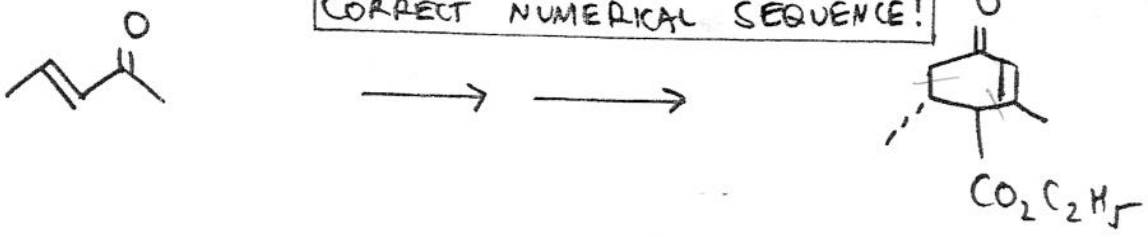
CHM 129/239 FINAL EXAM (3 hours) 2003

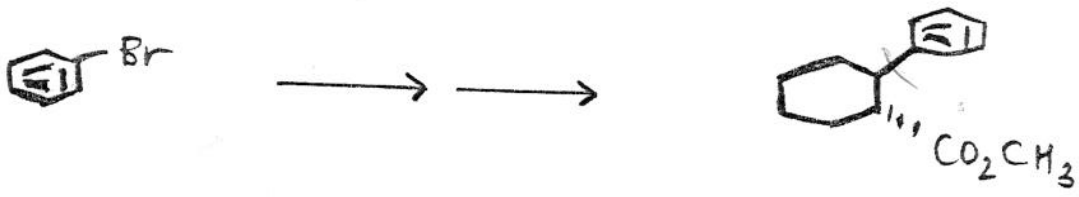
(molecular models may be used in this examination)

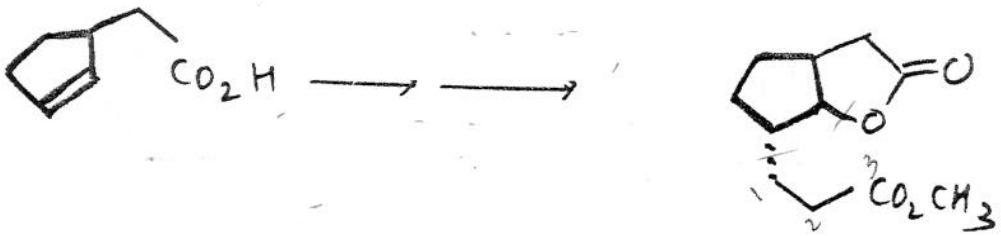
PROPOSE DIRECT, SHORT AND STEREOCONTROLLED ROUTES TO EACH TARGET COMPOUND, SPECIFYING ANY STANDARD REAGENTS OR "ALDRICH" CHEMICALS REQUIRED. TARGETS ARE RACEMIC EXCEPT AS NOTED. PLACE BLUEBOOK ANSWERS IN THE CORRECT NUMERICAL SEQUENCE!

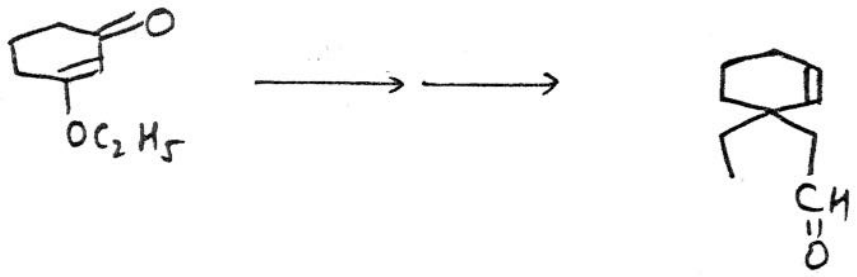
1. 

2. 

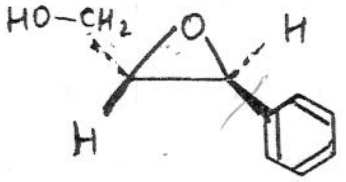
(enantiopure)

3. 

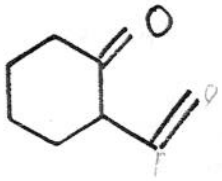
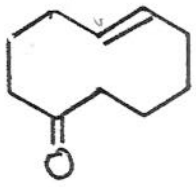
4. 

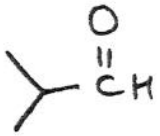
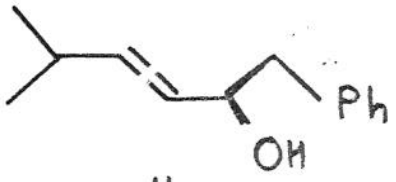
5. 

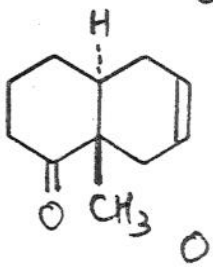
6. Ph_2 t-BuSi $OCH_2-C\equiv CH$ ⟶ ⟶



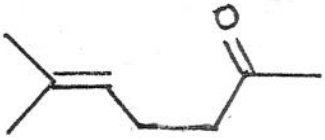
(enantiopure)

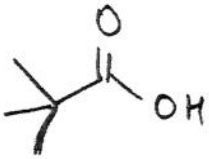
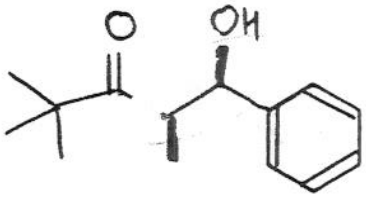
7.  ⟶ ⟶ 

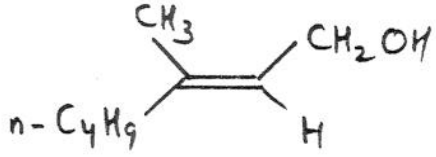
8.  ⟶ ⟶ 

9.  ⟶ ⟶ 

10. $C_2H_5NH_2$ ⟶ ⟶ 

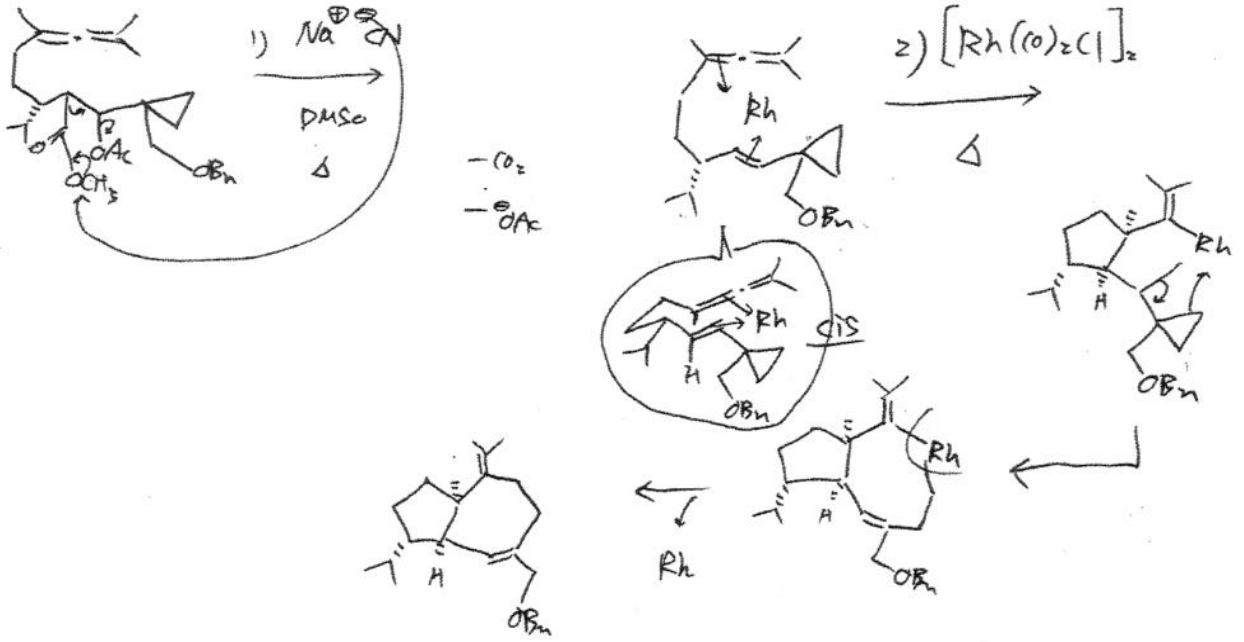
11.  ⟶ ⟶ 

12.  ⟶ ⟶ 

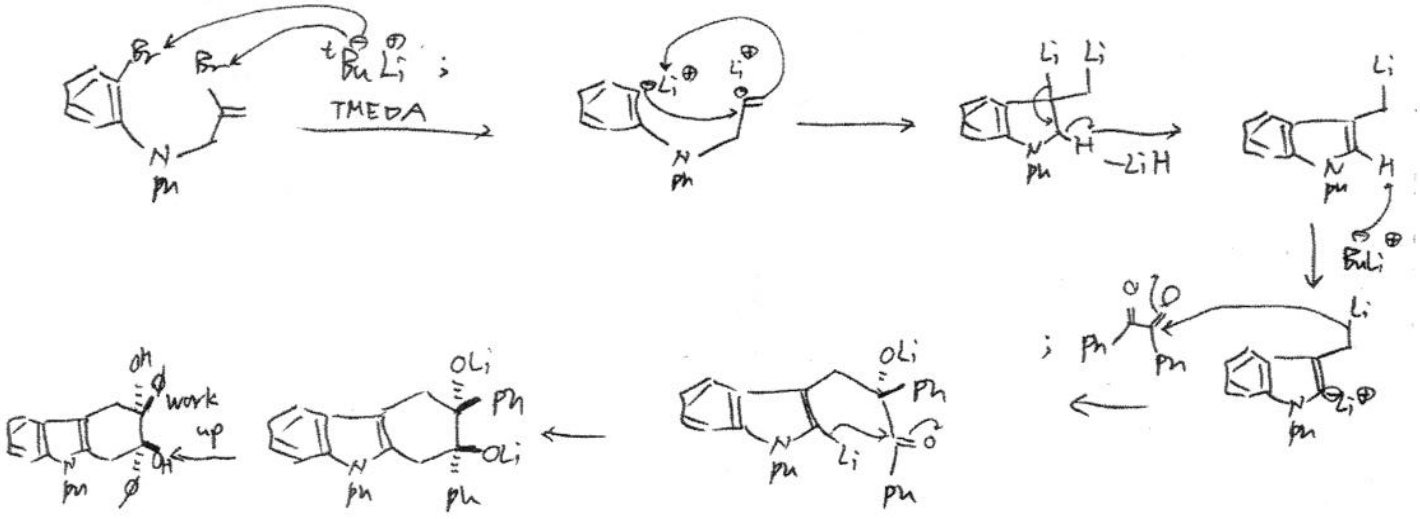
13. $n-C_4H_9C\equiv CH$ ⟶ ⟶ 

9/5/01 Problems Answer

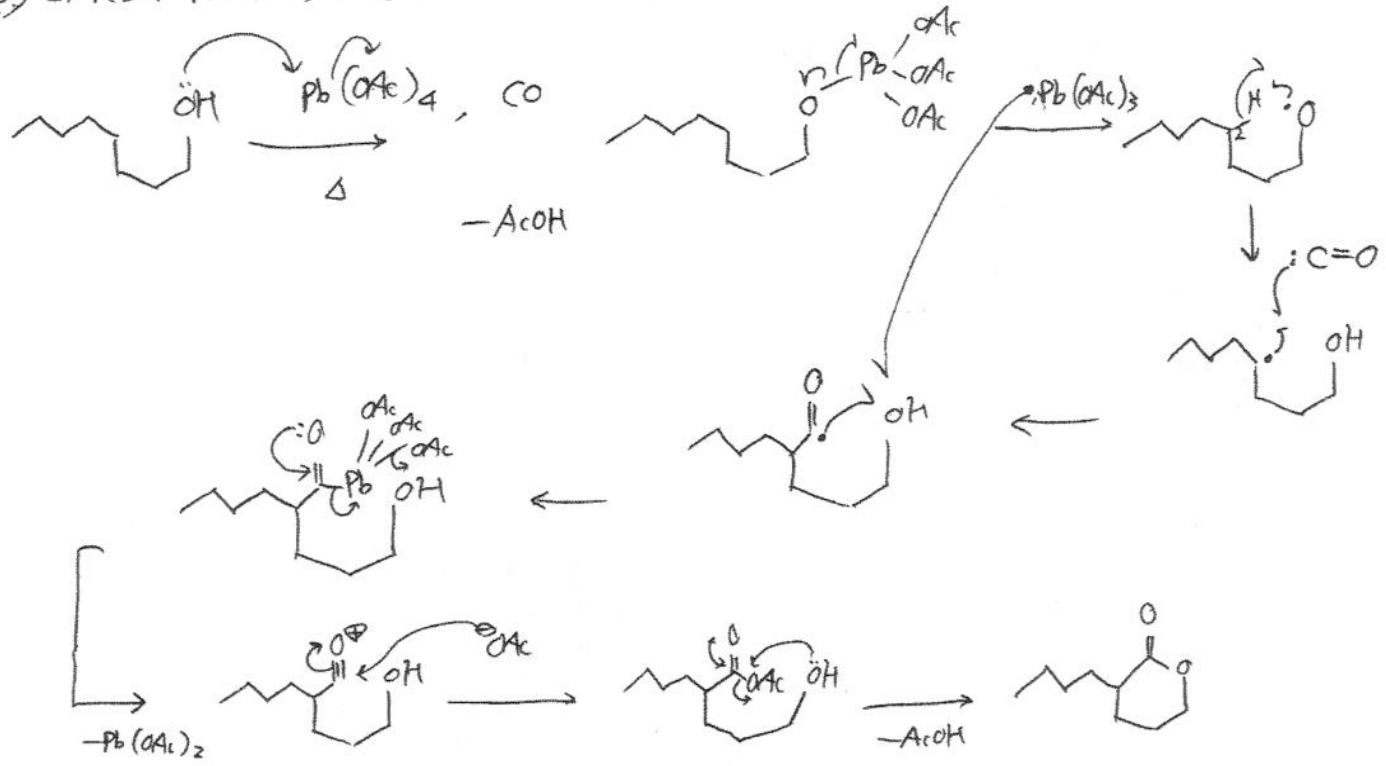
① OL. 2000. vol 2 No 15. 2323–2326



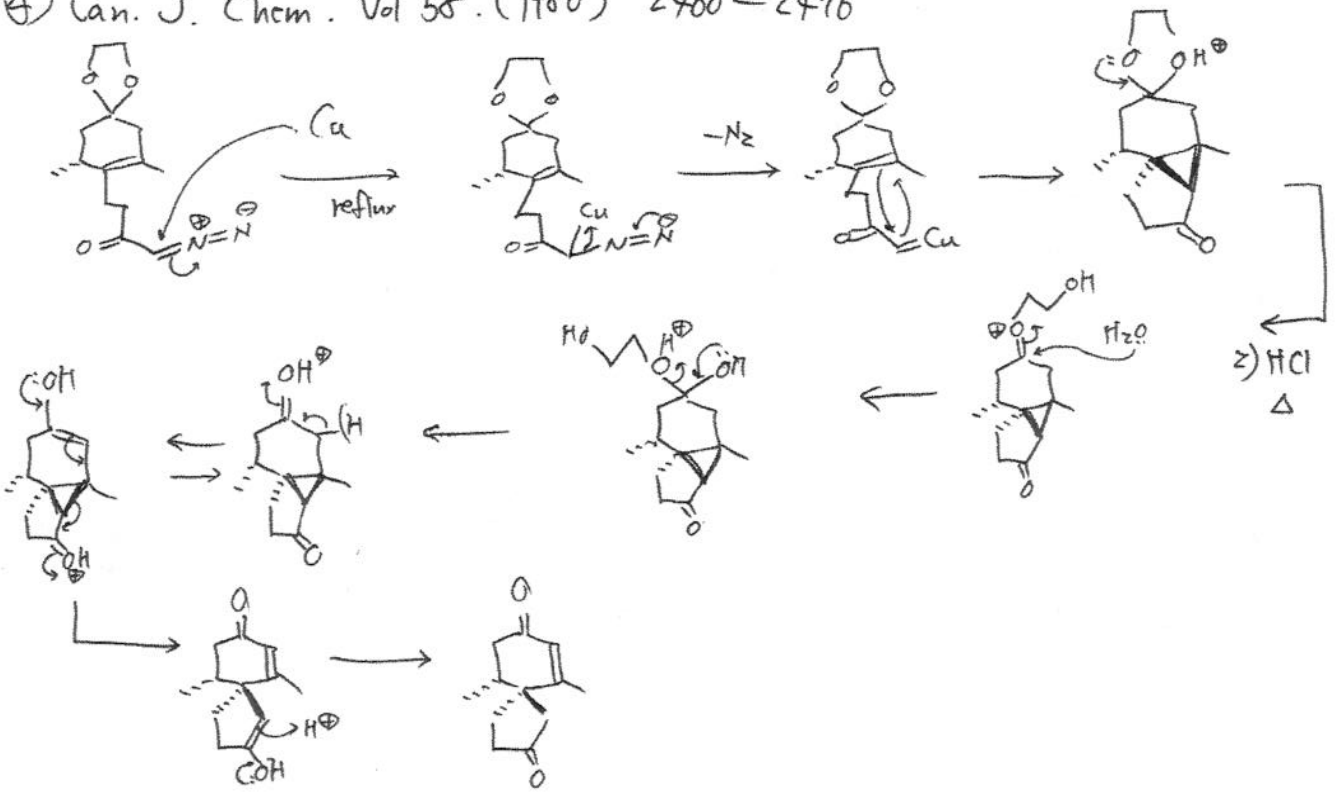
② Chem. Eur. J. 2001. 7 (13) 2896–2907



③ JACS. 120(34). 8893 (1998)

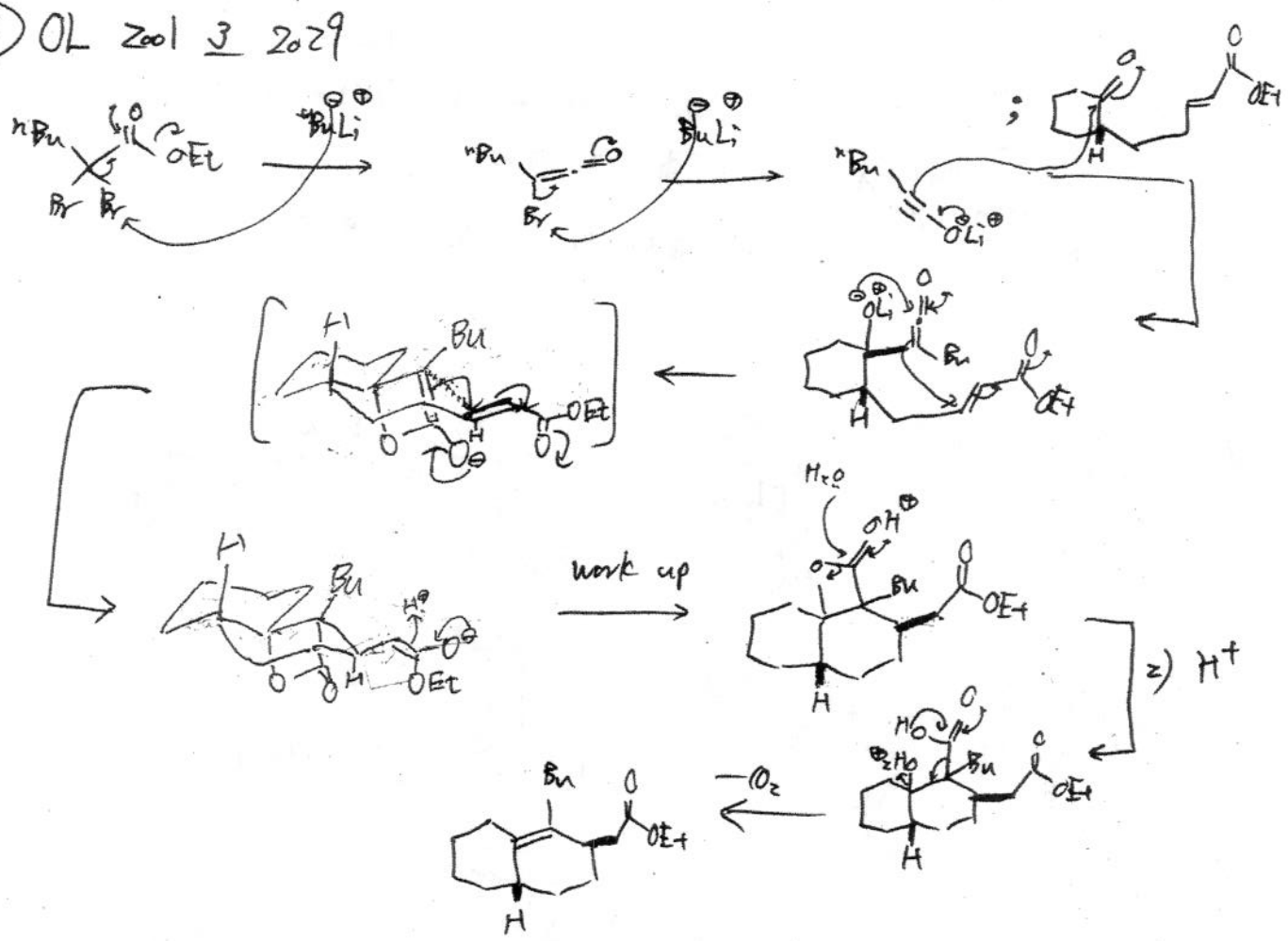


④ Can. J. Chem. Vol 58. (1980) 2460 − 2476



9/5/01 Answer-2

(5) OL Zool 3 2029



Group Meeting Problems — Solution 09/12/2001

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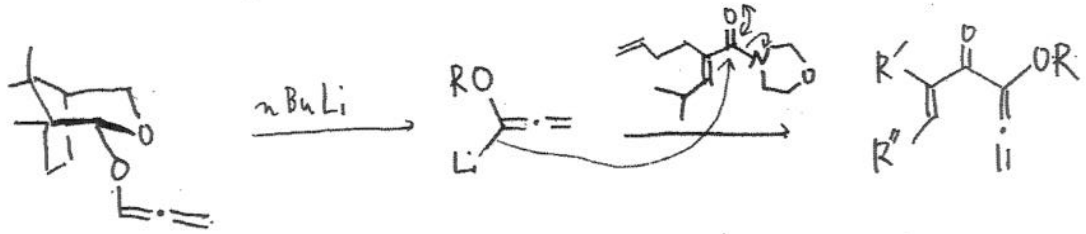
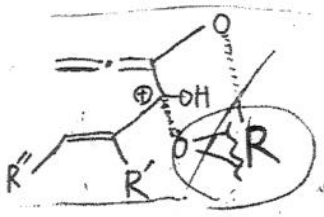


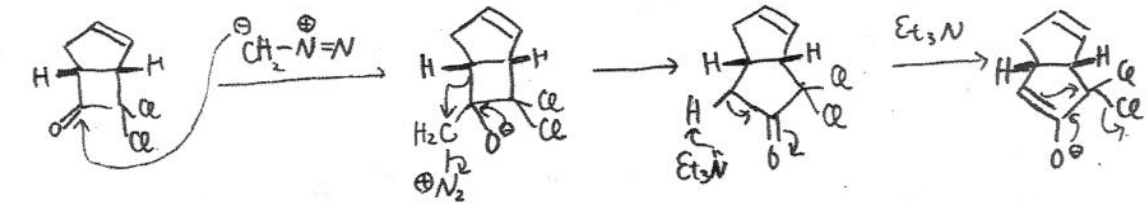
※立体

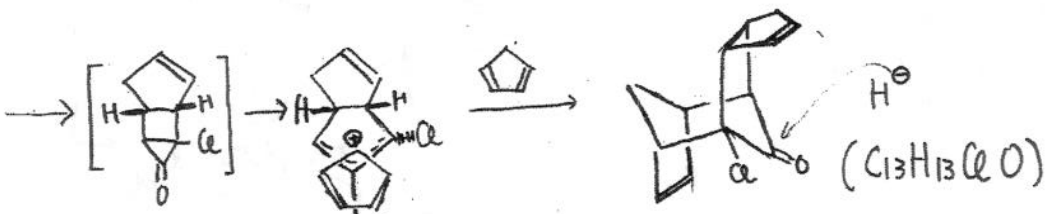


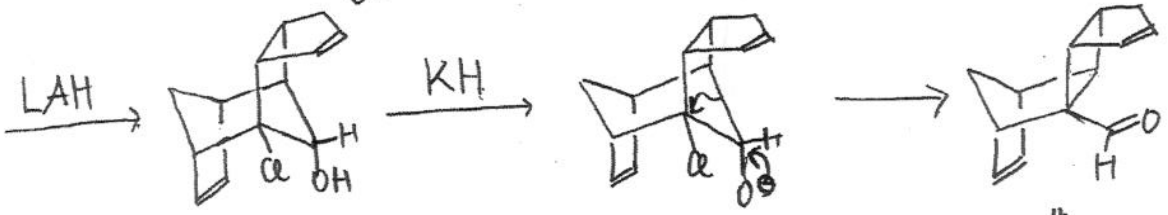
・平面より下に回ると、RとR'(R'')がぶつかるので、平面より上に回る。

・Rの○原子が⊕に入って、配座が固定される。

2.

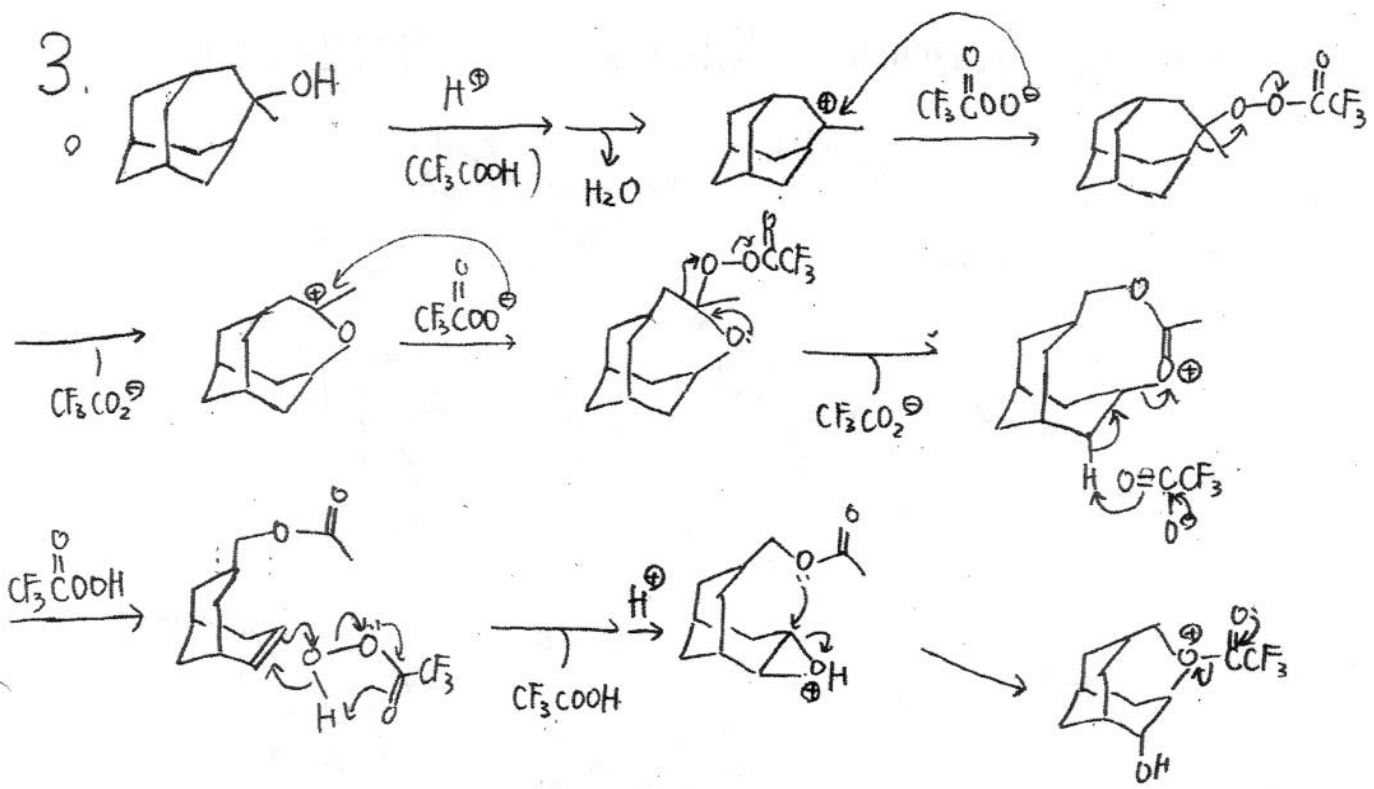




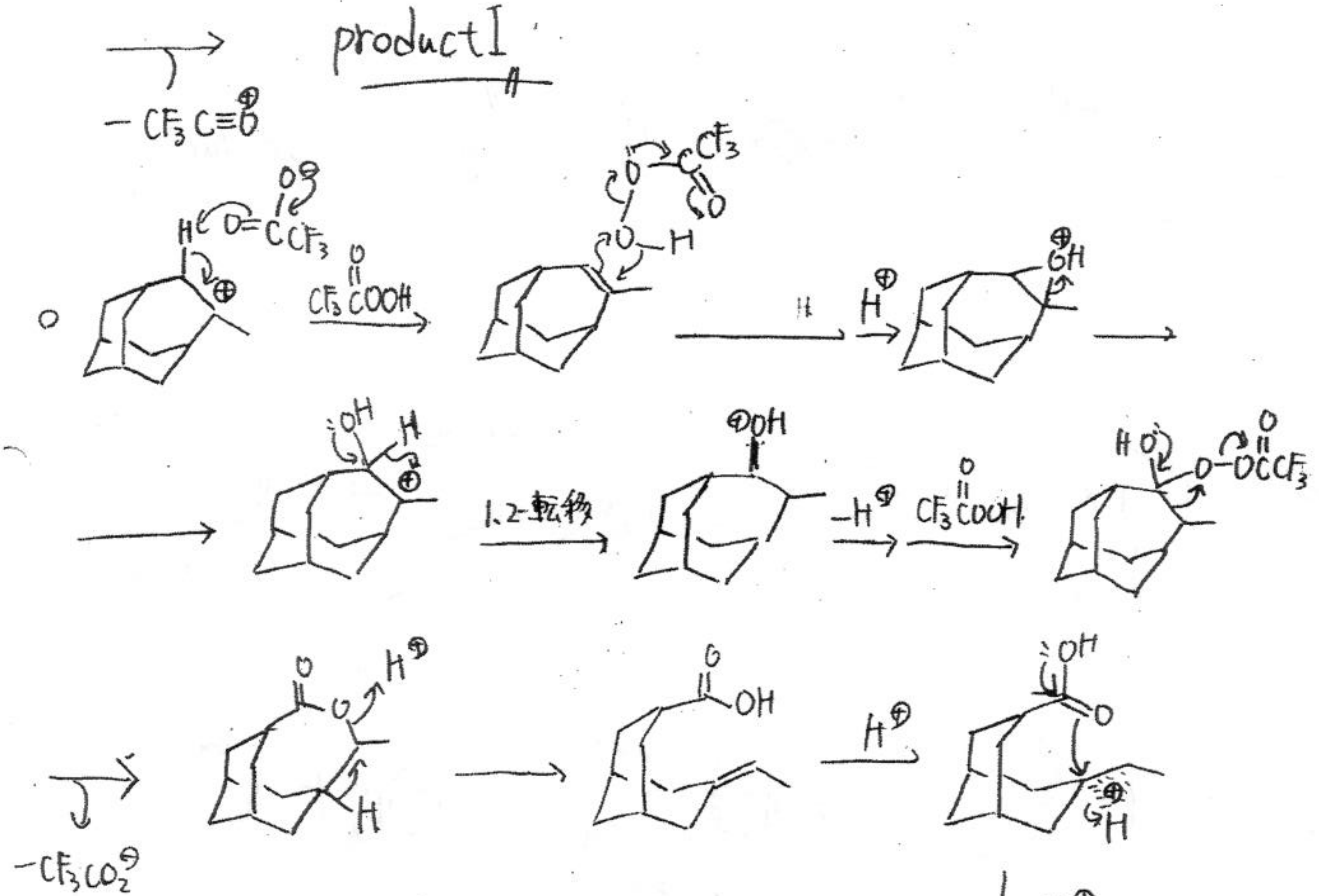


product

3.



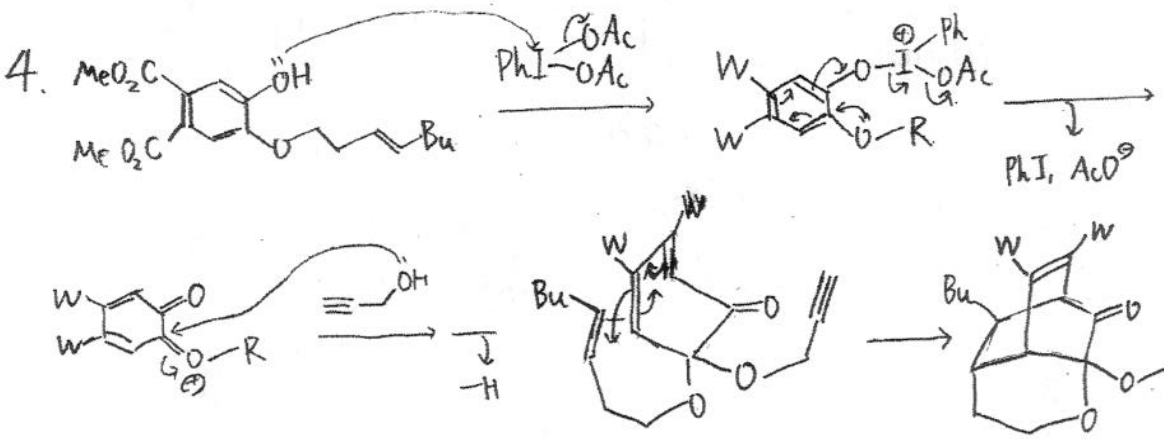
product I

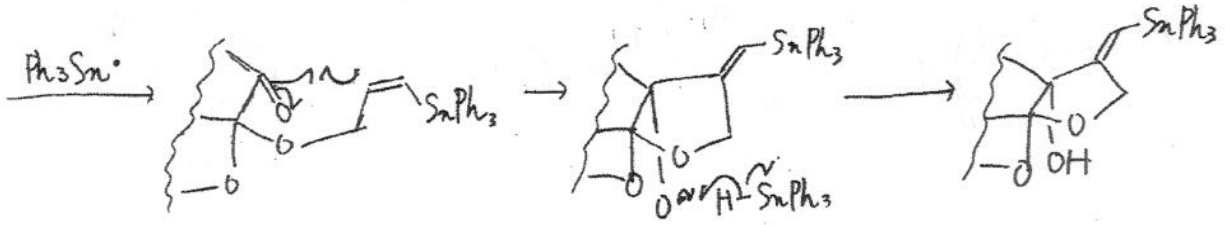


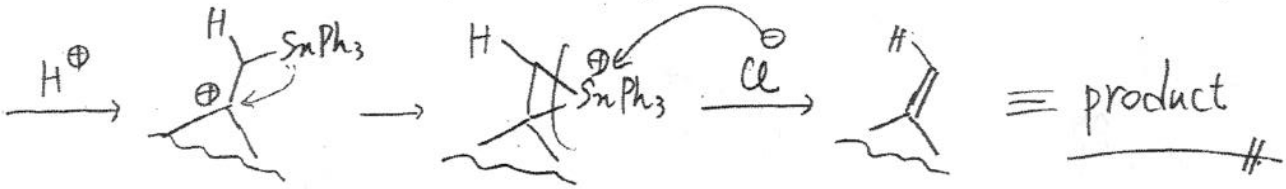
product II

Group Meeting Problems — Solution 09/12/2001

4.







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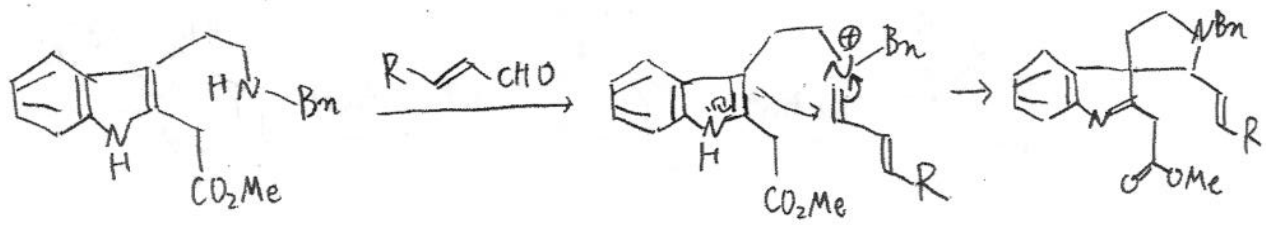
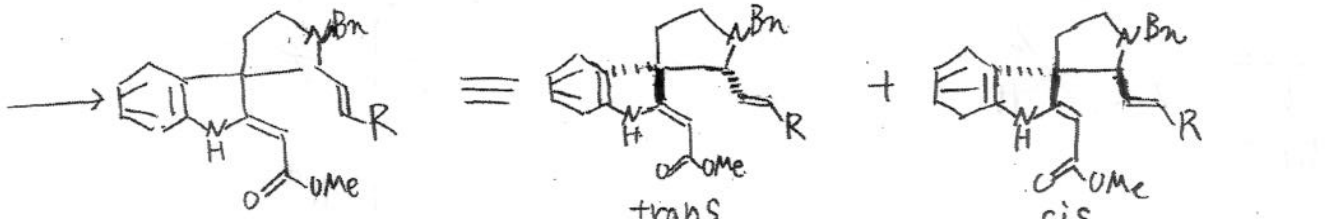
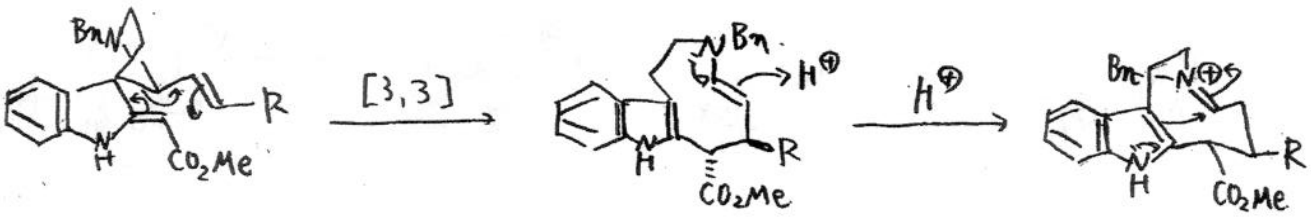




(not suitable for sigmatropic rearrangement) → no reaction

(Optimum geometry for a [3,3] sigmatropic rearrangement) → つづく

5. つづき



$\xrightarrow{-H^{\oplus}}$ product.

Group Meeting Problems Solution 09/19/2001

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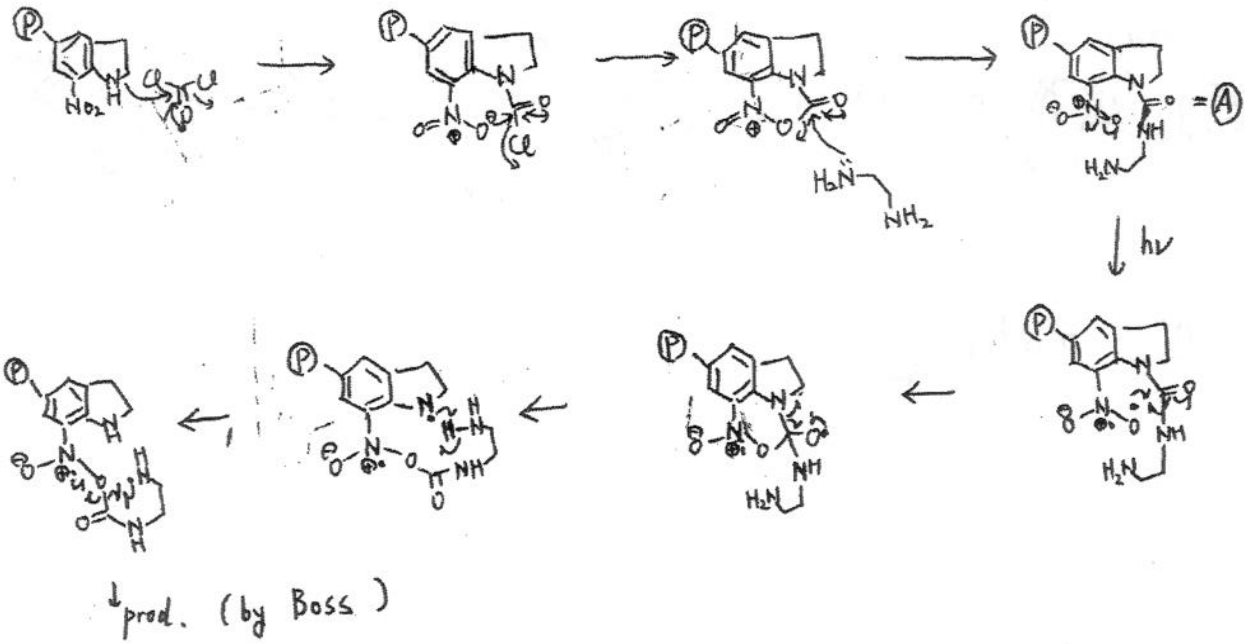
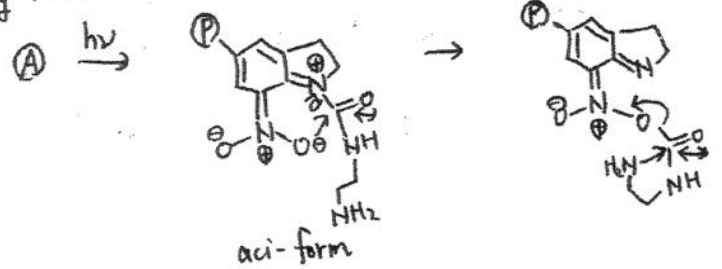


↓ prod. (by Boss)

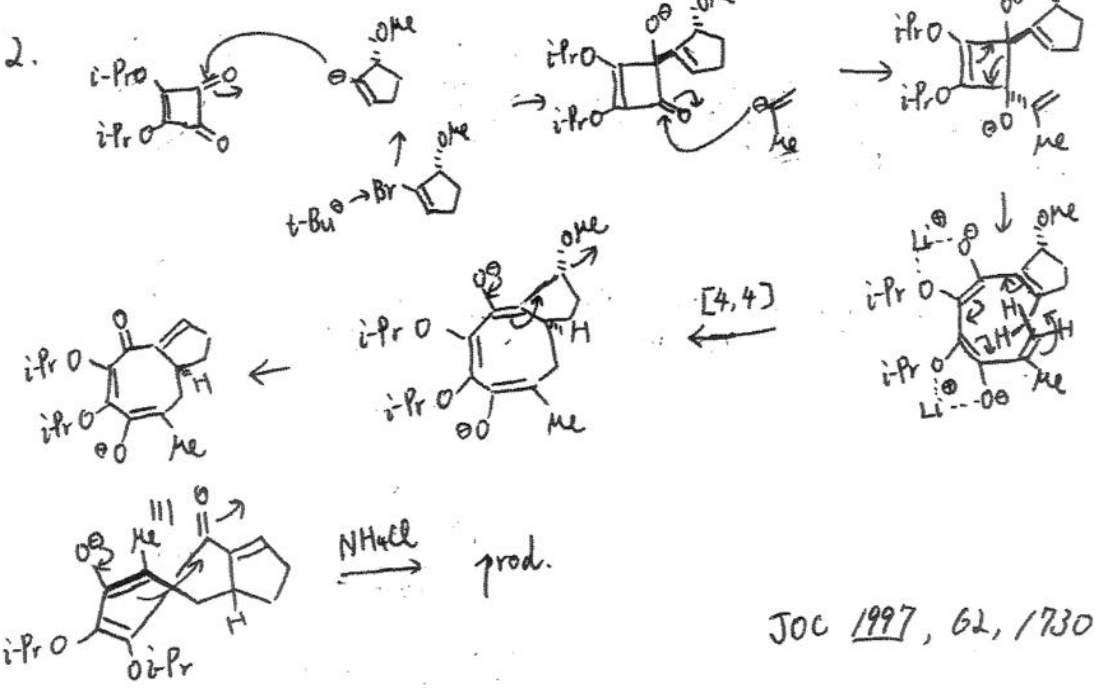
by Authors



aci-form

Synlett 2001, 900

2.



JOC 1997, 62, 1730

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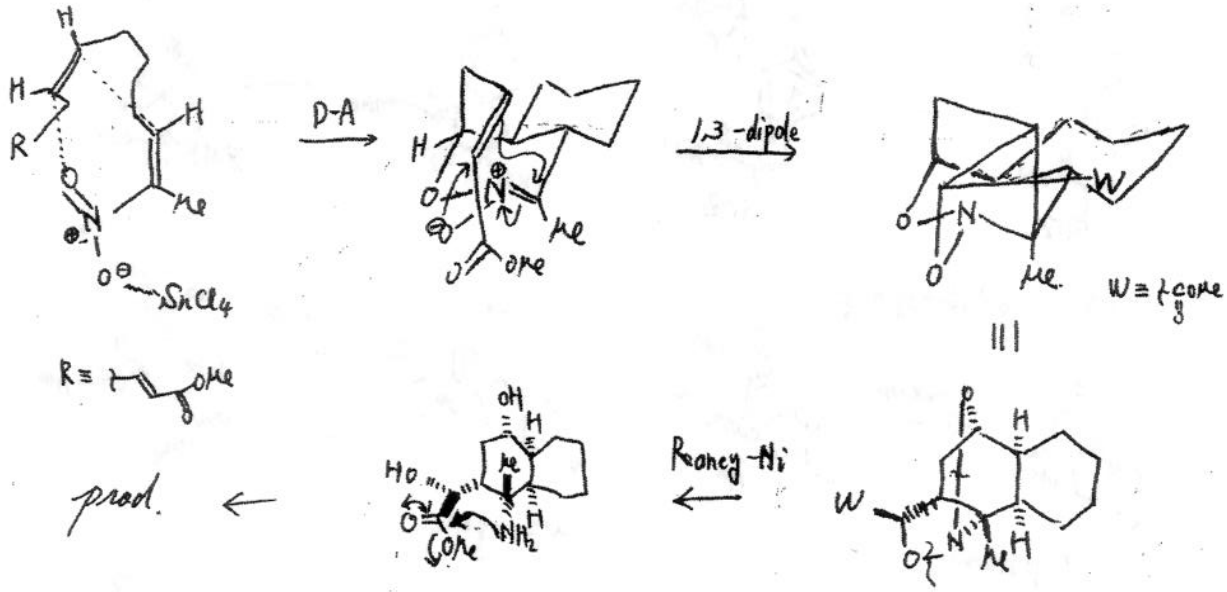

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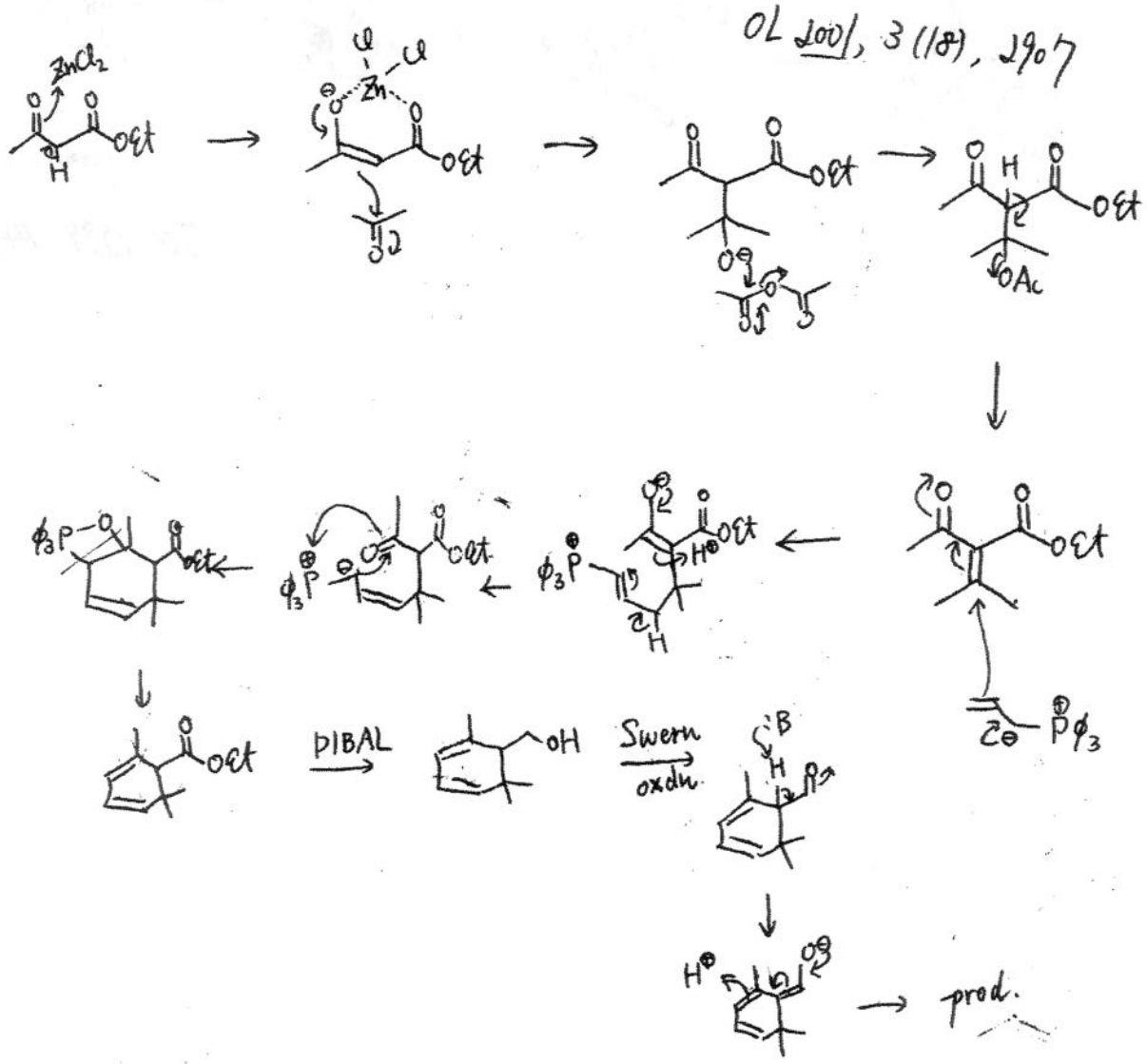

OL 2001, 3(18), 2907

T.L 1997, 38(44), 7793-6

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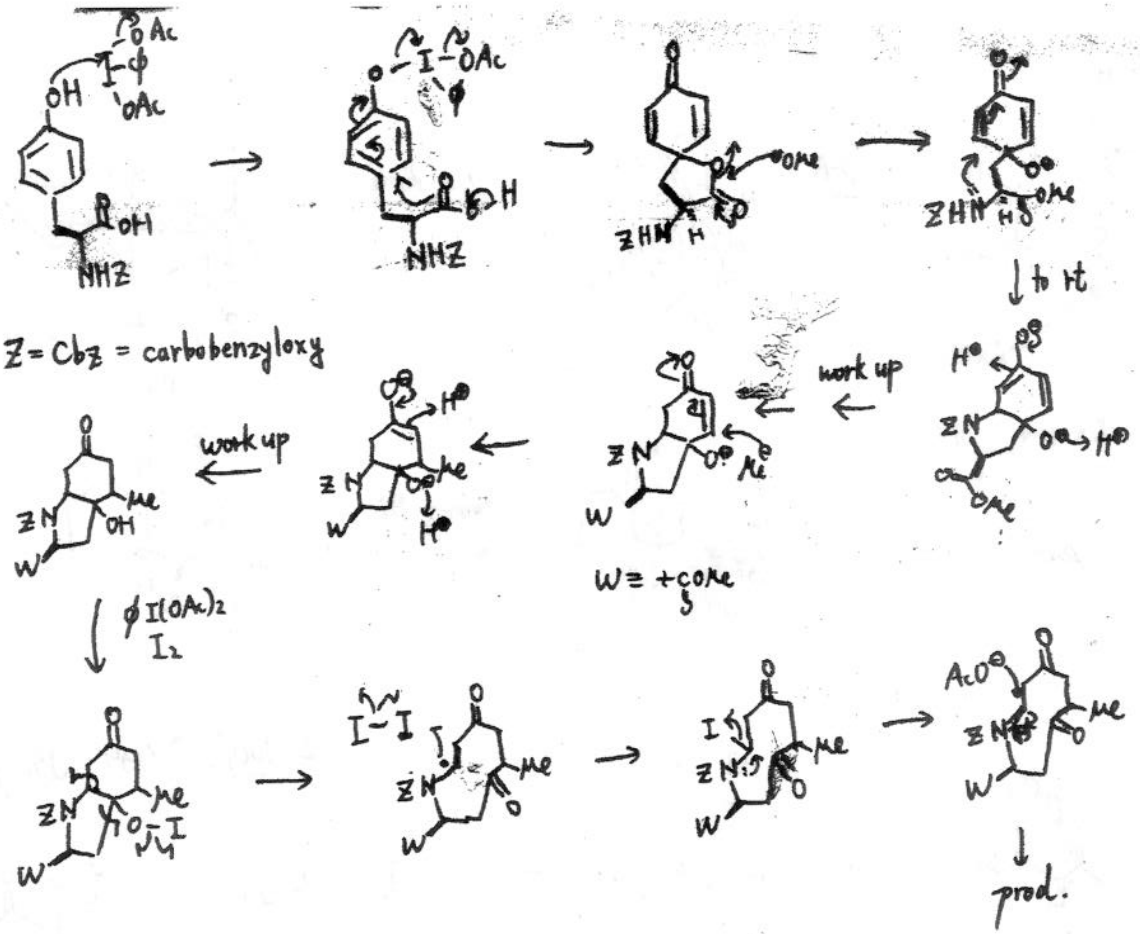

JOC 1999, 64, 4576

Group Meeting Problems Solution

2001 / 9 / 26

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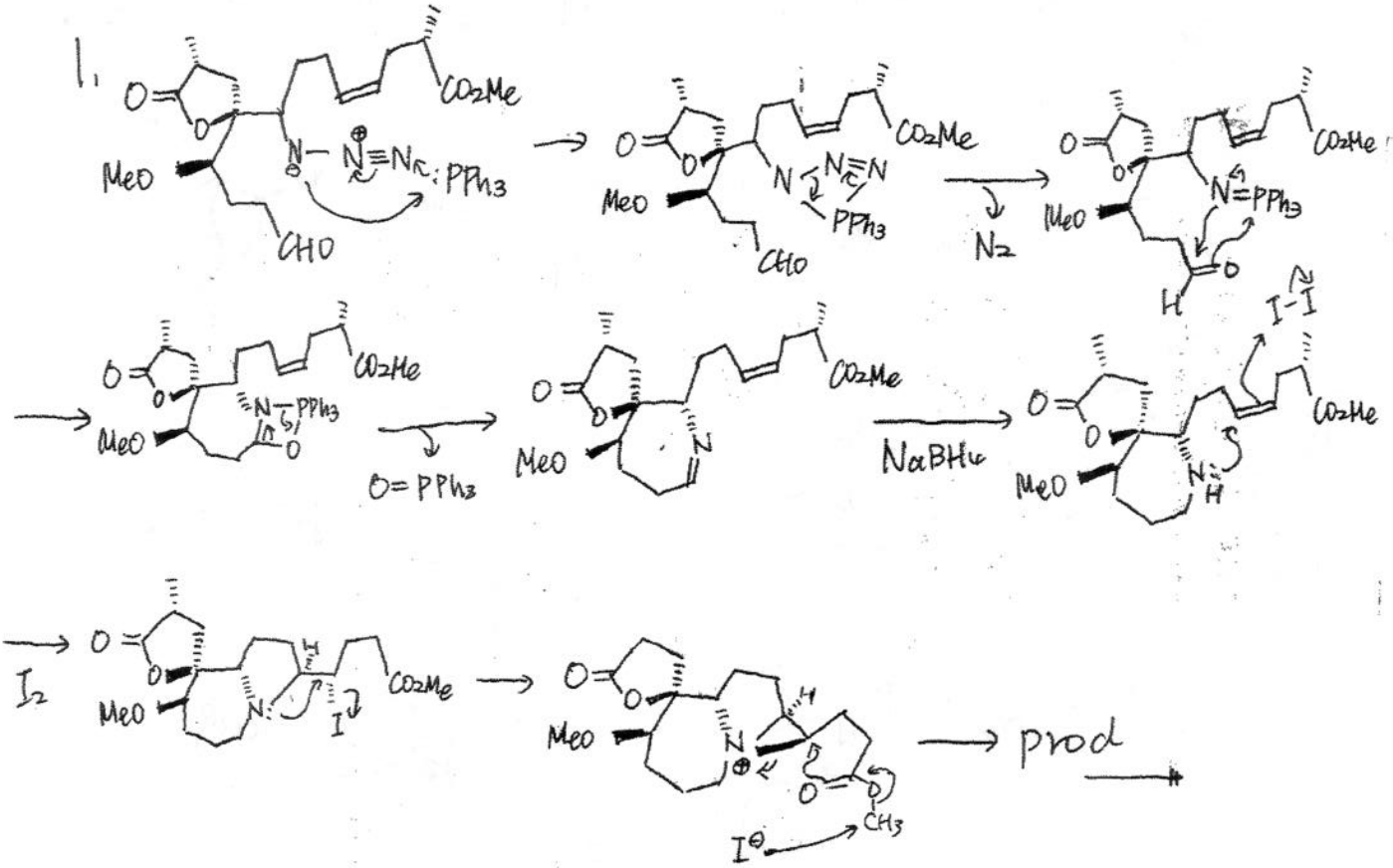

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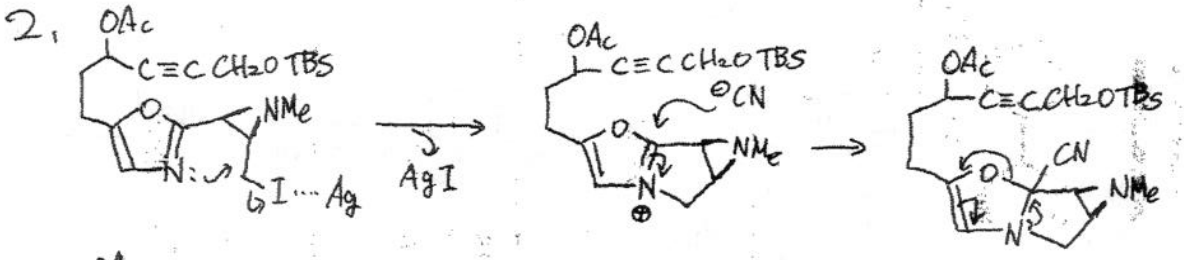

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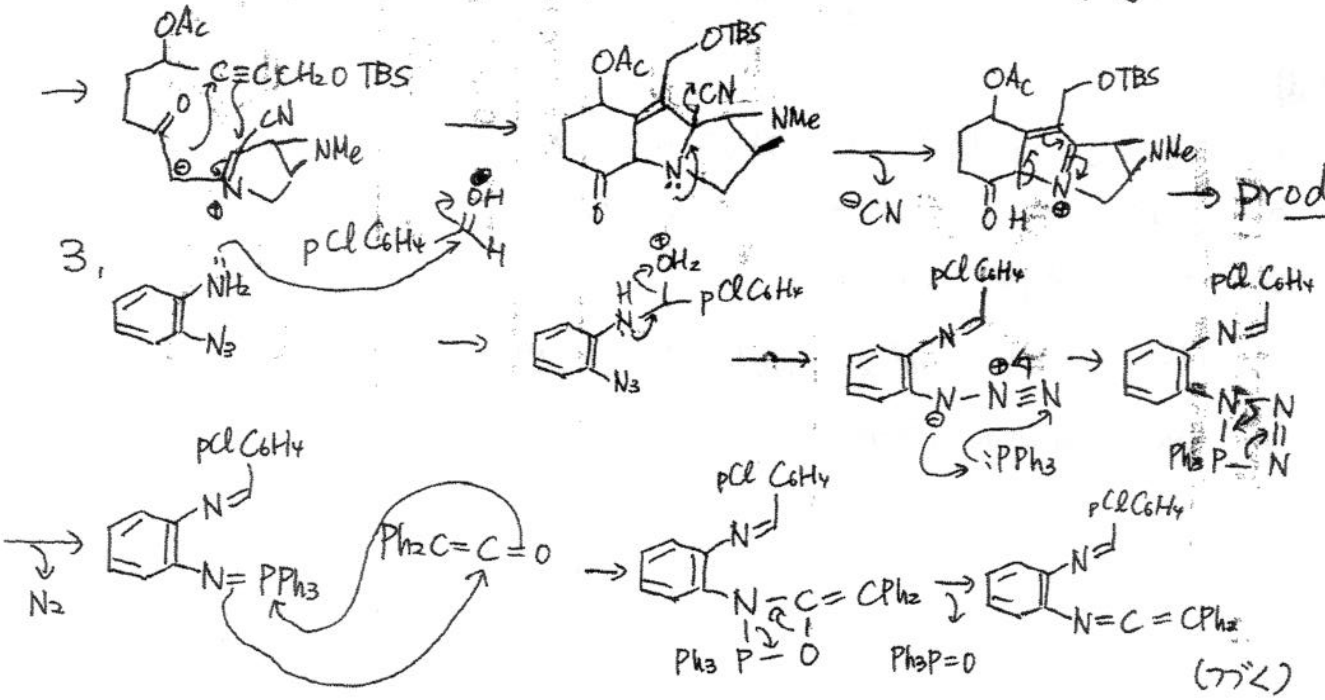
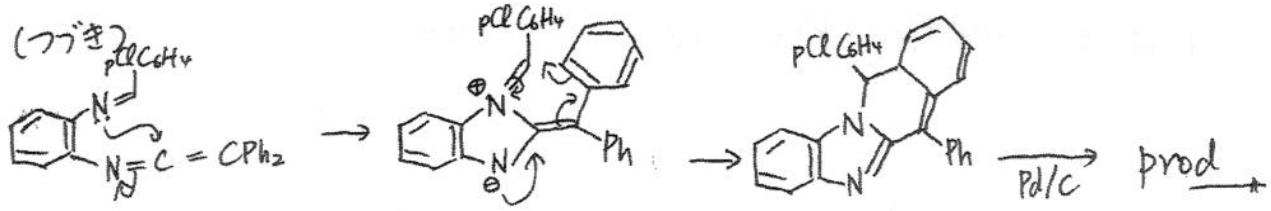


(つづく)

3 (つづき)



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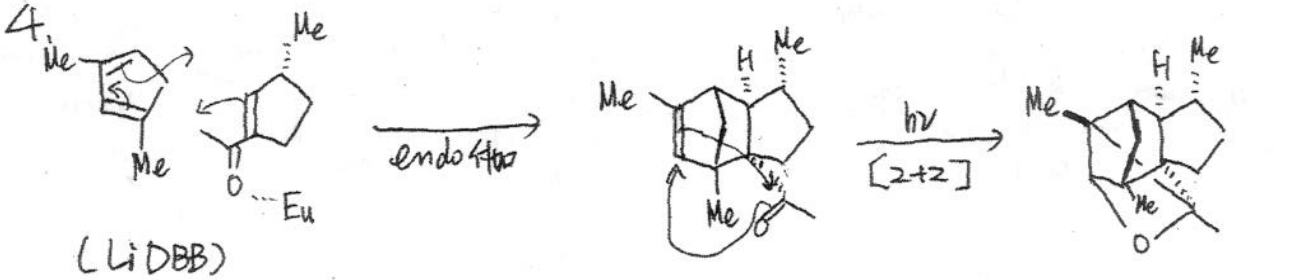
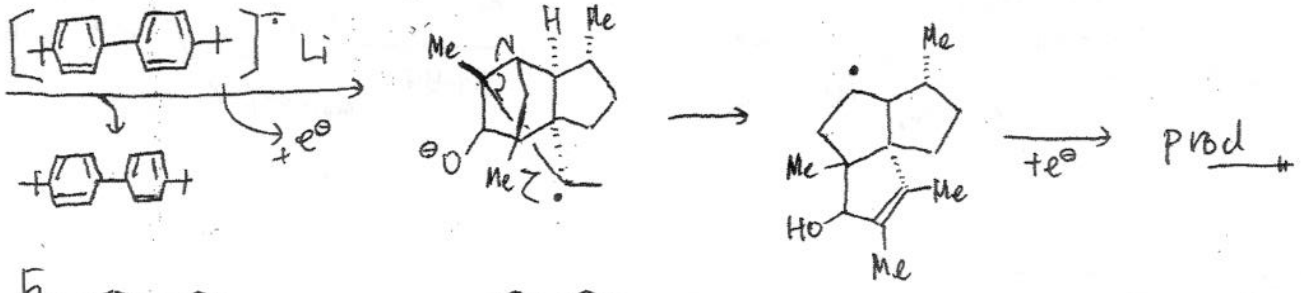


(LiDBB)



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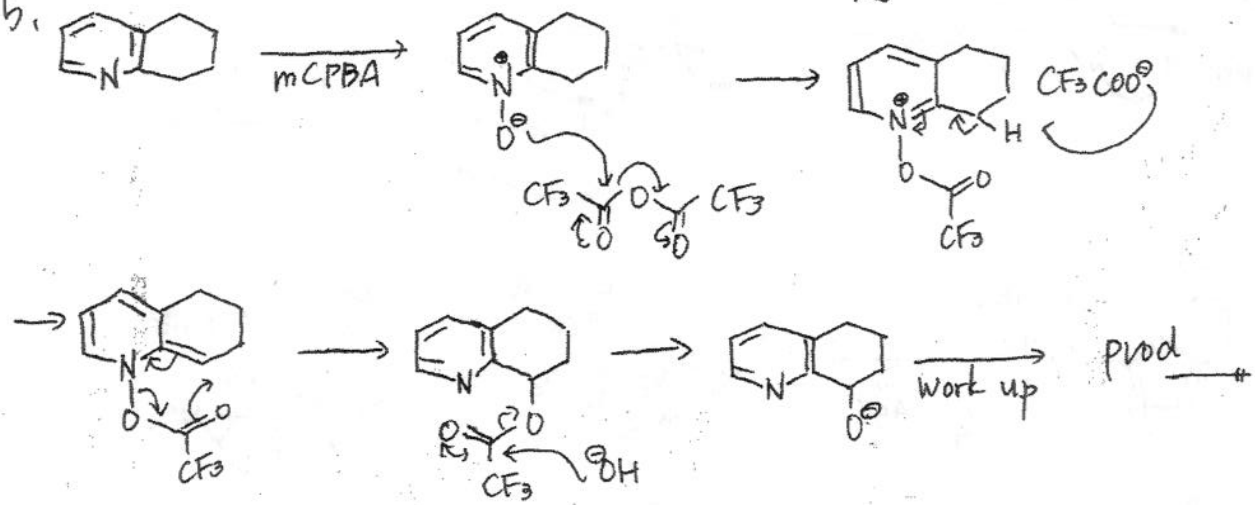


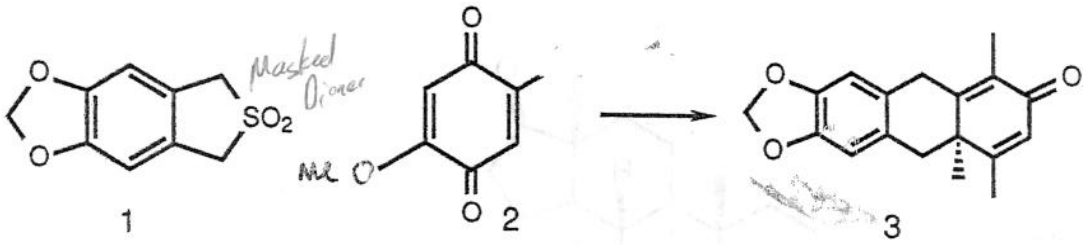
出典

1. OL. 2001, Vol3. 17. 2725 ~ 2728
2. JACS. 2000, 122, 5401 ~ 5402
3. TL, 1999, 6127
4. OL. 2000, vol2, No17, 2711 ~ 2712
5. Syn. Commun. 1995, 25, 629

Diels-Alder

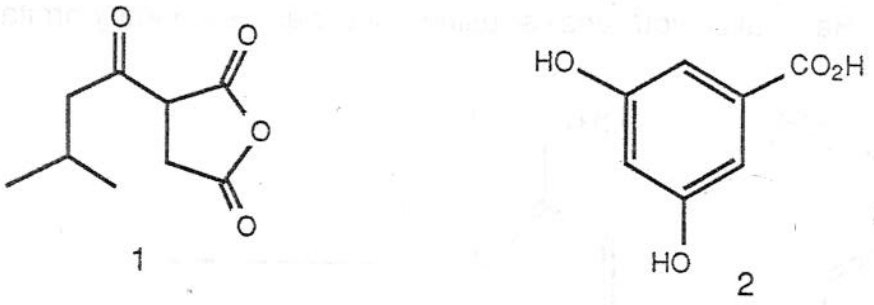
Problem Set Chemistry 435 October 22, 1986

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



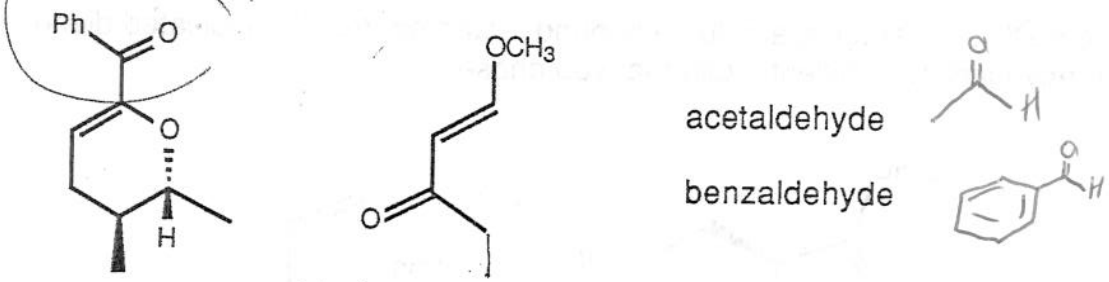
1 2 3

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



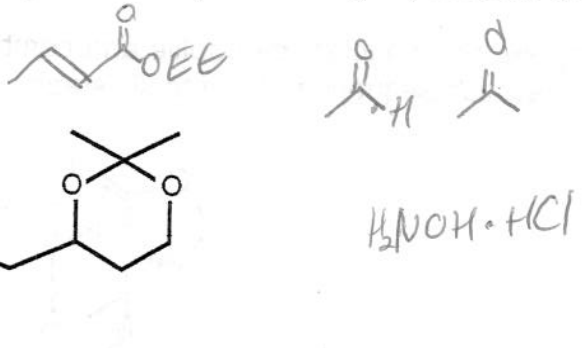
1 2

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



1 2

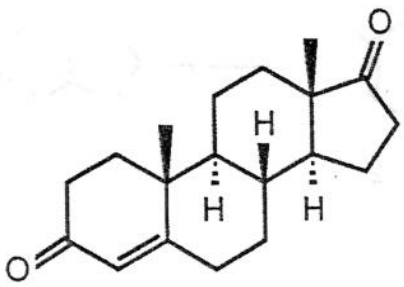
8. How would you make comopund 1 from ethyl crotonate, acetaldehyde, acetone and hydroxylamine hydrochloride?



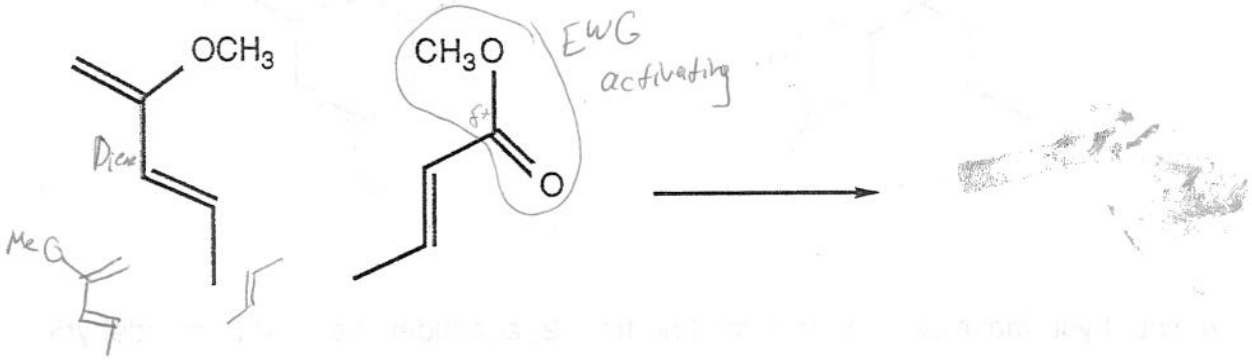
1

Problem set Chemistry 435 October 22, 1986

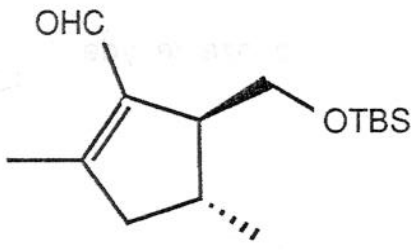
1. Draw as the 3D structure the steriod given below.



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.

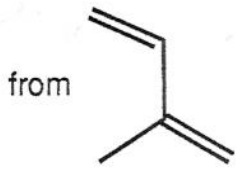


3. Give a Diels-Alder approach to compound 1 starting from the indicated diene. Use any electron deficient olefin that you chose.

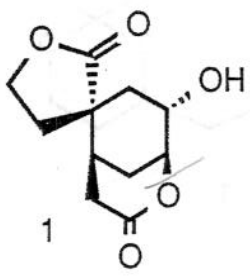


1

from



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

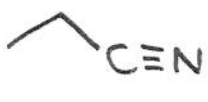
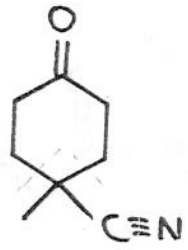


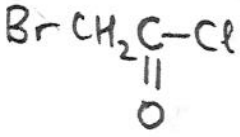
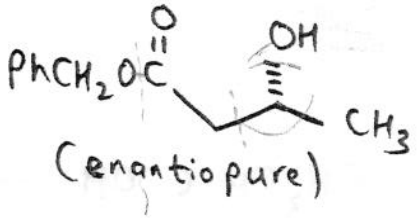
1

2ND "HOUR EXAM"

(YOU MAY USE MOLECULAR MODELS!) final 18+4

Propose short, efficient and stereocontrolled syntheses of each target from the starting material shown. Use any Aldrich intermediates or standard reagents. Assume products are racemic/achiral unless otherwise specified! Write answers in blue book, specifying all reagents. Put your name (PRINT!) on blue book.

1.  ⟶ 

2.  ⟶ 
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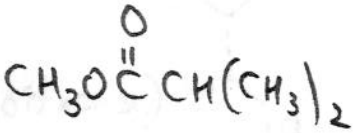
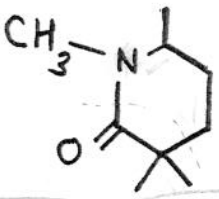
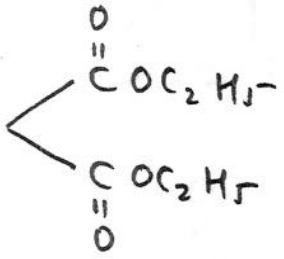
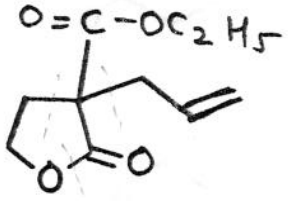
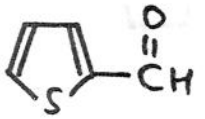
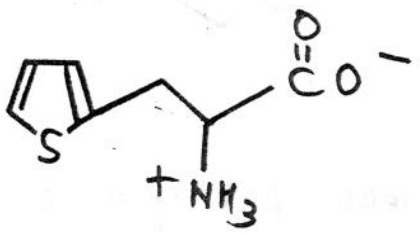
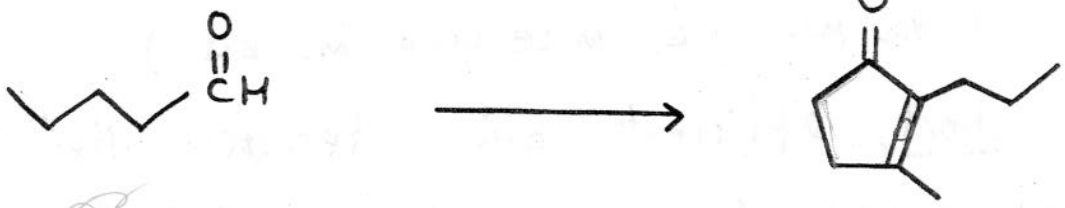
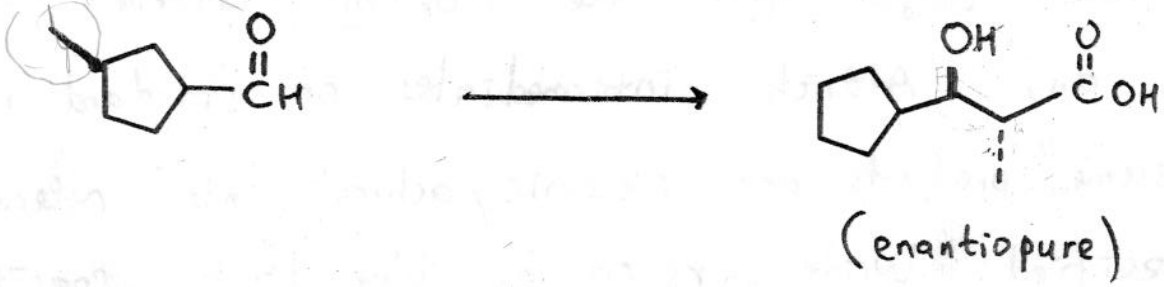
3.  ⟶ 

4.  ⟶ 

5.  ⟶ 

6. 

7. 

(enantiopure)

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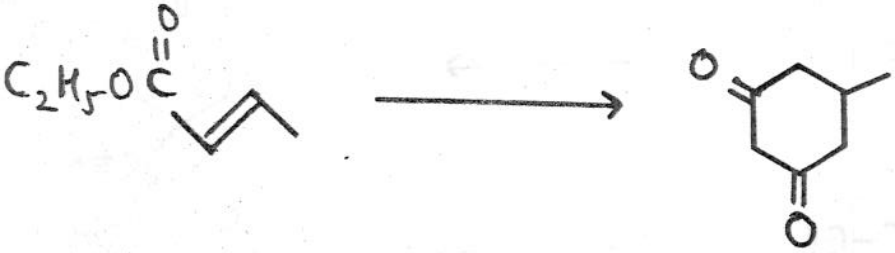
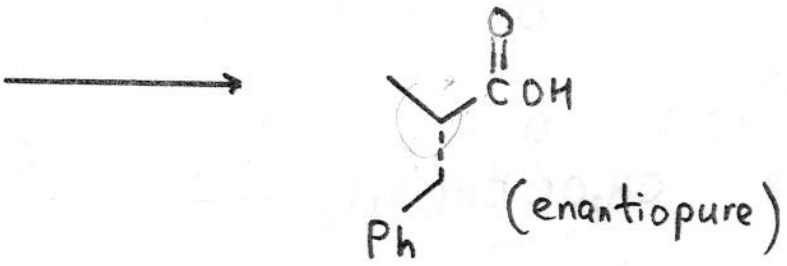
9. 

10. CH_3CH_2COOH 

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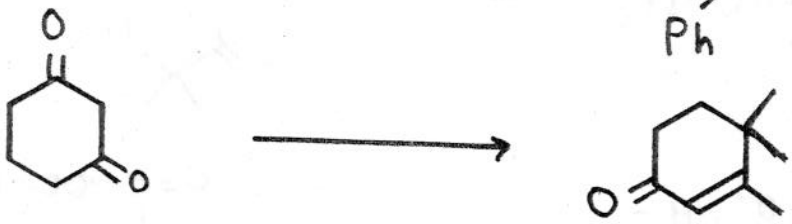
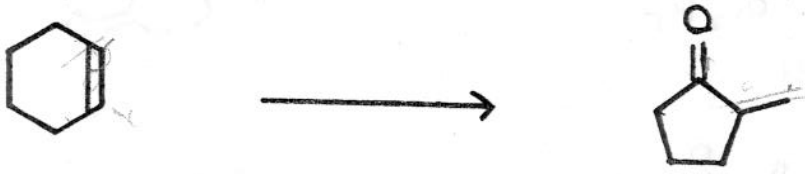
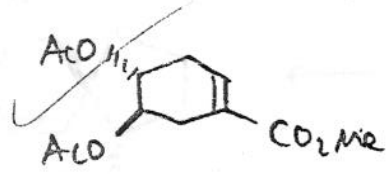
11. 

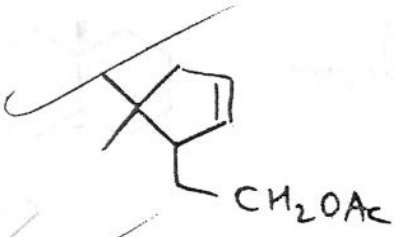
12. 

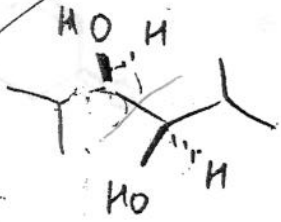
(Please put your name on the blue book.)

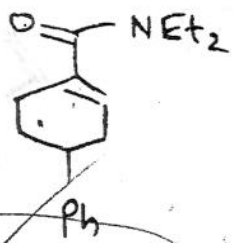
PROBLEM SET 2 CHM 435 9/25/90

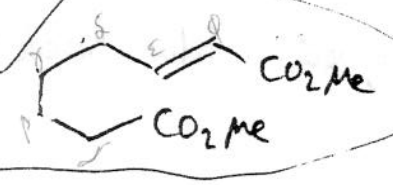
Starting from Aldrich precursors, and using at least one of the general reaction types discussed in class, propose efficient syntheses for each of the following compounds. Assume they are racemic if not otherwise specified.

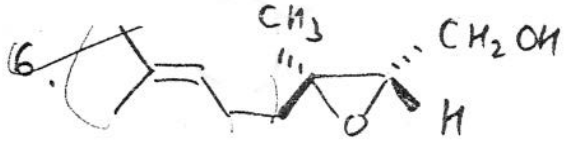
1. 

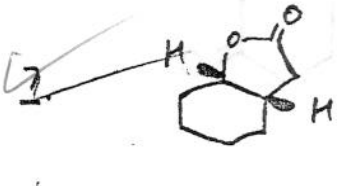
2. 

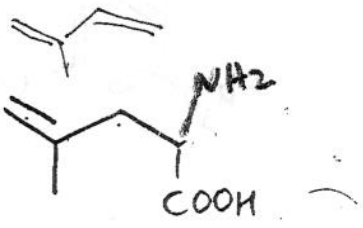
3. 

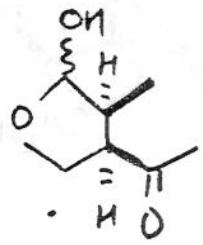
4. 

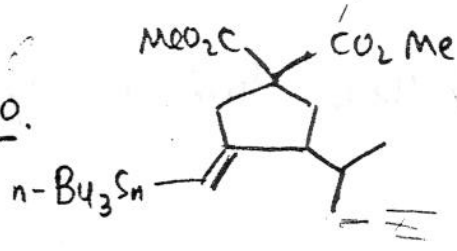
5. 

6. 
(enantio. pure)

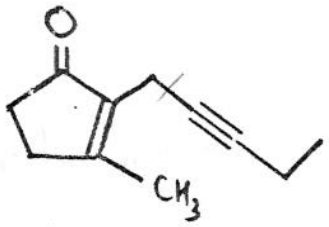
7. 

8. 

9. 

10. 

14. $CH_3CH_2C\equiv CH$ ⟶⟶



15.

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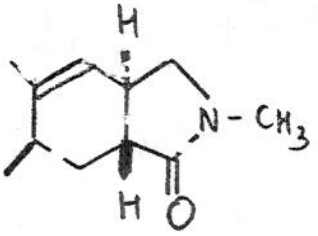
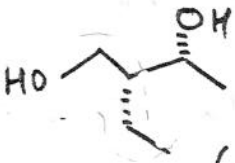


16. $HO_2C\,CH_2CH_2\,CH_3$ ⟶⟶



(enantiopure)

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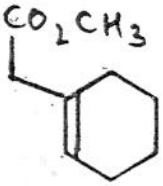

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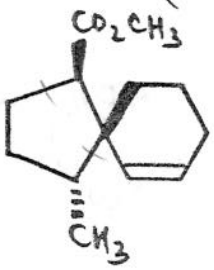
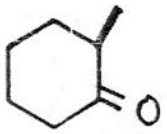


one hint!

18.



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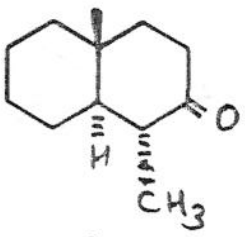

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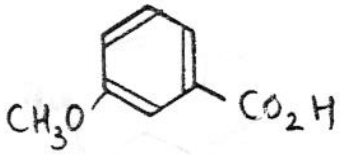

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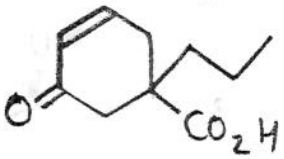

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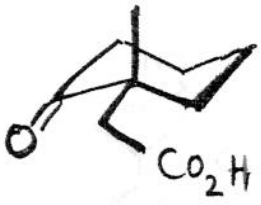

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(Please turn in your signed blue book(s) only.)