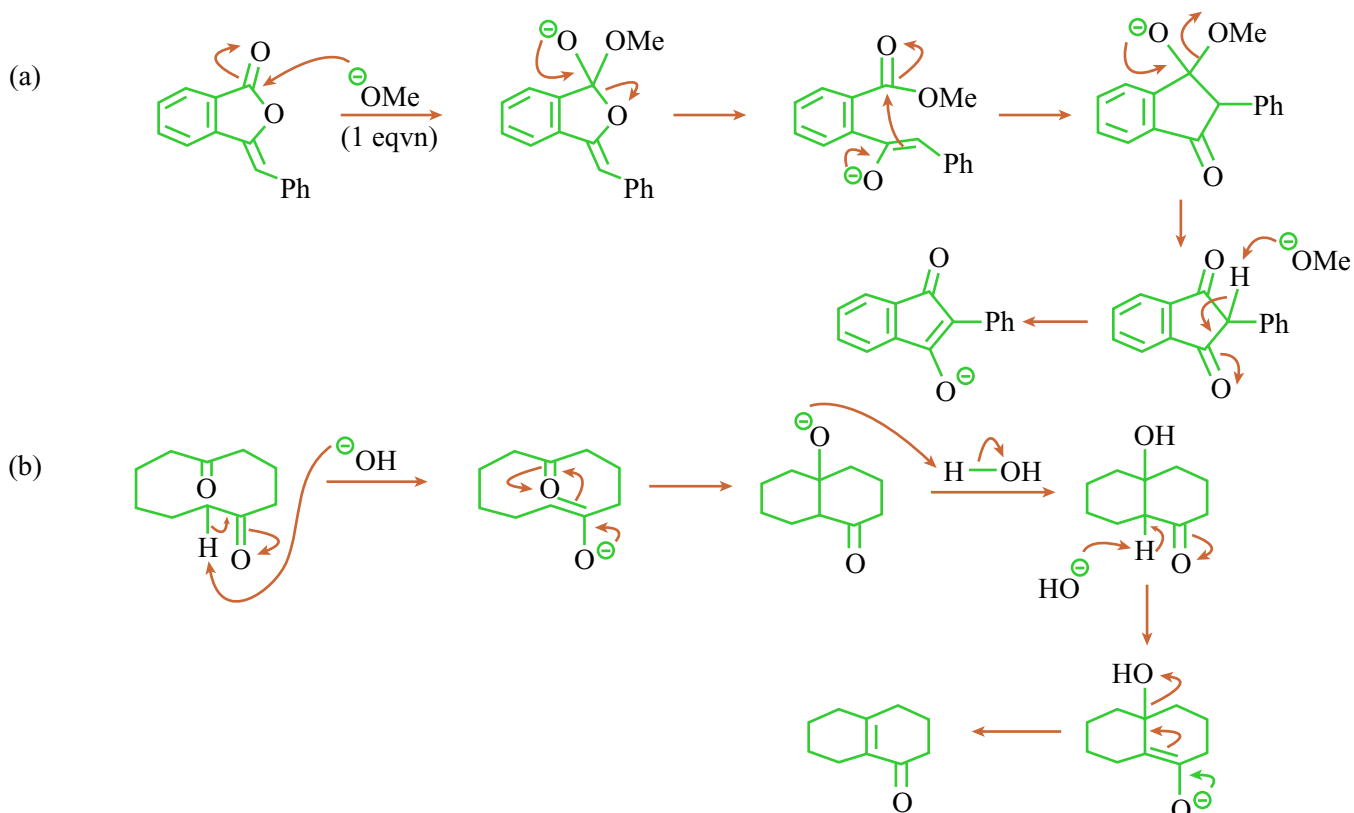
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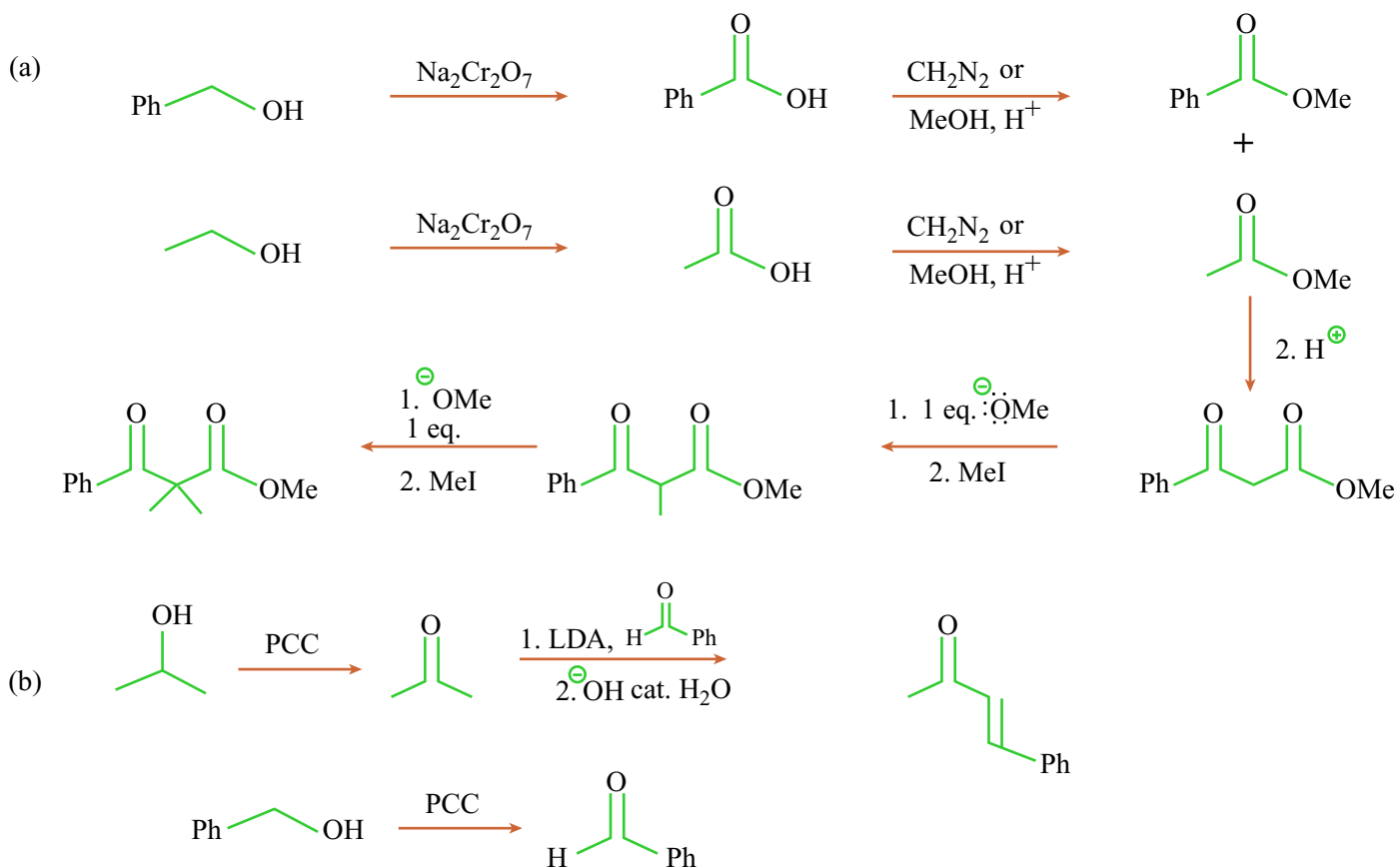
Figures by MIT OCW.

## 5.13: Organic Chemistry II

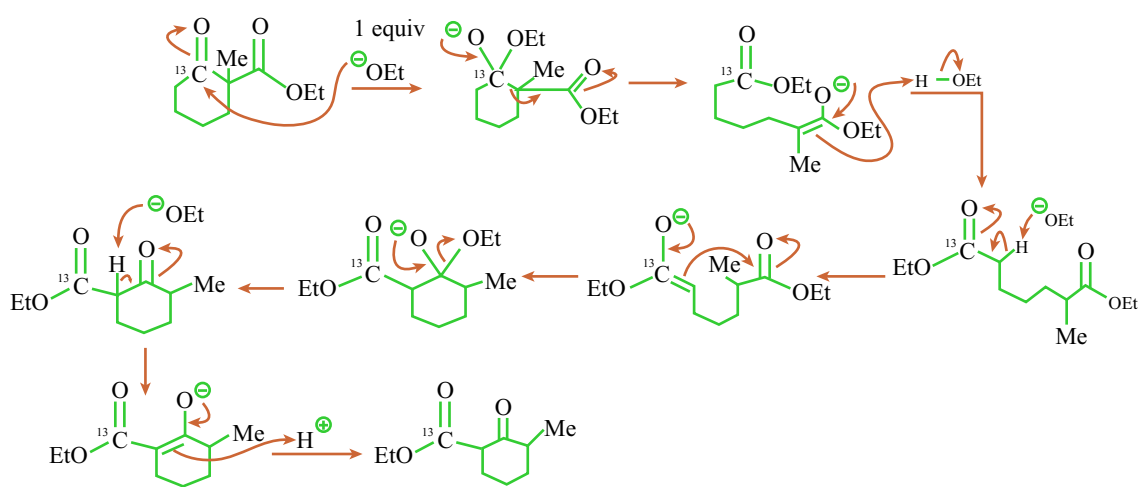
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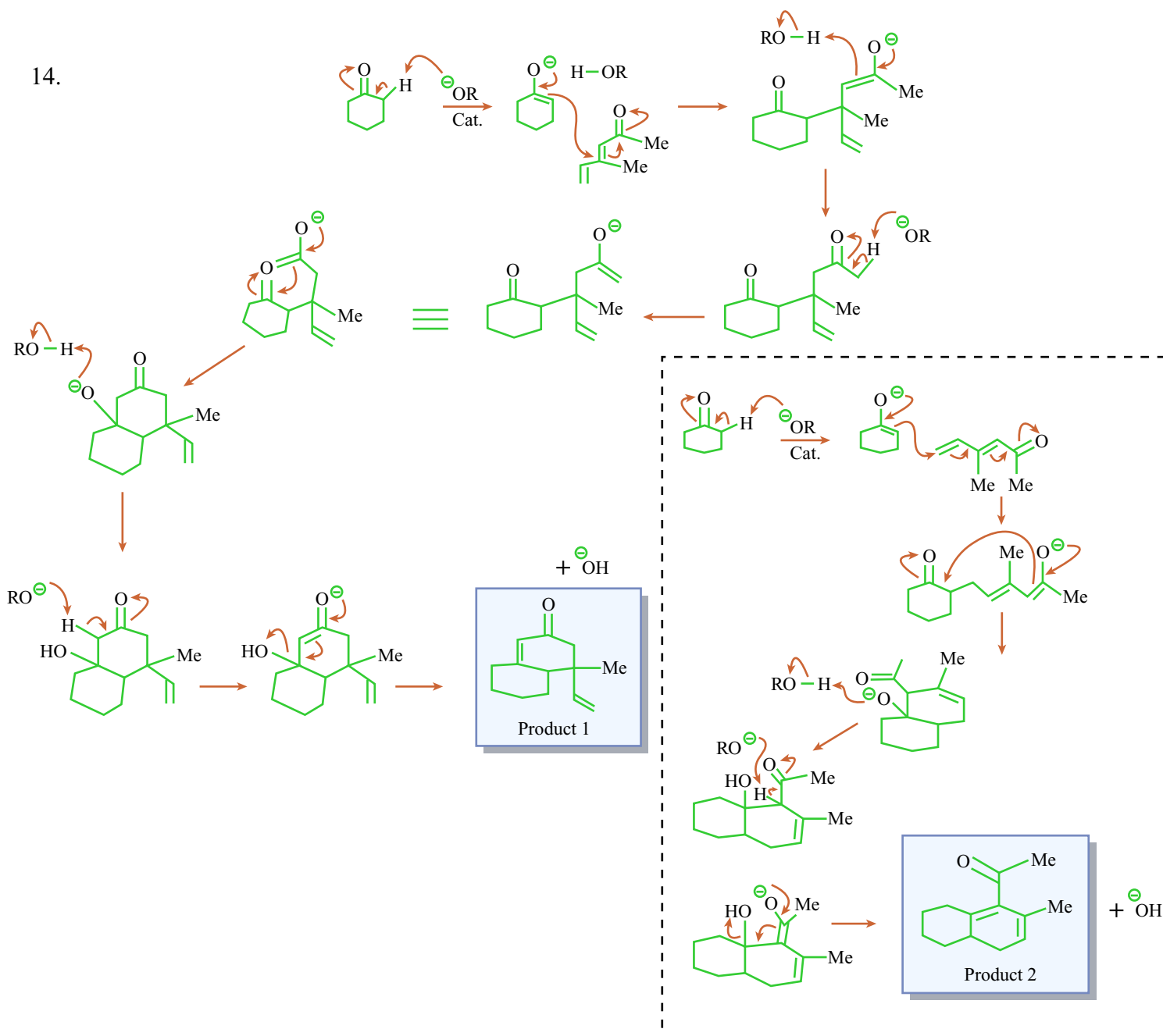
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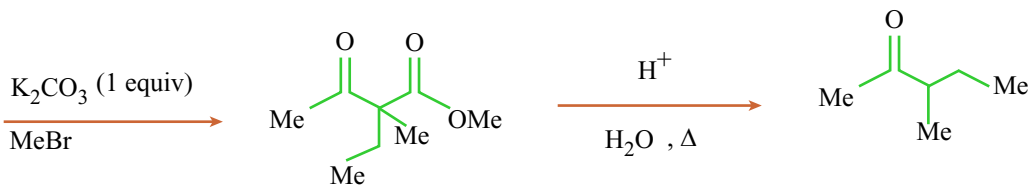
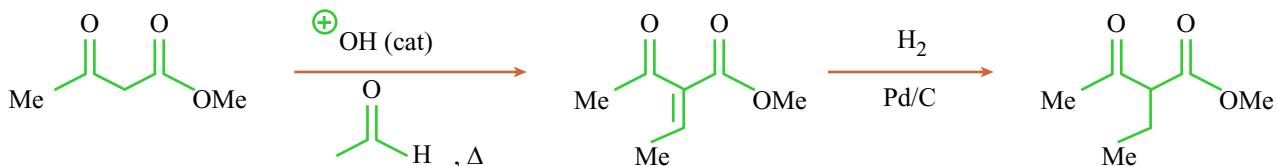
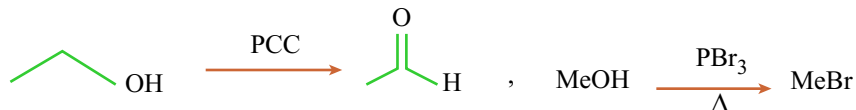
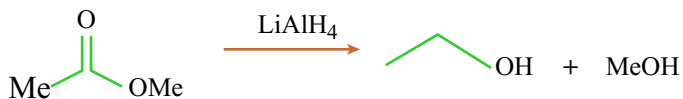
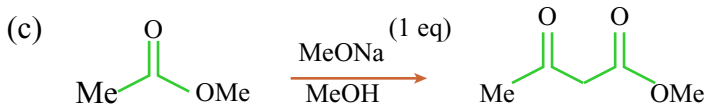
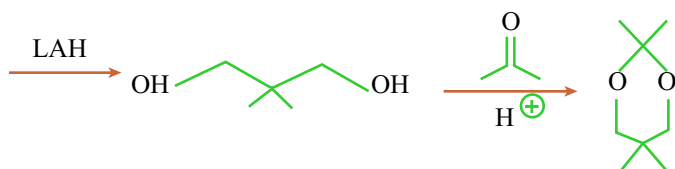
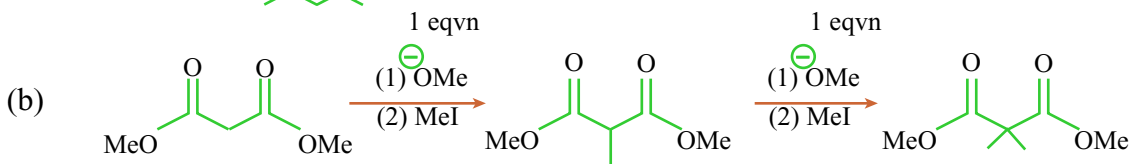
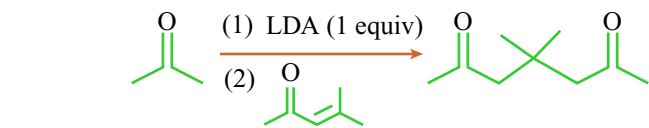
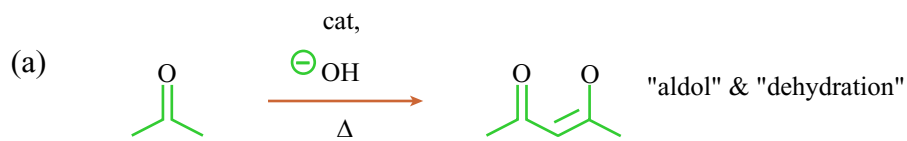
13.



14.

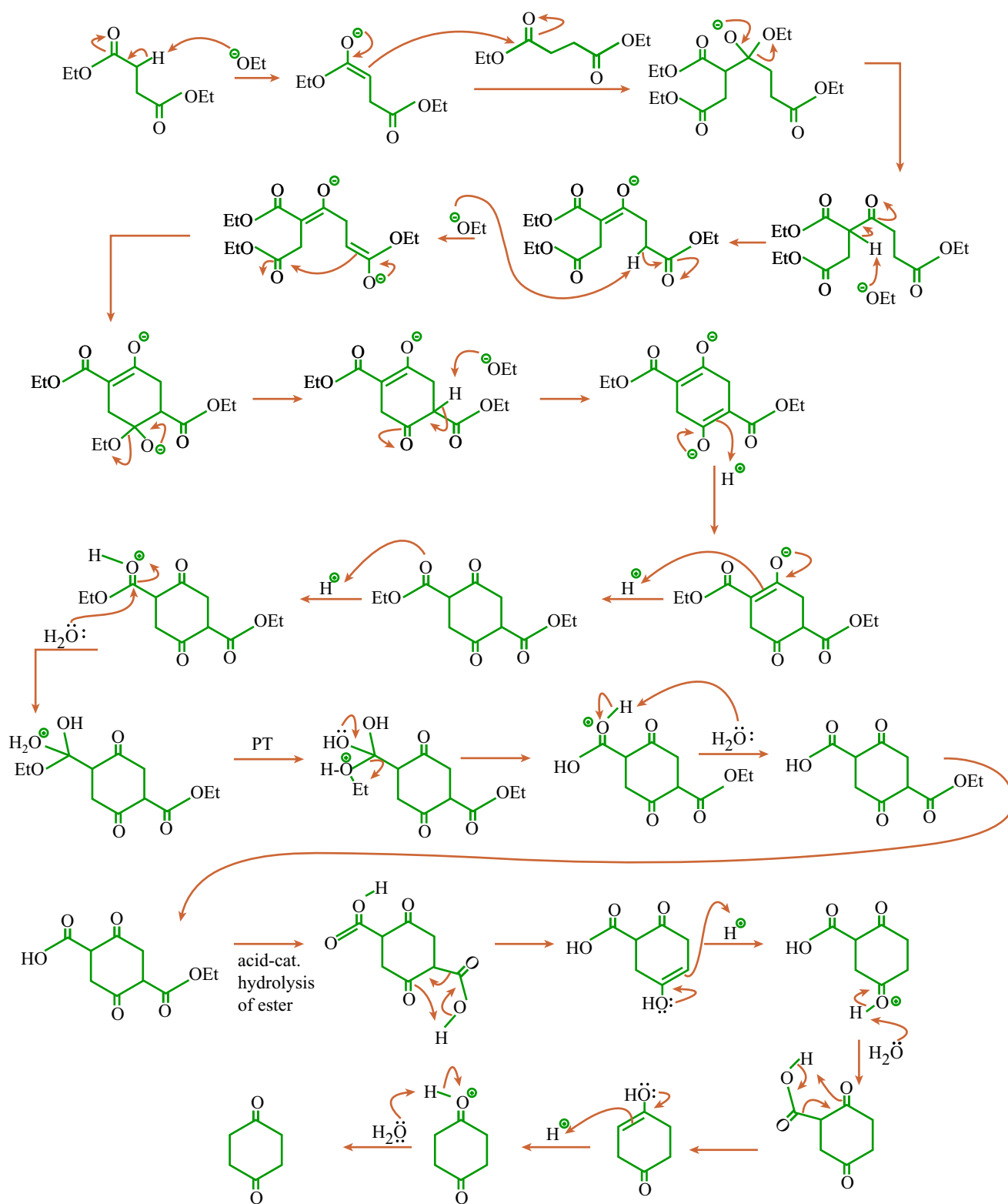


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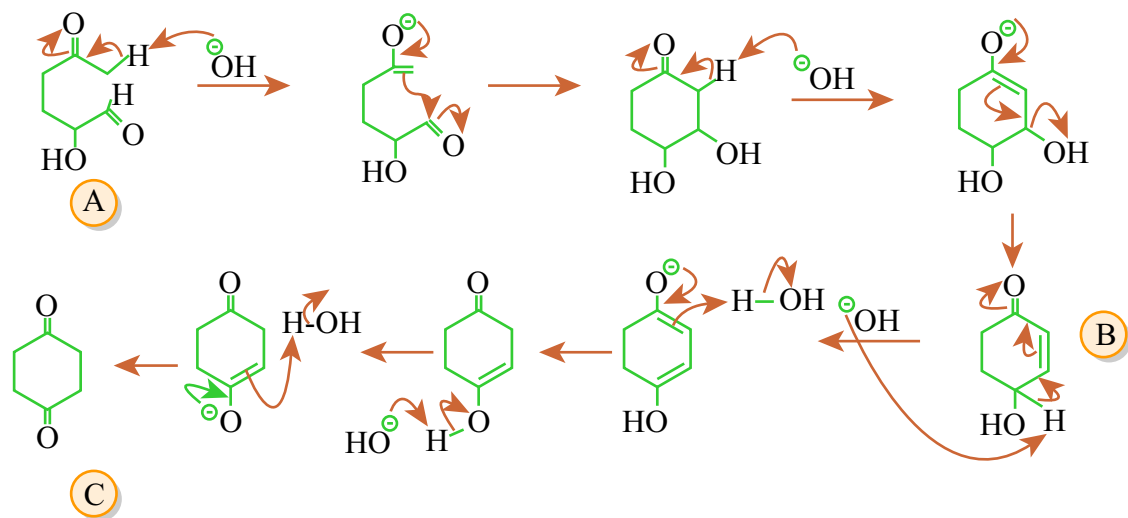
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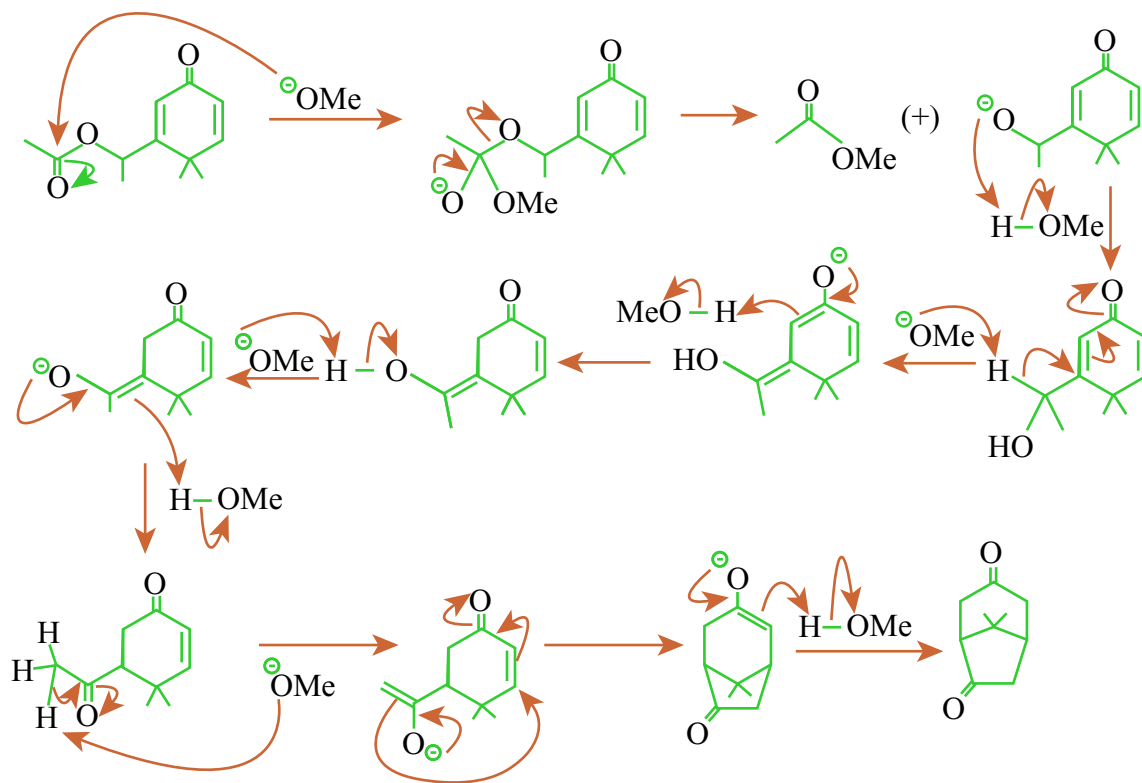


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17

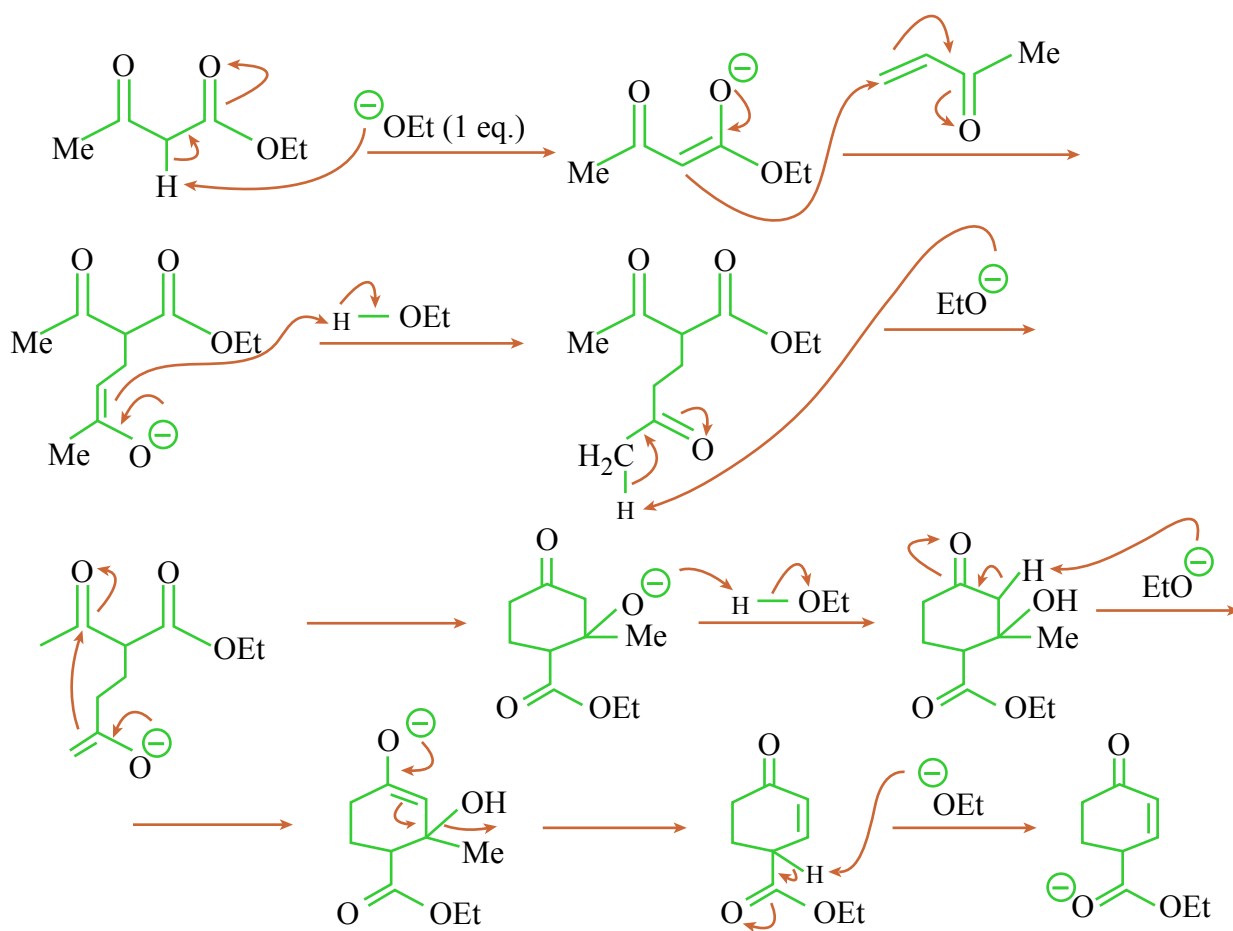


18



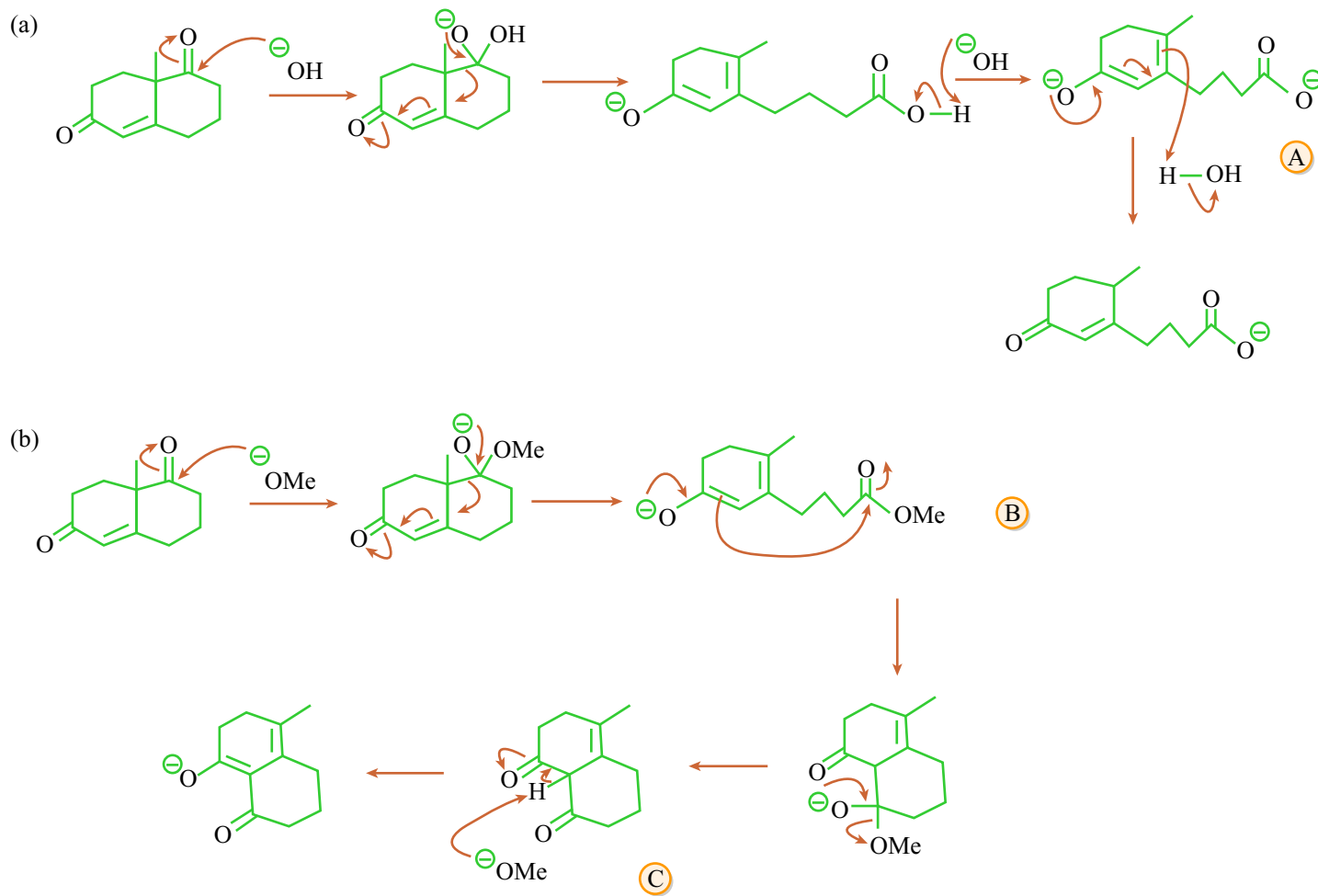
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19.



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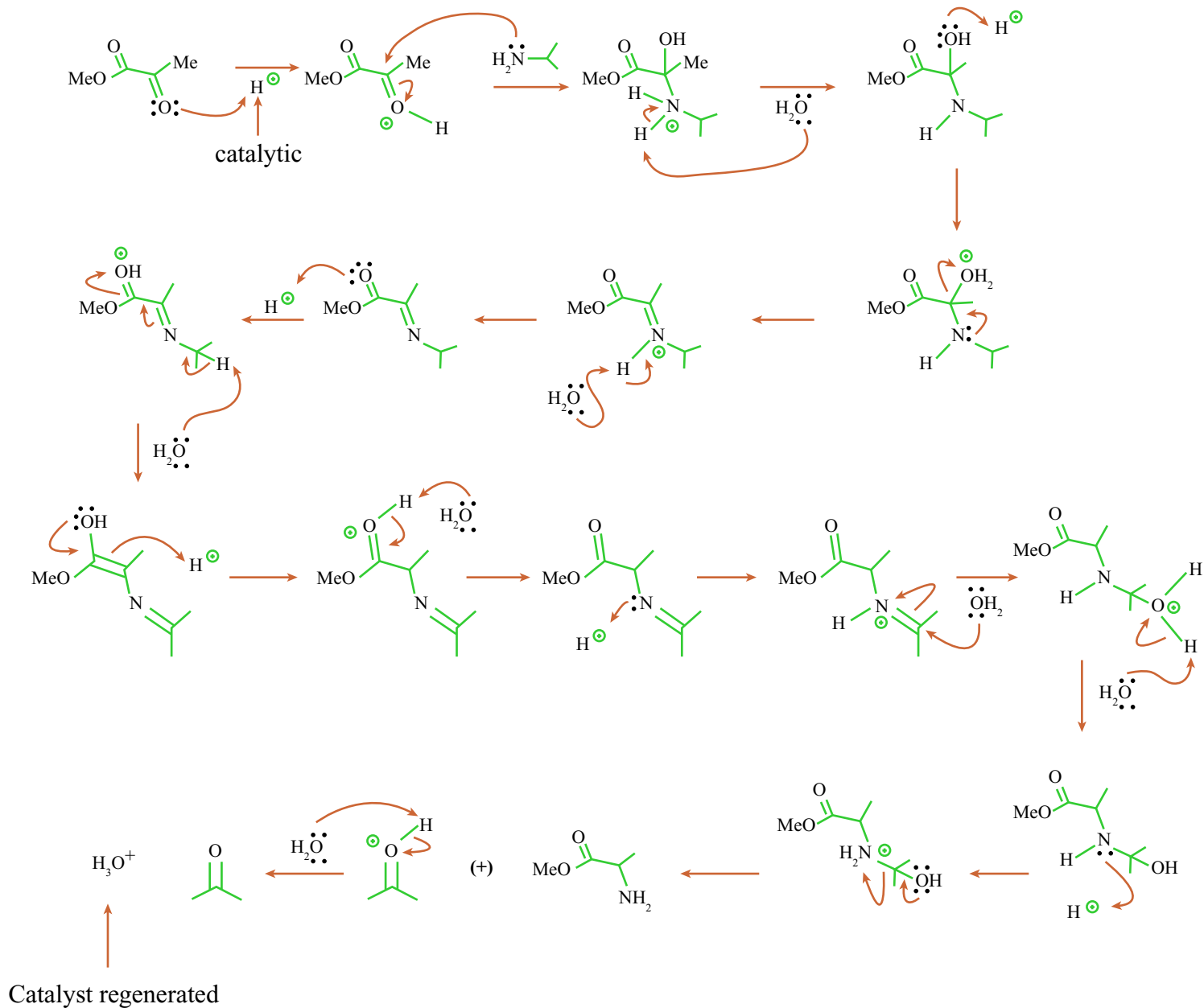


(c) Carboxylate **(A)** generated from rapid deprotonation is not reactive toward nucleophilic attack by enolates. In contrast, **(B)** can do further condensation generating **(C)** which can be deprotonated under rxn condition.

Figures by MIT OCW.

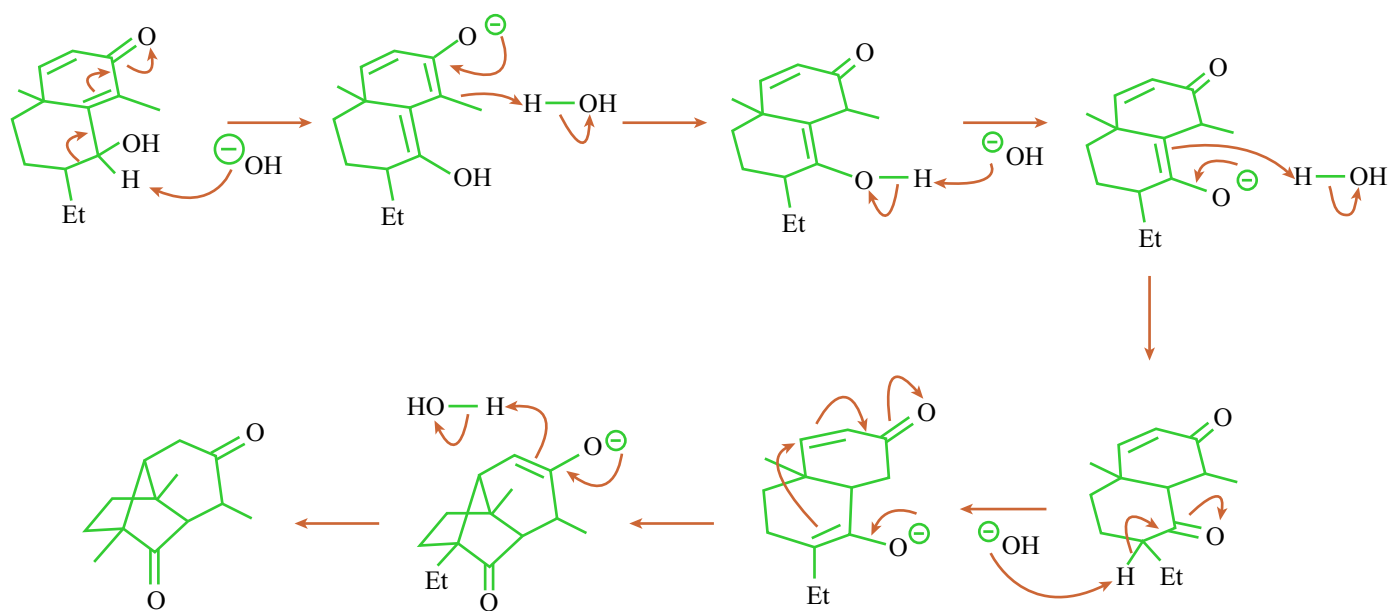


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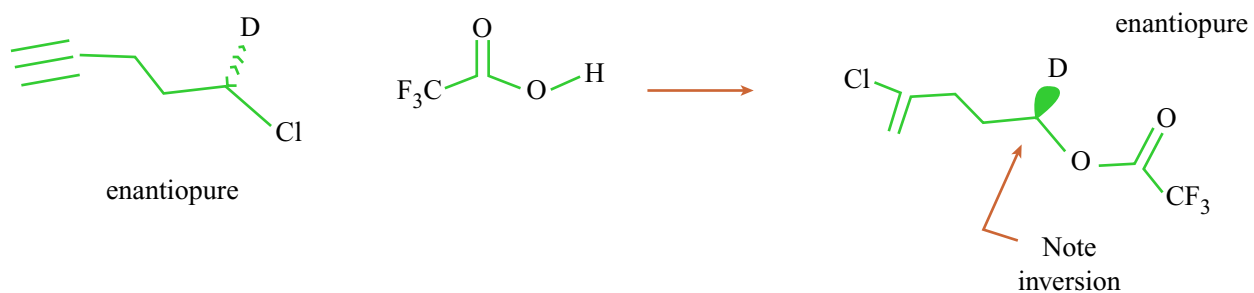
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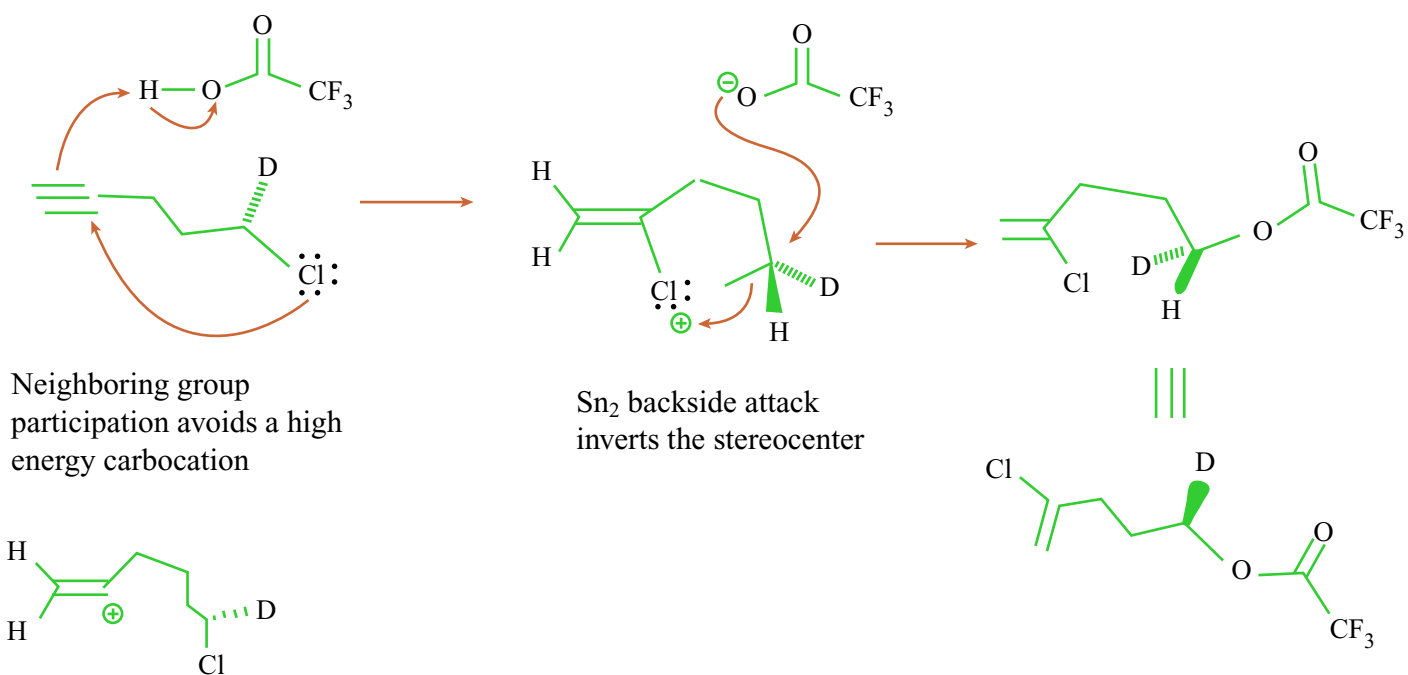


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23.

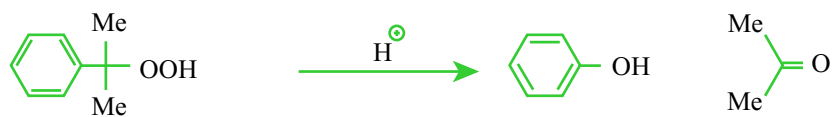


Mechanisms

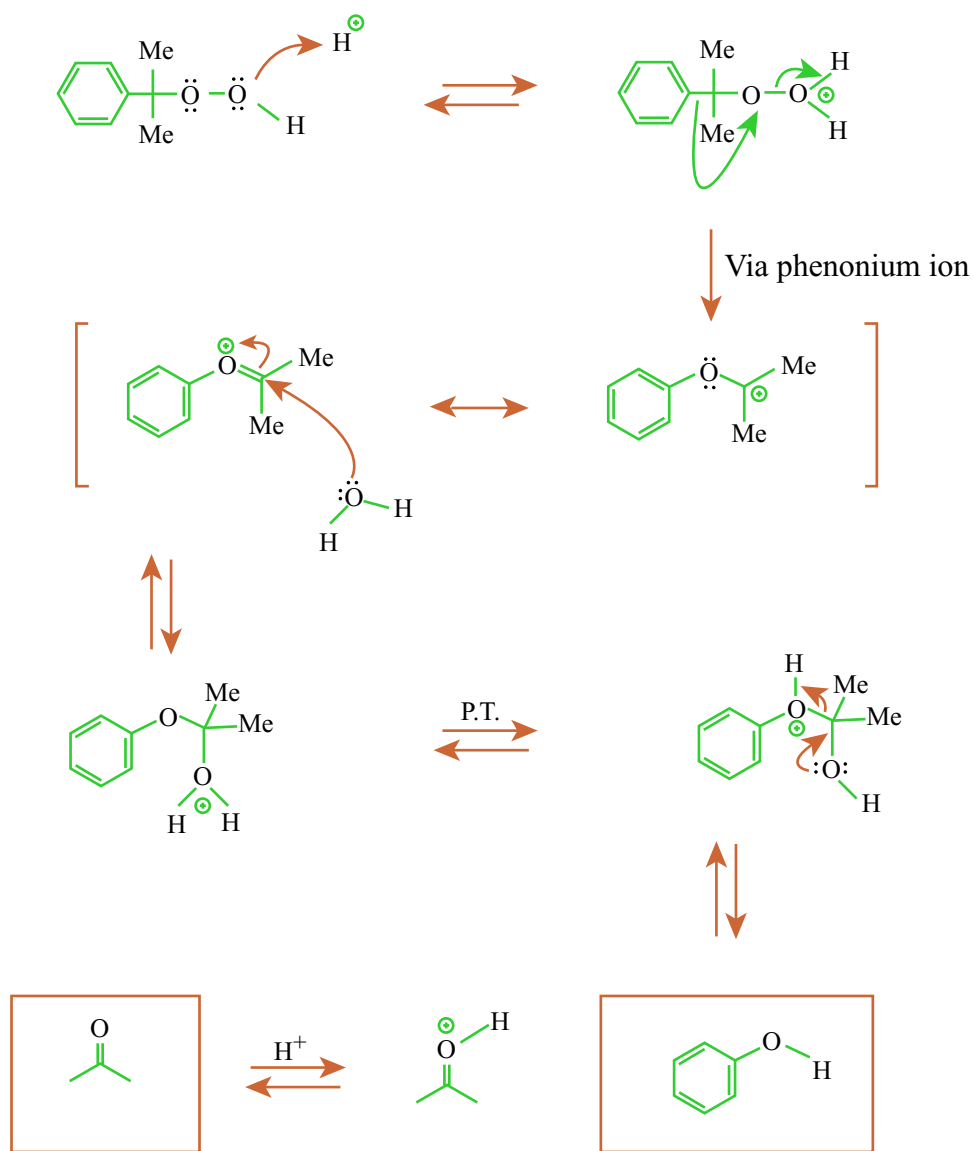


Figures by MIT OCW.

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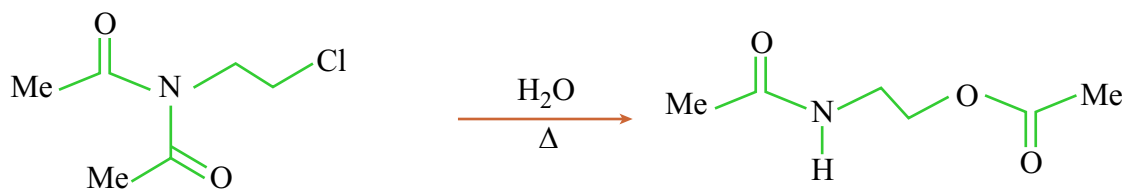


Mechanism:

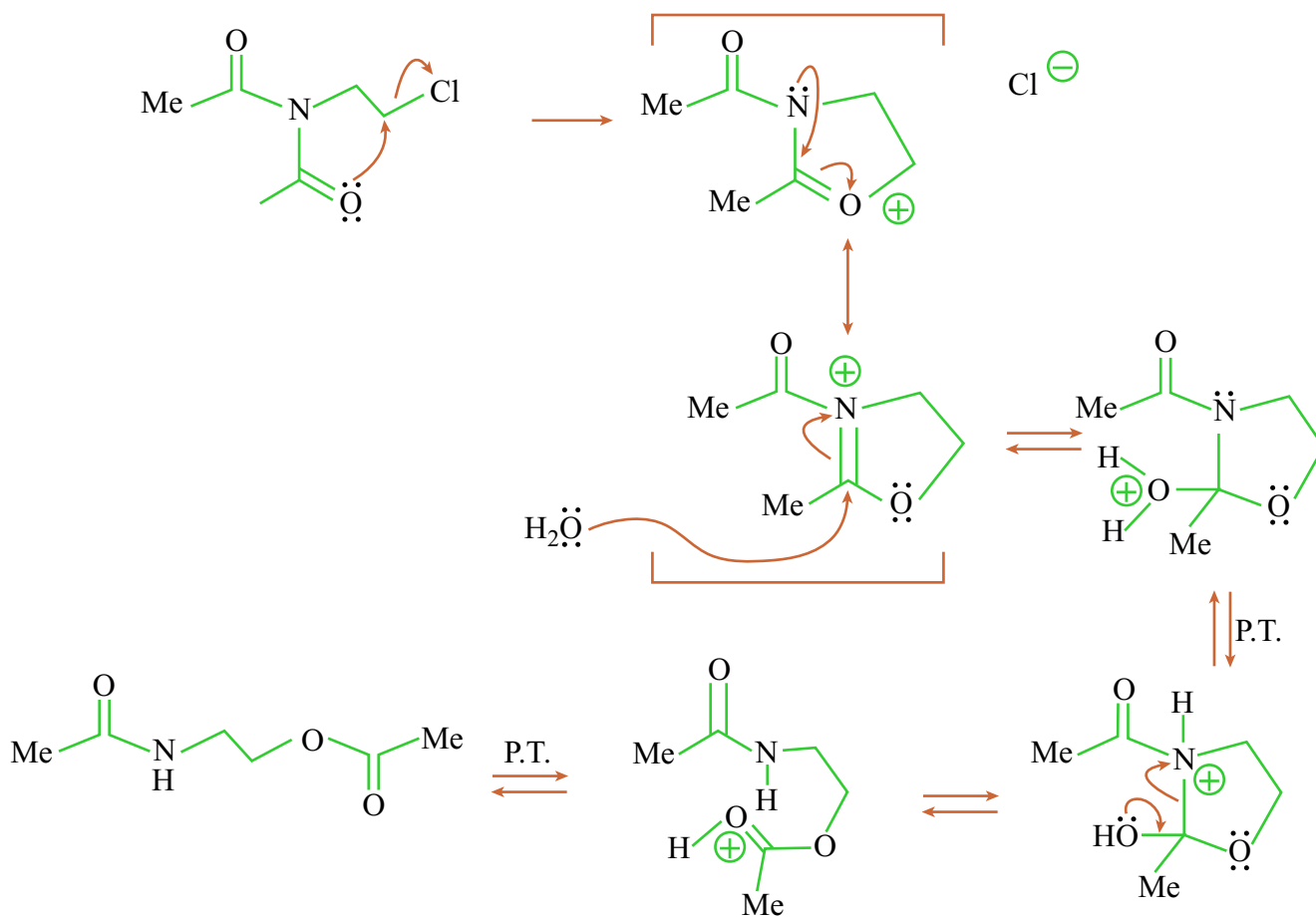


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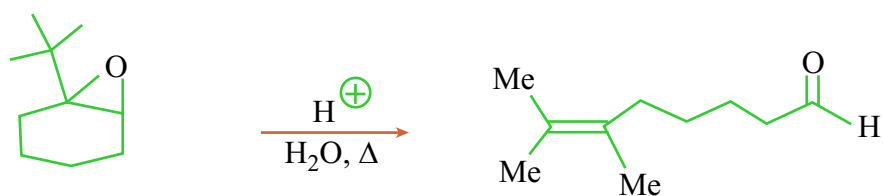


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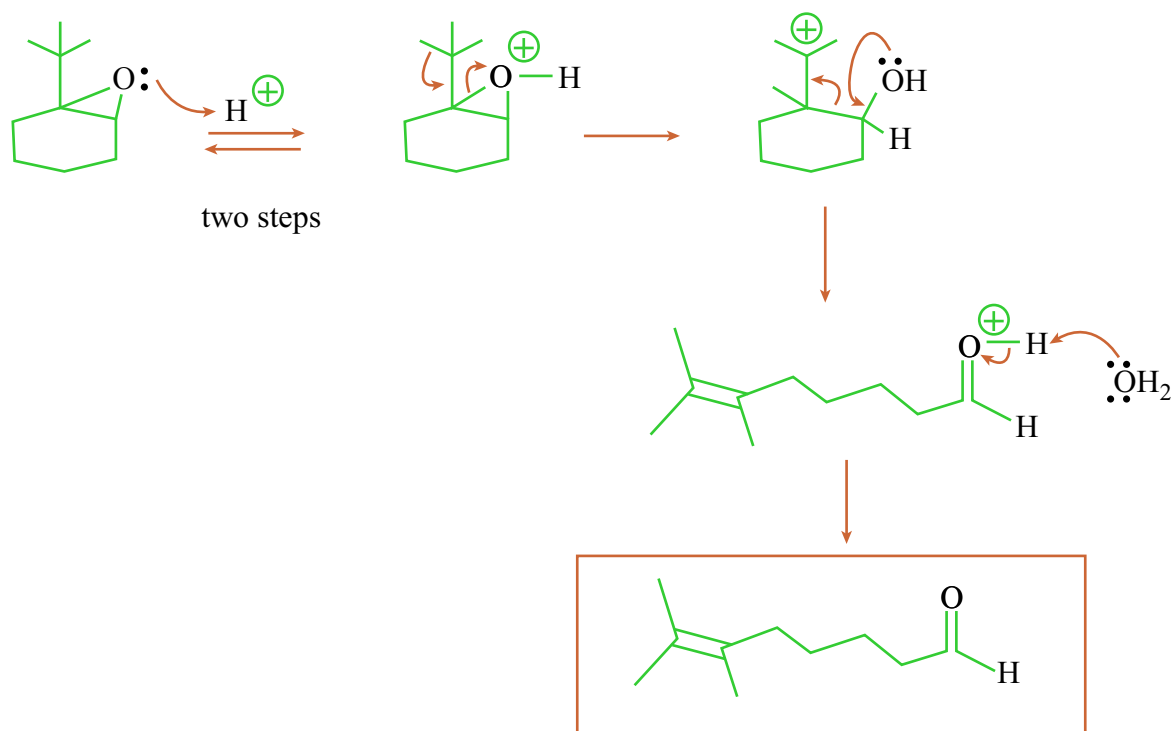


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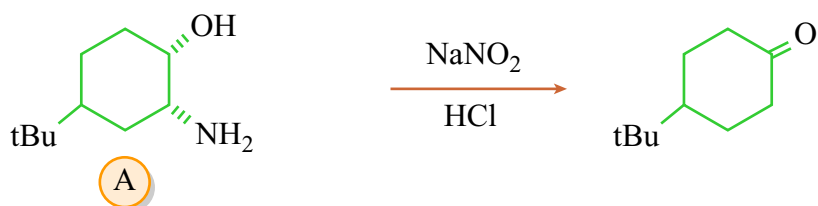


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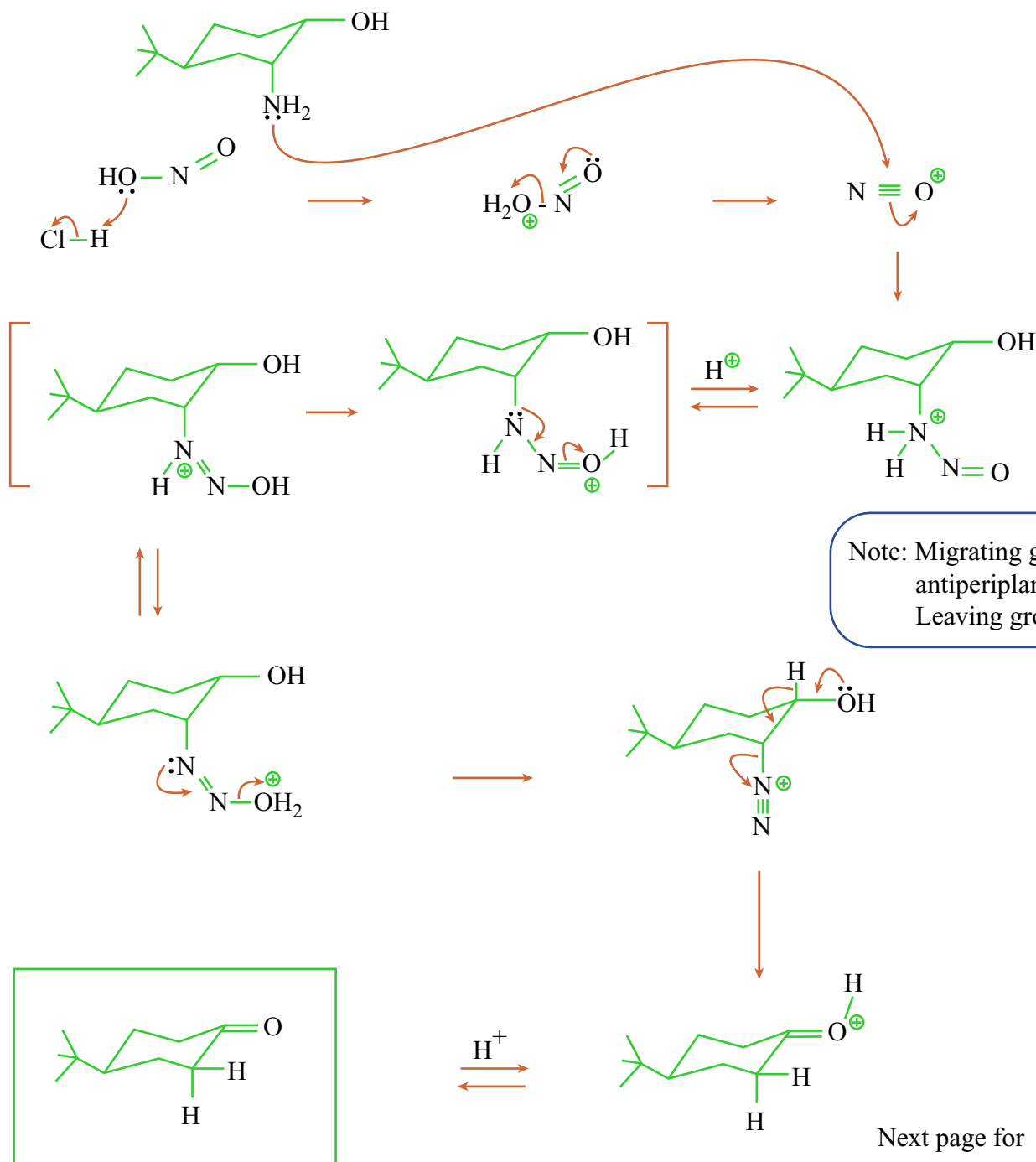


Figures by MIT OCW.

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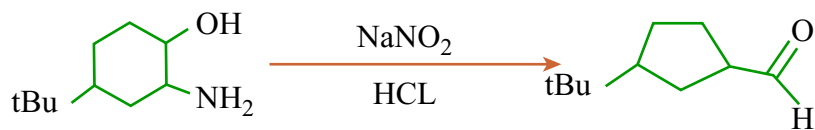


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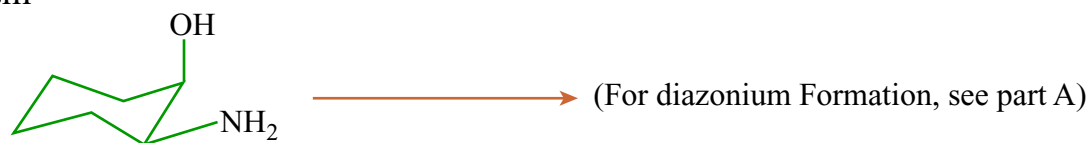


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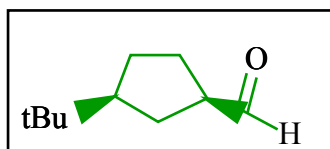
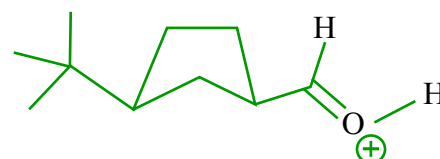
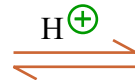
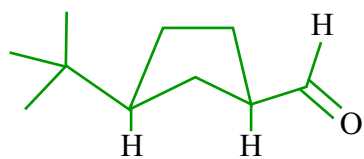
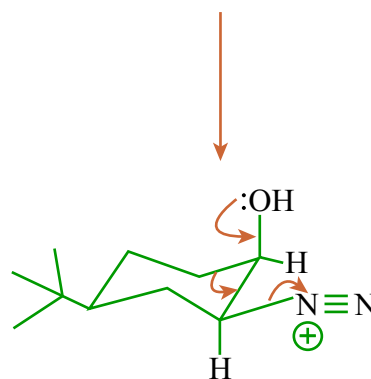
# 27 Part B



Mechanism



★ Once again:  
The migrating group is anti-periplanar to the leaving group.



Figures by MIT OCW.