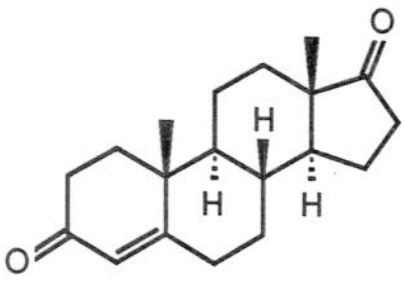
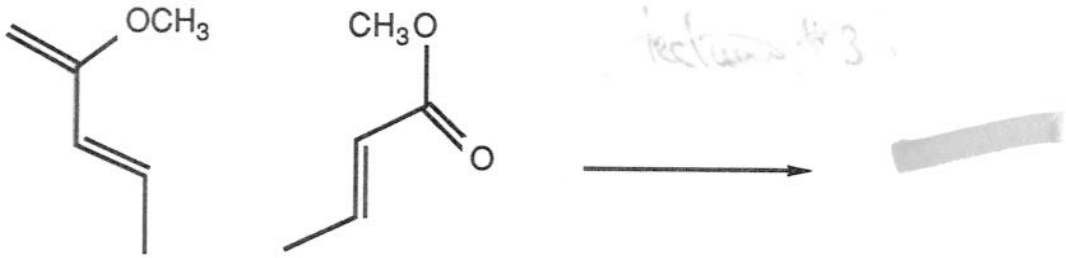
Problem set Chemistry 435 October 22, 1986

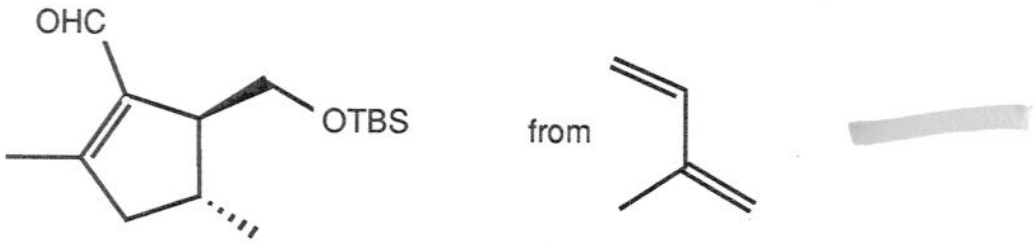
1. Draw as the 3D structure the steriod given below.



2. Give the regio and stereochemical orientation for the product of the Diels-Alder reaction shown below. Rationalize your answer using frontier and secondary orbital interactions.

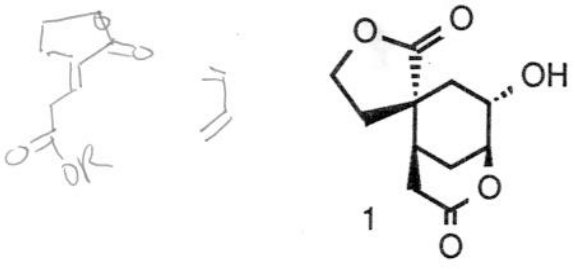


3. Give a Diels-Alder approach to compound 1 starting from the indicated diene. Use any electron deficient olefin that you chose.



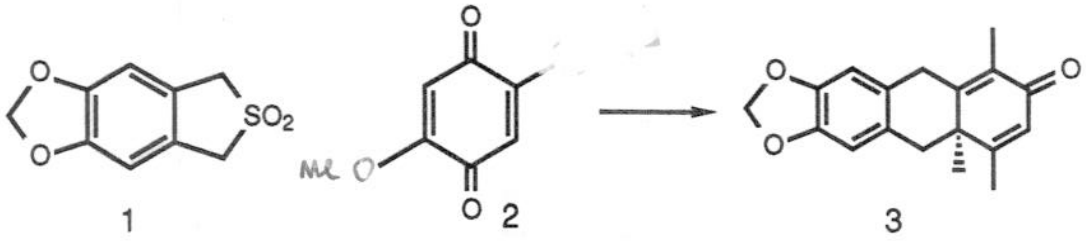
1

4. From any electron deficient dienoplile and combination of dienes you chose prepare 1. Try for a reaction sequence of five to six steps.



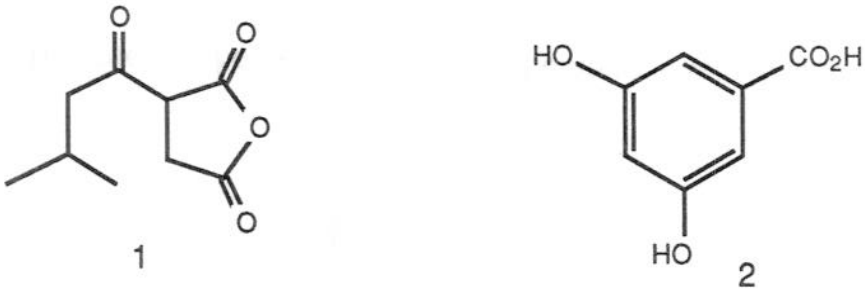
Problem Set Chemistry 435 October 22, 1986

5. From compounds 1 and 2 show how you would prepare 3.



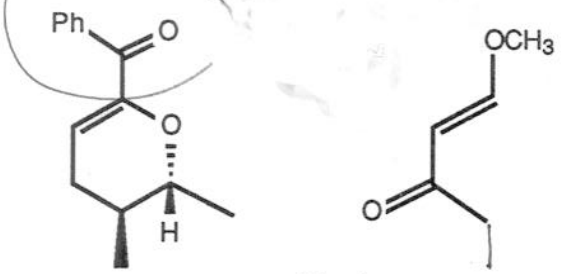
1 2 3

6. How would you make 1 from the benzene derivative 2?



1 2

7. How would you make compound 1 starting from 2, acetaldehyde, and benzaldehyde?

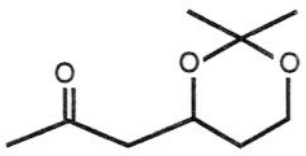


1 2

acetaldehyde

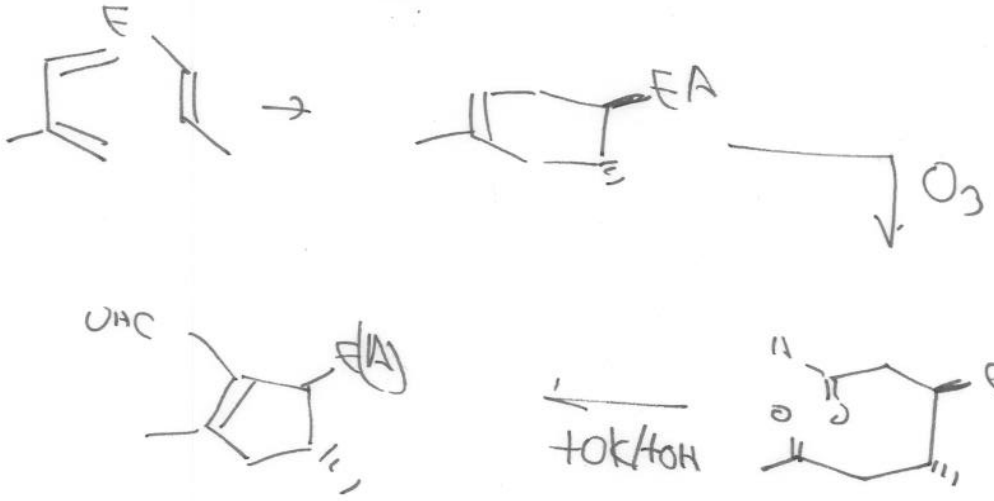
benzaldehyde

8. How would you make comopund 1 from ethyl crotonate, acetaldehyde, acetone and hydroxylamine hydrochloride?

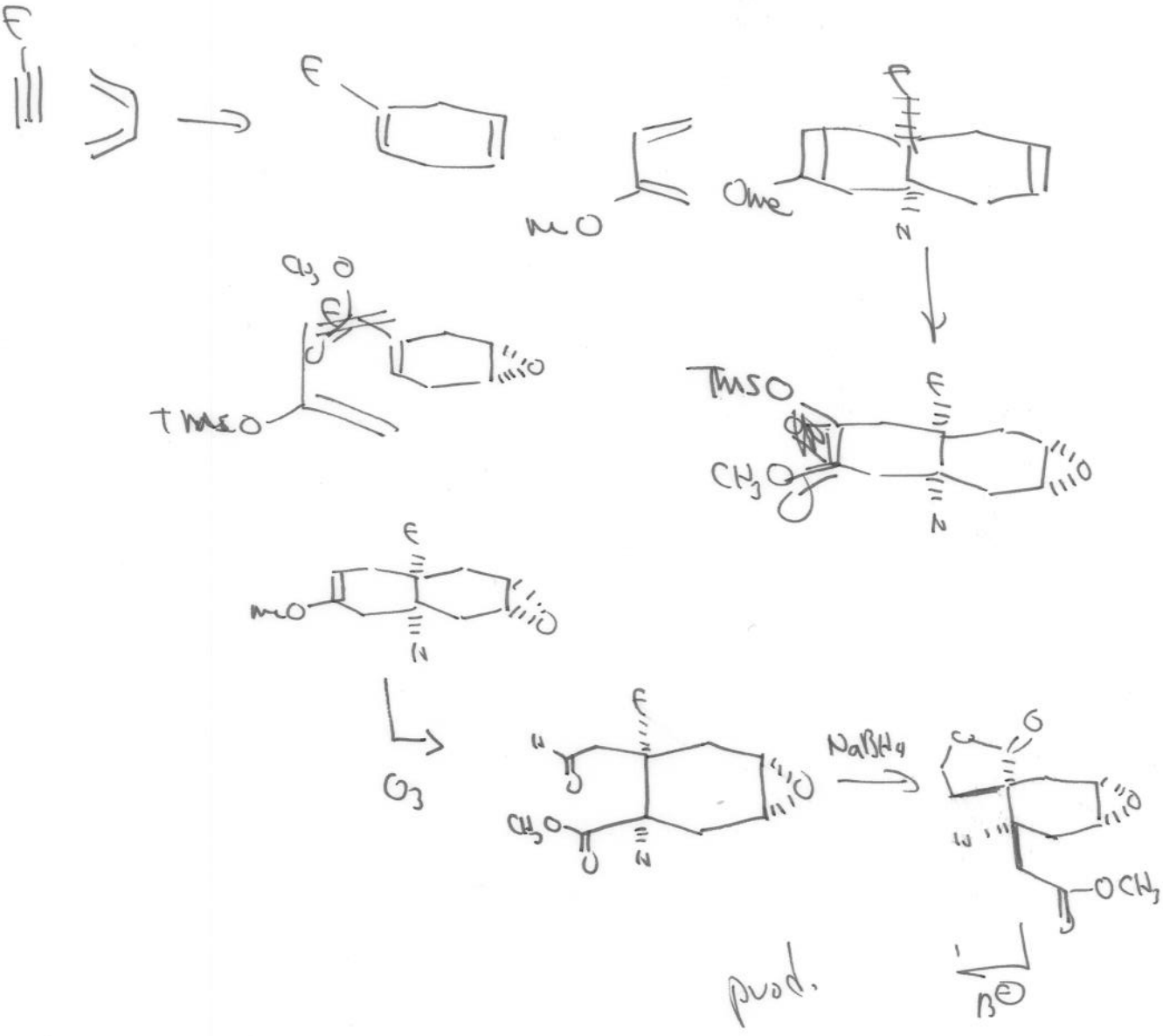


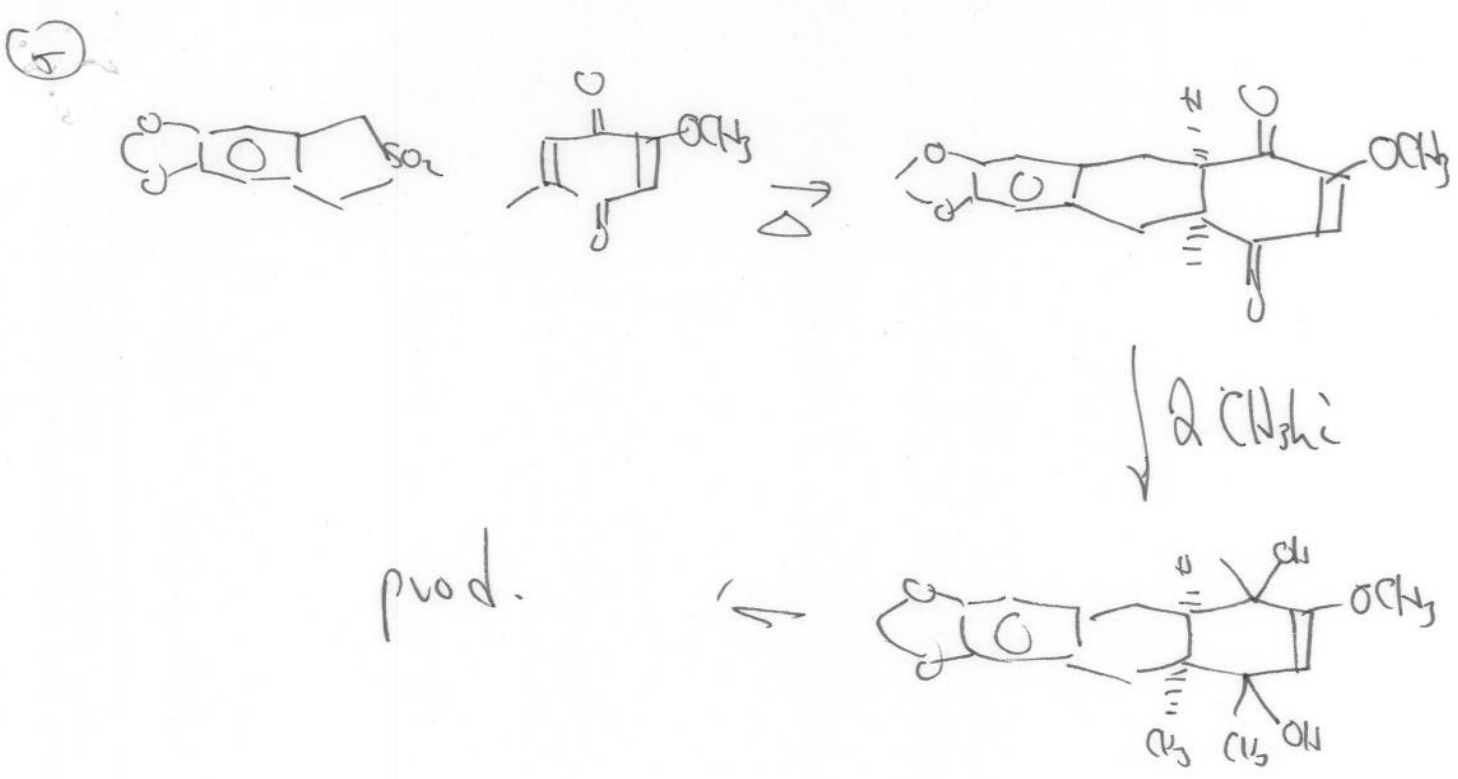
1

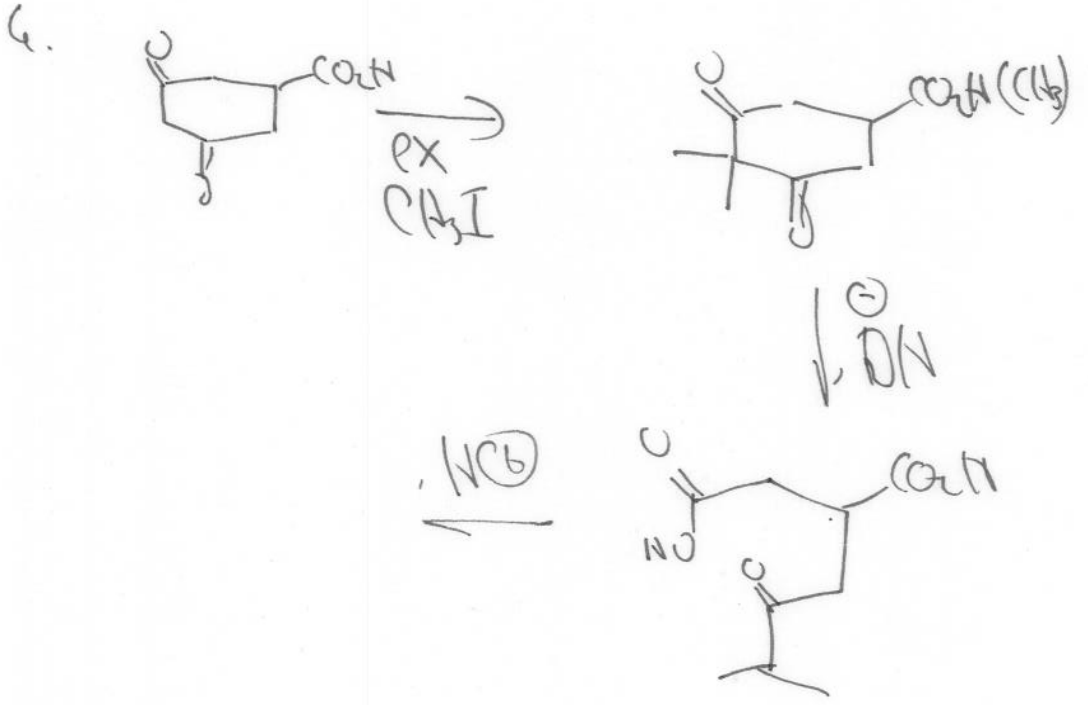
3.

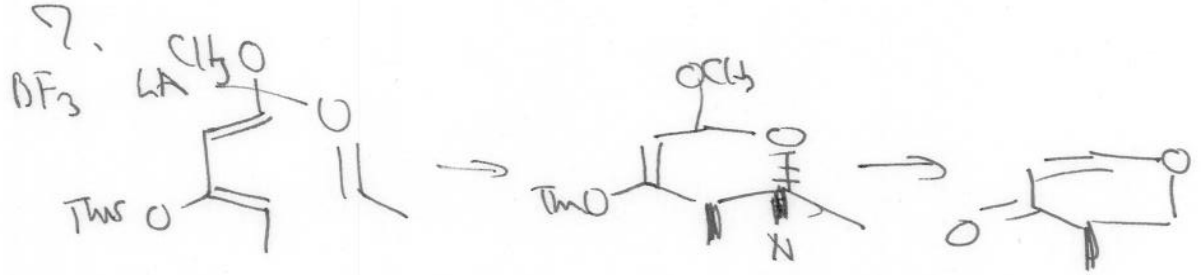

F
EA
O_3
OHC
F(A)
+OK/HOH
O
F(A)

4).

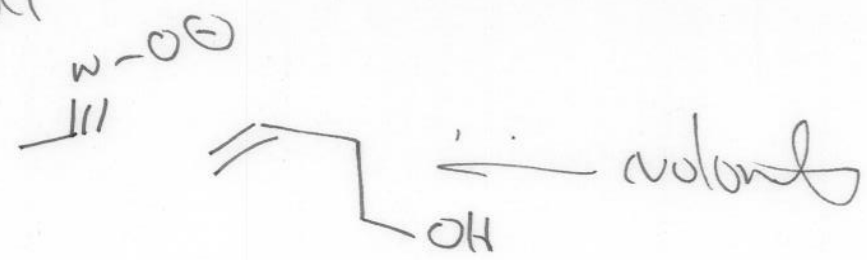

F
F
MeO
OMe
N
O_3
O
TMSO
TMSO
F
CH_3
O
N
F
MeO
N
O_3
F
O
CH_3O
O
N
$NaBH_4$
O
O
OCH_3
prod.
$B^{\ominus}$


2 CH3Li
prod.

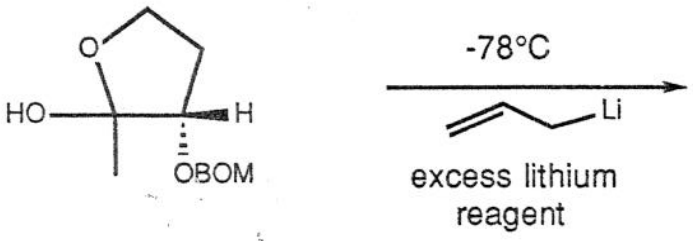

4.
ex
CH3I
1. DIN
2. NCB


7.
BF3 LA
THS

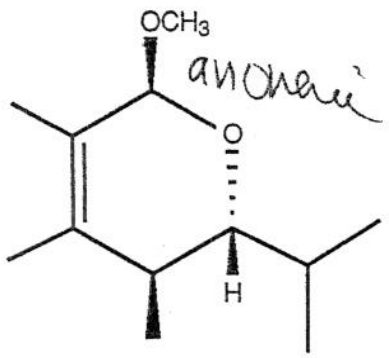
(8) NaOCl



9. What is the structure of the product, including stereochemistry that you would obtain from the reaction indicated below?

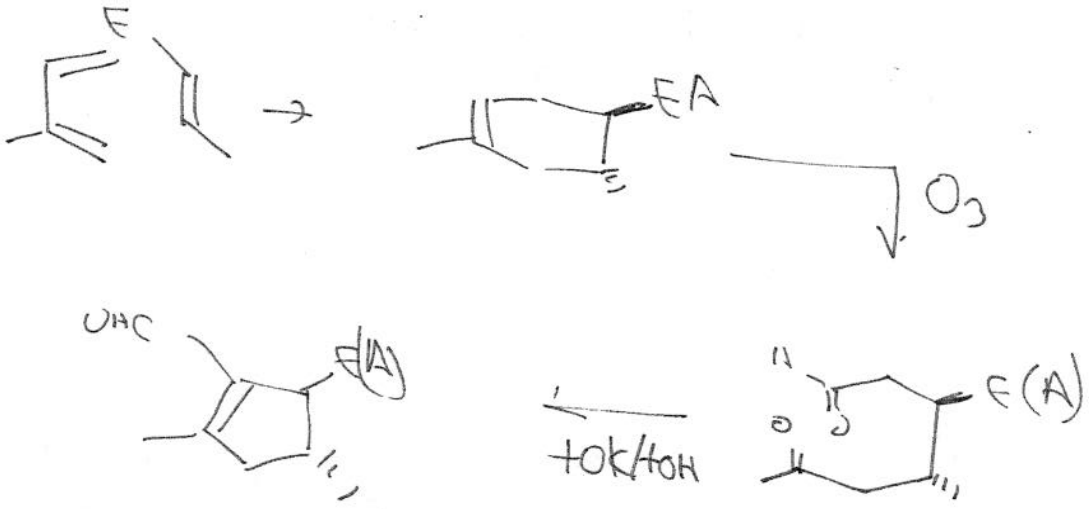


10. How would you prepare compound 1 from from 3-pentanone and isobutyraldehyde?

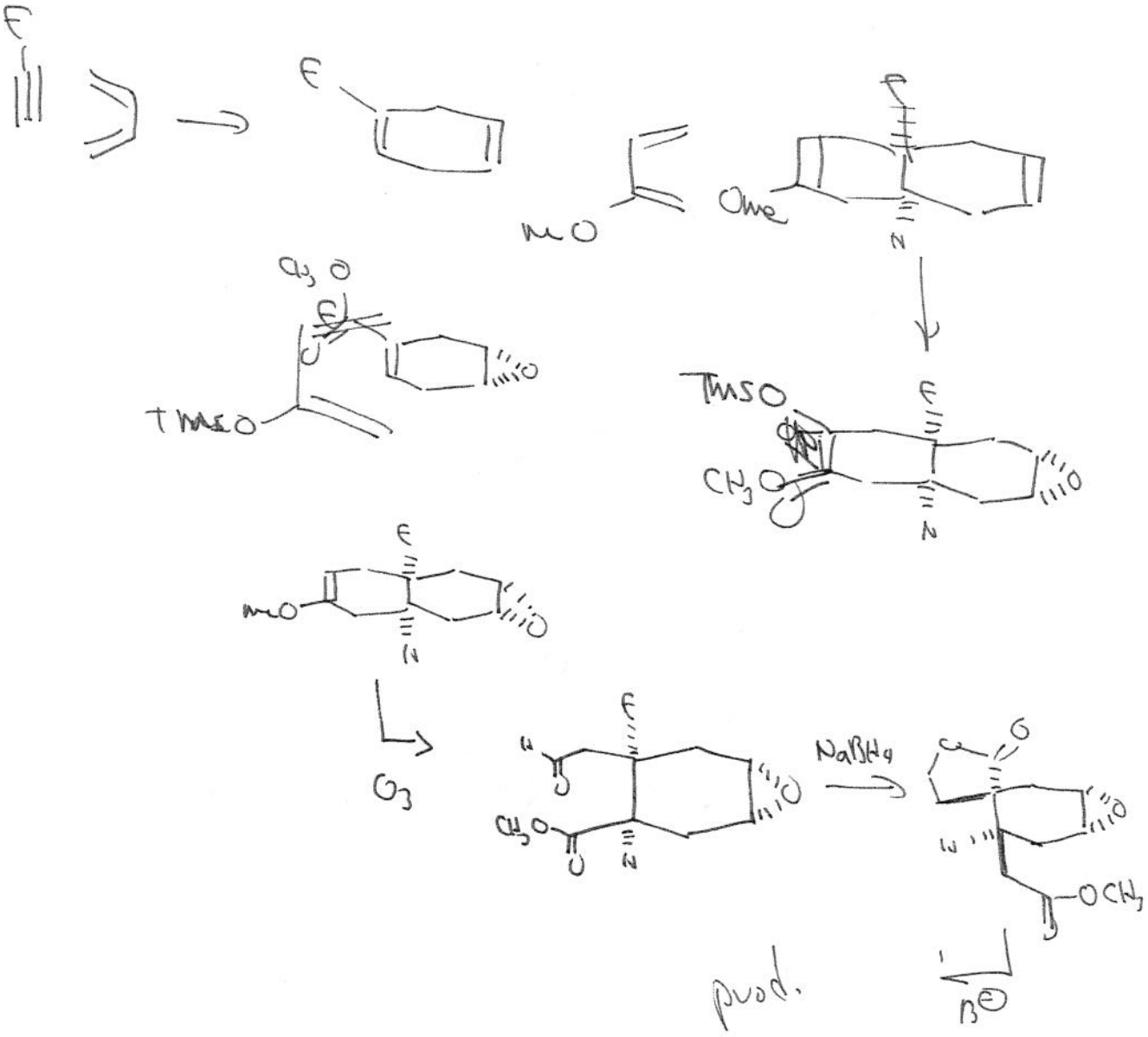


1

3.


E
EA
O_3
OHC
E(A)
tOK/tOH
E(A)

4).

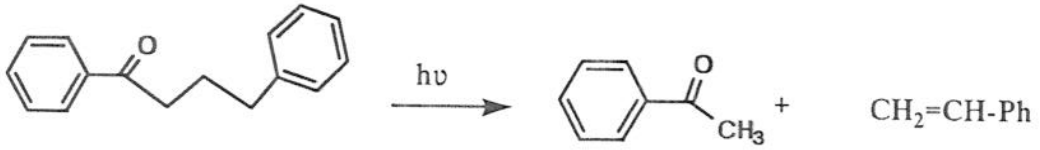

E
E
MeO
OMe
N
O_3
TMSO
TMSO
E
CH_3O
N
E
MeO
N
O_3
E
CH_3O
N
$NaBH_4$
OCH$_3$
prod.
$B^{\ominus}$

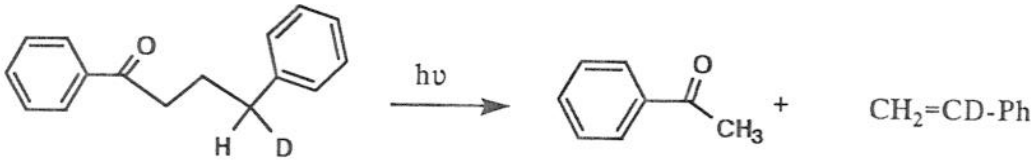
(8) NaOCl

Electron Pushing Tutorial

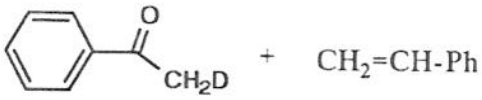
Provide Mechanisms for the following reactions. Show all steps carefully and distinctly in your mechanisms

1.

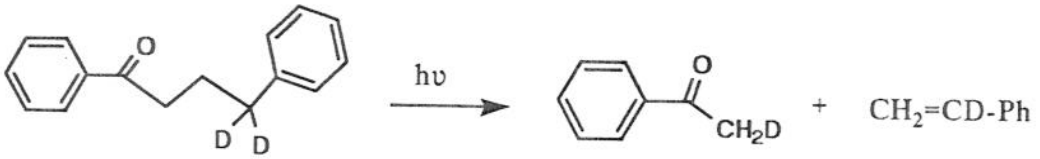




major (85%)

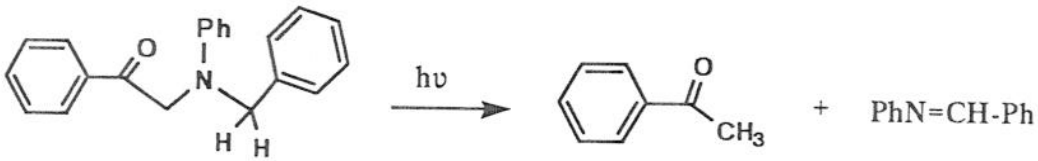


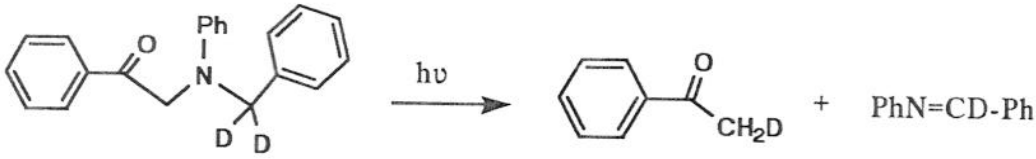
minor (15%)



Reaction Much Slower in this case.

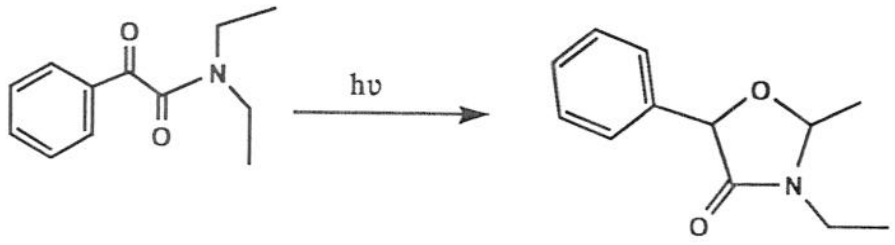
2.



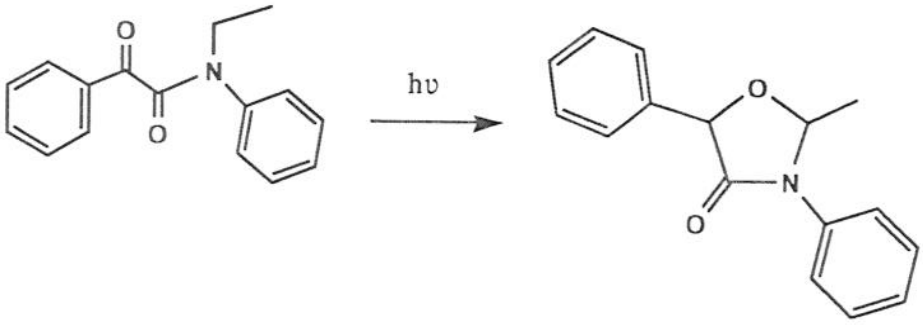


Deuterated compound reacts at nearly the same rate

3.



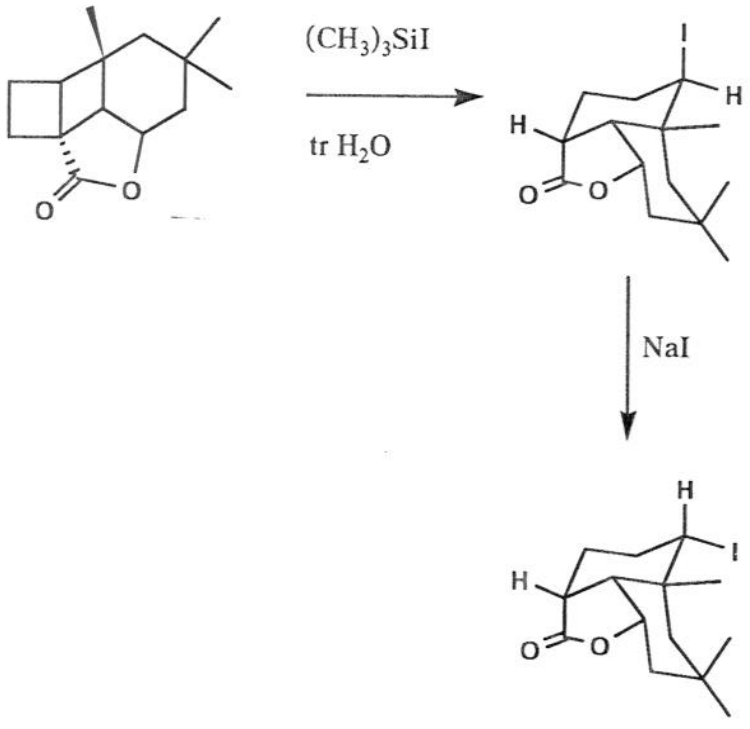
100%, $\phi = 0.24$



EXPLAIN

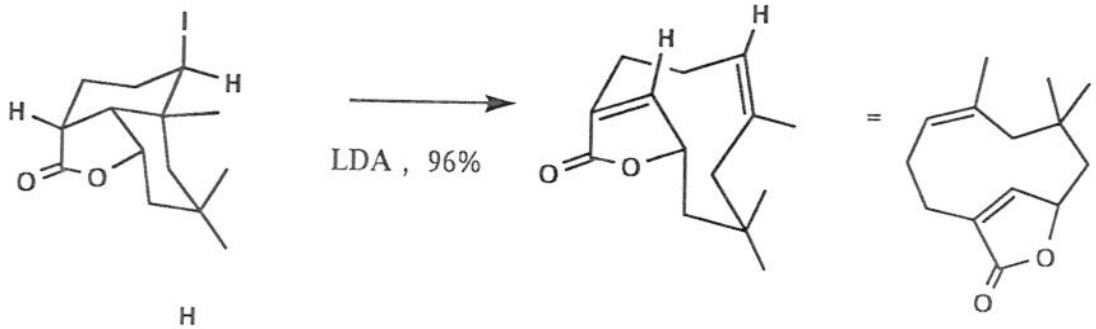
~ 50%, $\phi = 0.01$

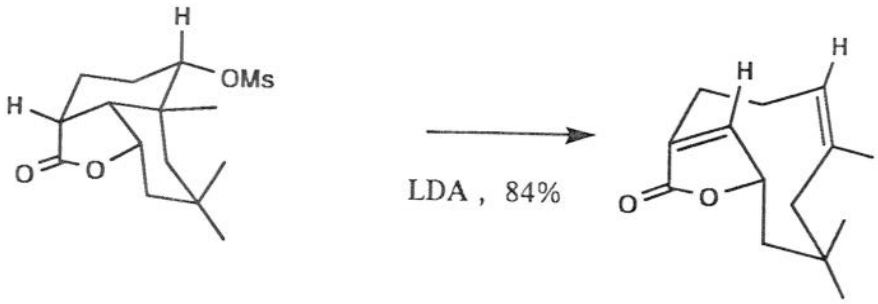
4. Rationalize the Following Transformations:

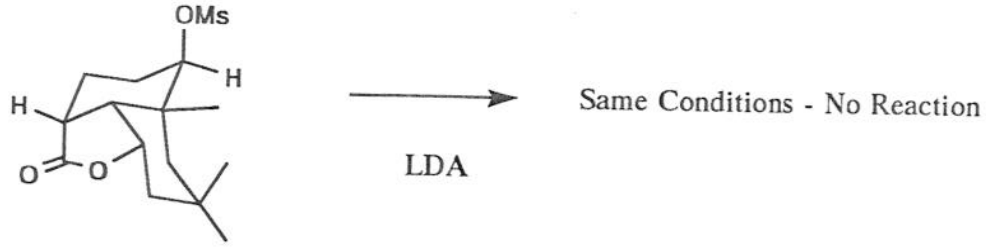


5.

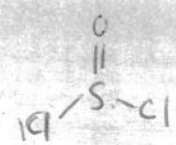

H
I
H
O
O
LDA , 91%
H
H
O
O

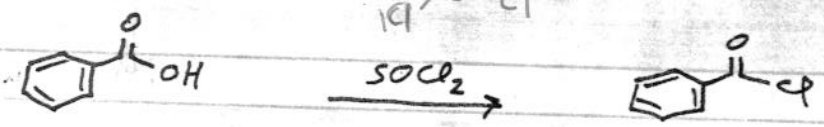

I
H
H
O
O
LDA , 96%
H
H
O
O
=
O
O

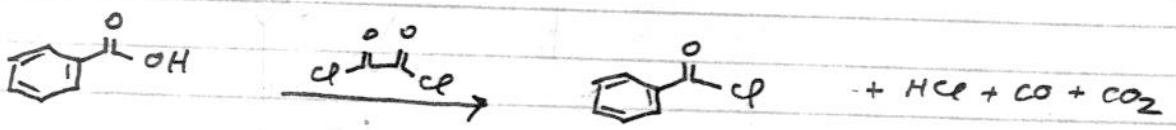

H
OMs
H
O
O
LDA , 84%
H
H
O
O

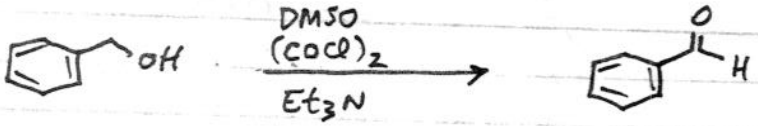

OMs
H
H
O
O
LDA
Same Conditions - No Reaction

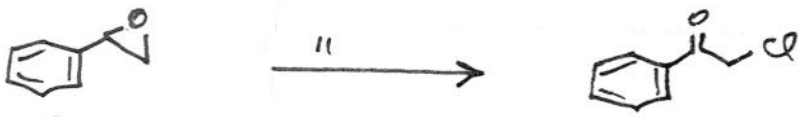
PROBLEM SET 4

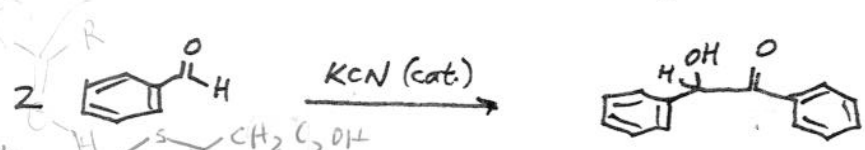


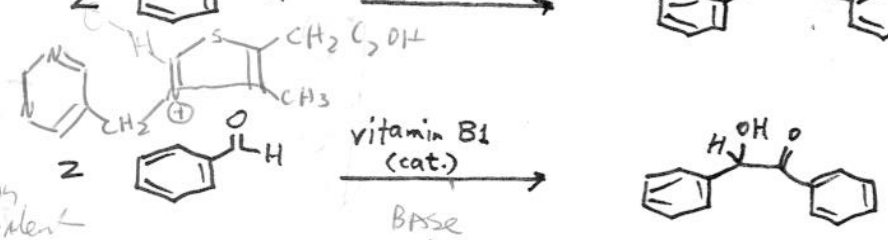
MARCH ① 

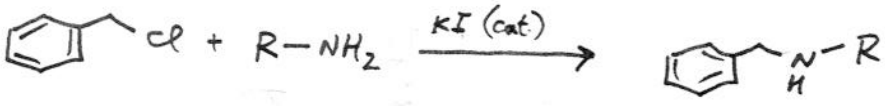
② 

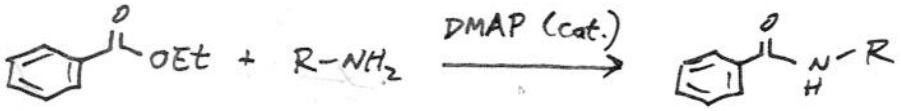
✓ ③ 

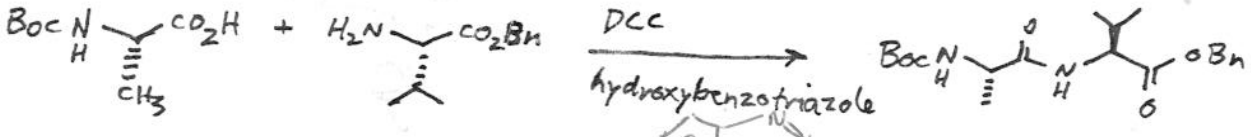
④ 

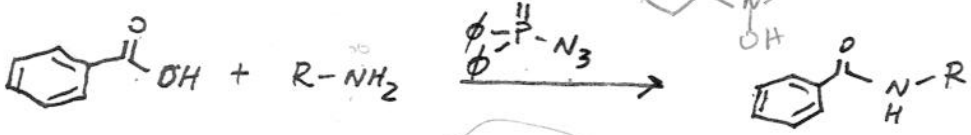
✓ ⑤ 

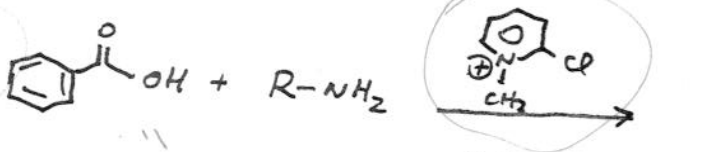
O'Neil ⑥ Acylation equivalent 

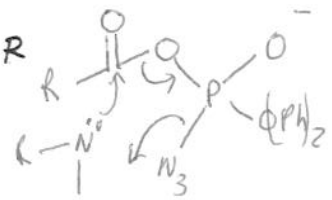
Finkelstein ⑦ 

⑧ Chem 

DEREK LEITHE ⑨ 

✓ ⑩ 

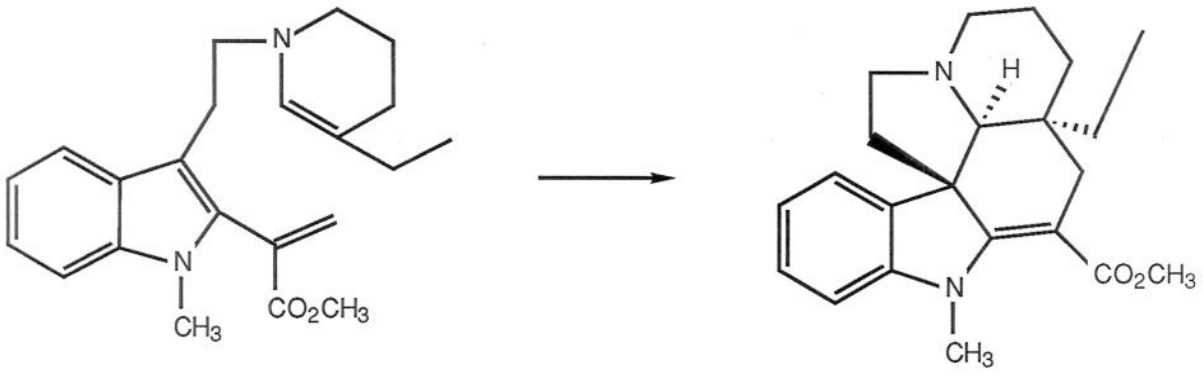
Mukaiyama ⑪ 



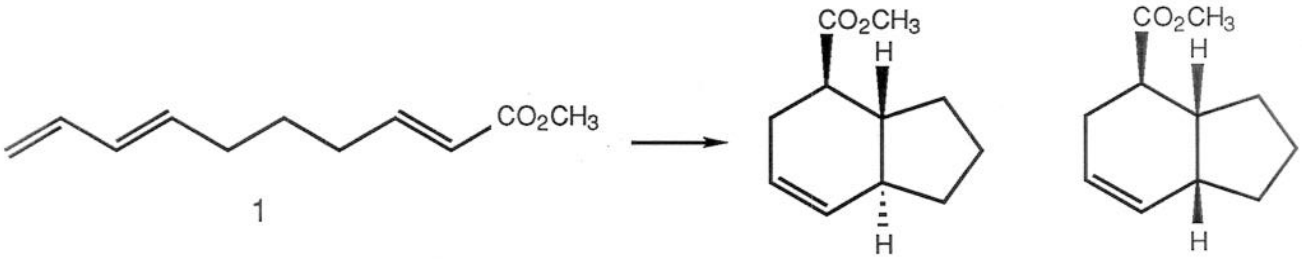
JACS 1972 6203

INTRAMOLECULAR DIELD-ALDER REACTIONS QUESTIONS RELATED THERETO

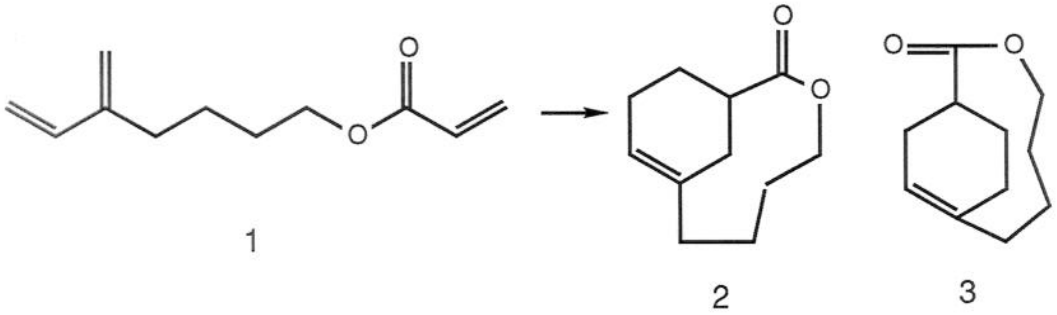
1. THE FOLLOWING TRANSFORMATION MAY BE VIEWED EITHER AS AN INTRAMOLECULAR DIELS-ALDER REACTION OR AS A MICHAEL ADDITION ACYLATION REACTION, WHICH IS MORE LIKELY AND WHY?



2. The unsaturated ester 1 gives a mixture of 2 and 3 in 39% and 26% yields, respectively at 150C. When the same reaction is carried out in the presence of menthoxyaluminum dichloride, at 23C only 2 is formed in 72% yield, why?



3. Compound 1 at 190°C gives 2 and 3. Show the transitions states leading to 2 and 3.



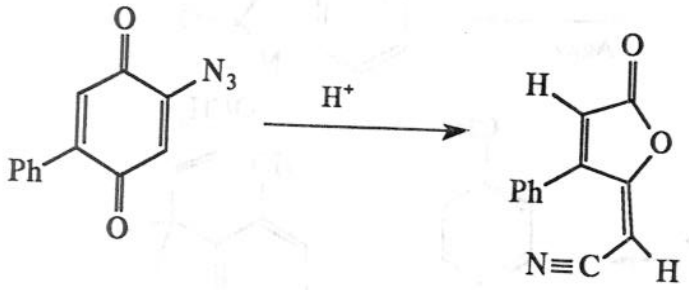
Organic Chemistry

Arrow Pushing Tutorial

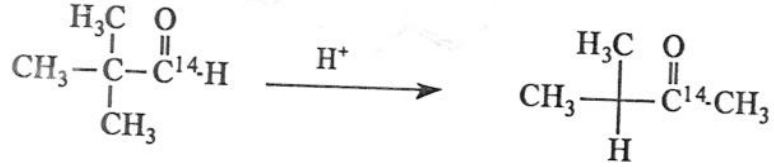
Fall 1990

Suggest reasonable mechanisms by which each of the following transformations could occur.

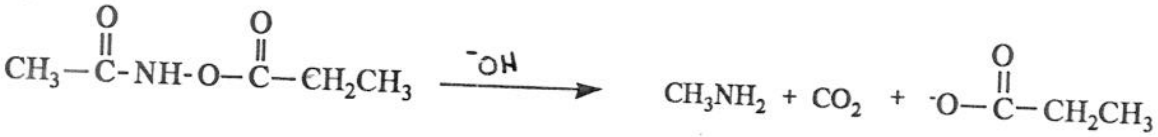
1.



2.



3.



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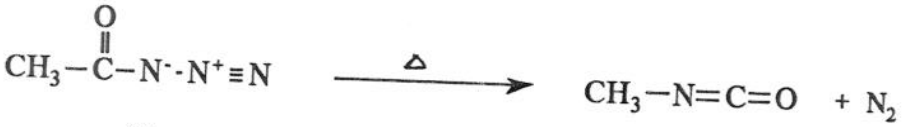

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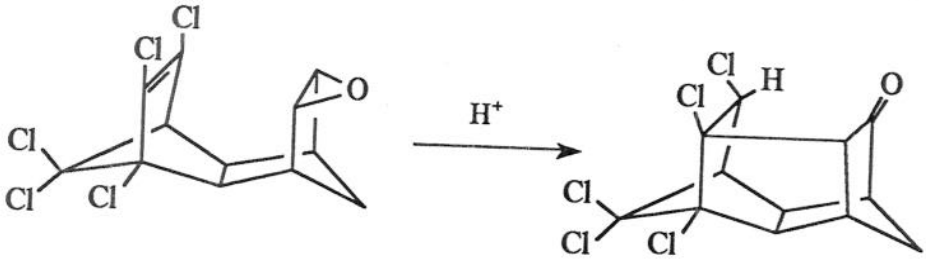

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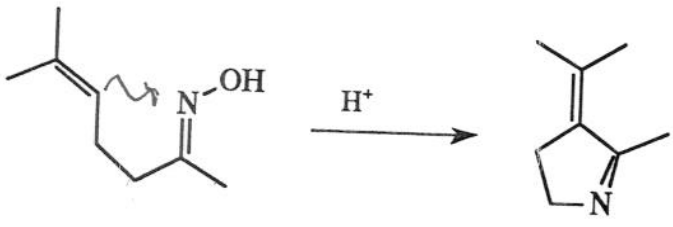

7.