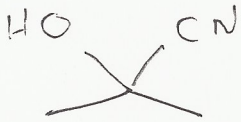
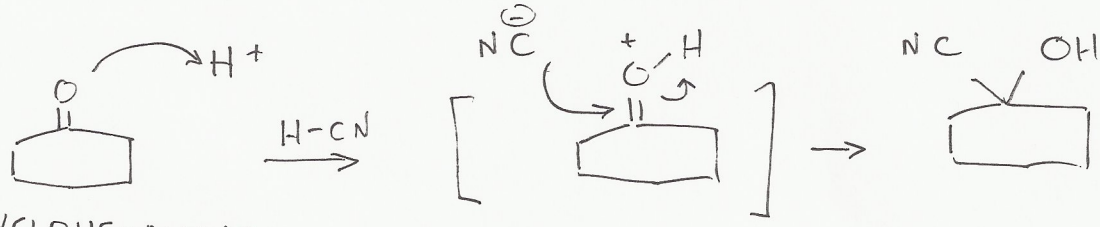
SOLUTIONS
PROBLEM SET
18

19.9 Cyanohydrin is derived from reaction of a ketone and ^-CN Nu: in a Nu: Acyl. Addition

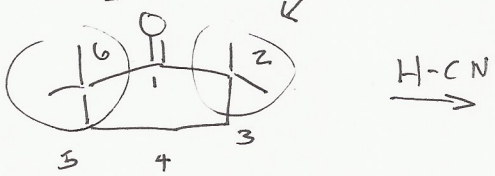


CYANOHYDRIN



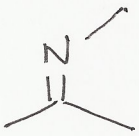
CYCLOHEXANONE

TOO STERICALLY CROWDED AROUND THE CARBONYL CARBON

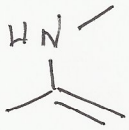


2, 2, 6, 6-TETRAMETHYL CYCLOHEXANONE

19.10 Reaction of a 1° or 2° Amine with a ketone occurs via a Nu: Acyl addition. The product of the reaction is an imine or enamine.

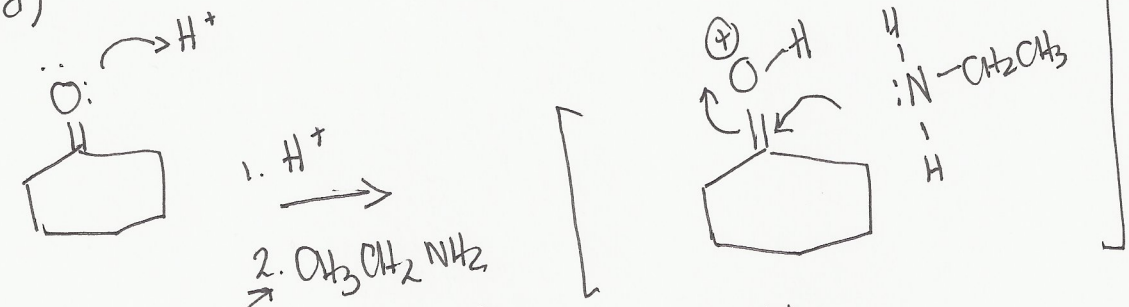


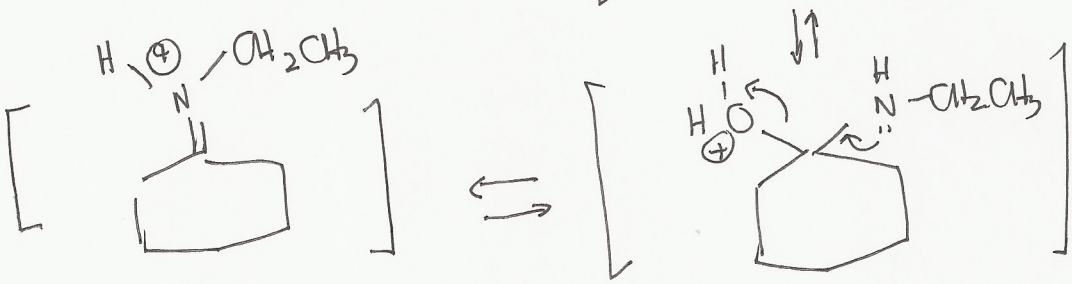
IMINE (from 1° AMINES)

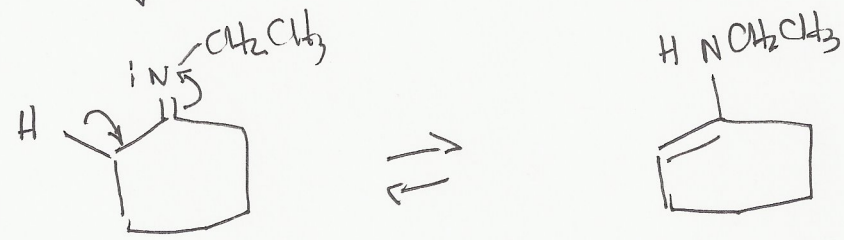


ENAMINE (from 1° or 2° AMINES)

19.10 (cont'd)

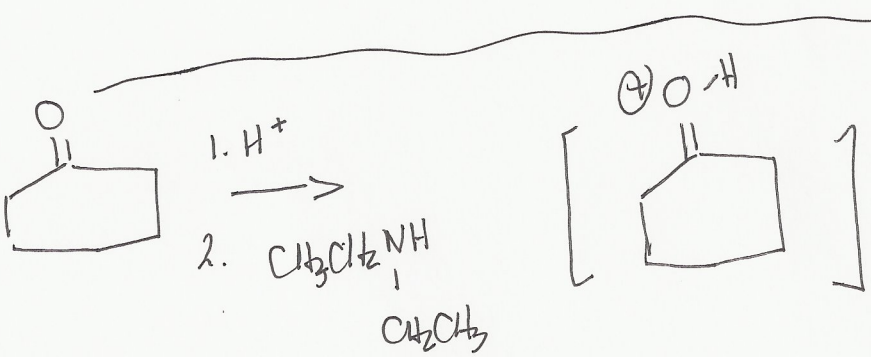






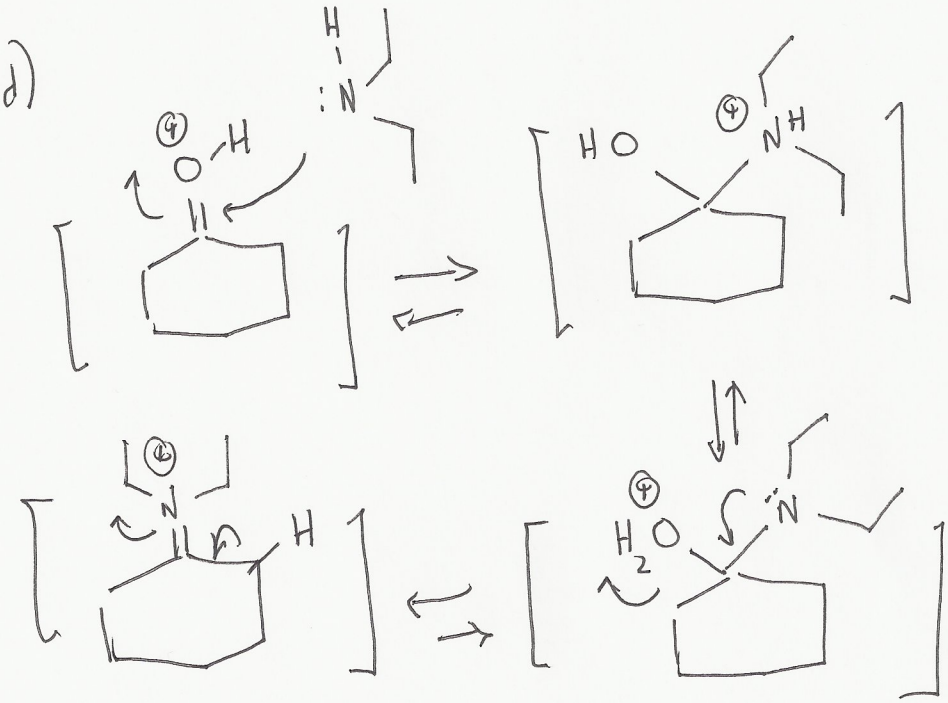
H transfers from N to O

(Similar to enol carbonyl rearrangement (TAUTOMERIZATION))



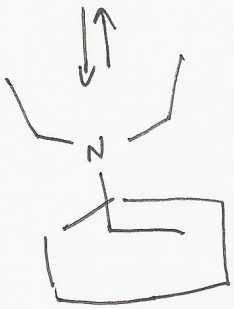
(cont'd)

19.10 (cont'd)



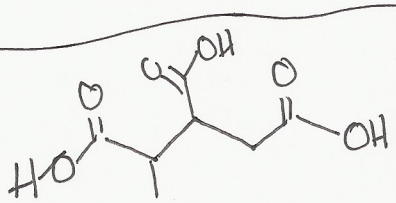
H transfers from N to O

IMINIUM ION

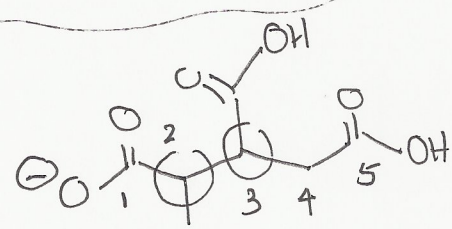


ENAMINE

19.20



OH
isocitric acid

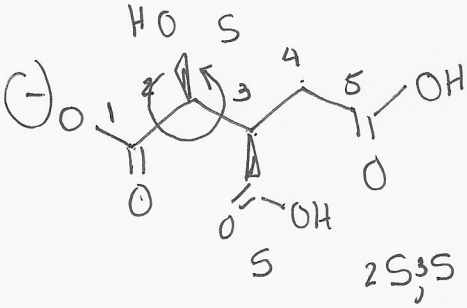


OH
Isocitrate

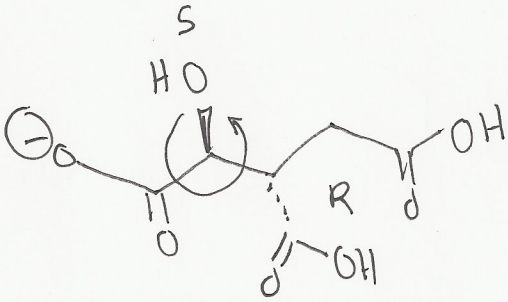
CHIRAL CENTERS are at C_2 or C_3

19.20 (cont'd)

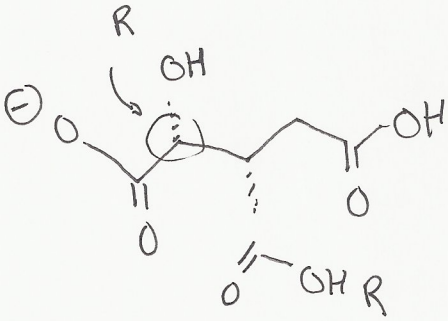
There are 4 possible stereoisomers of isocitrate



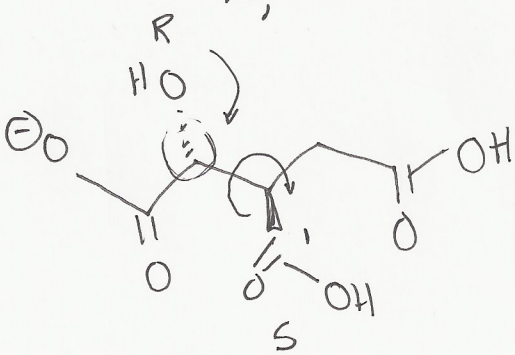
2S,3S



2S, 3R



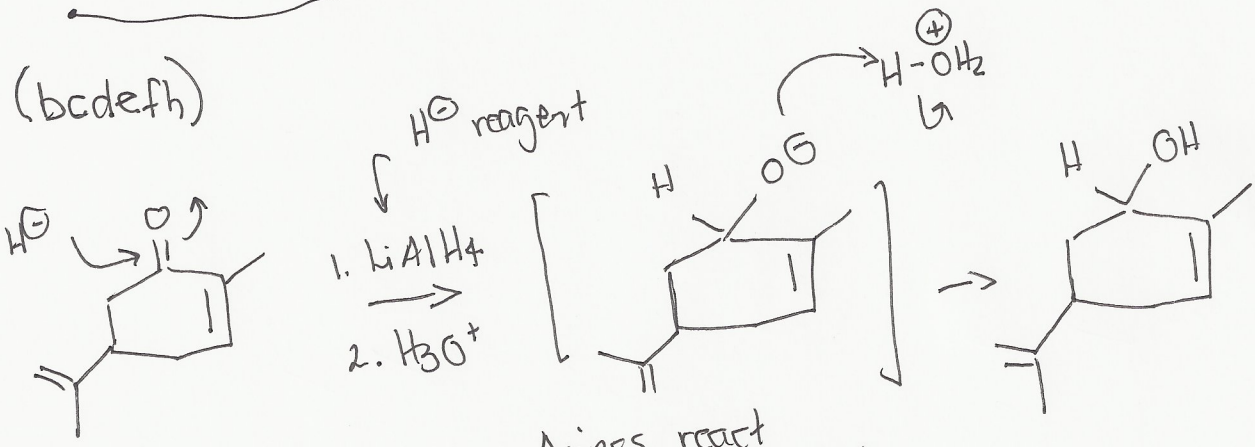
2R, 3R



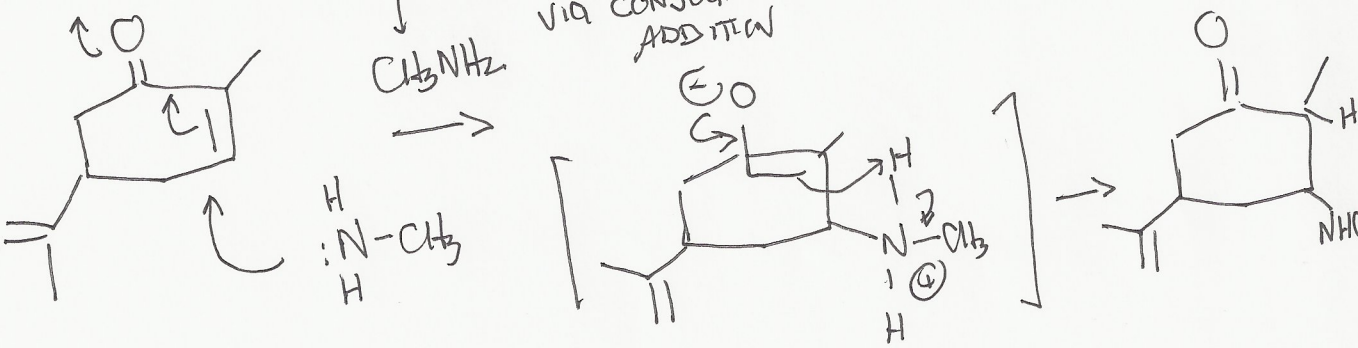
2R, 3S

19.40 (bcdefh)

b)

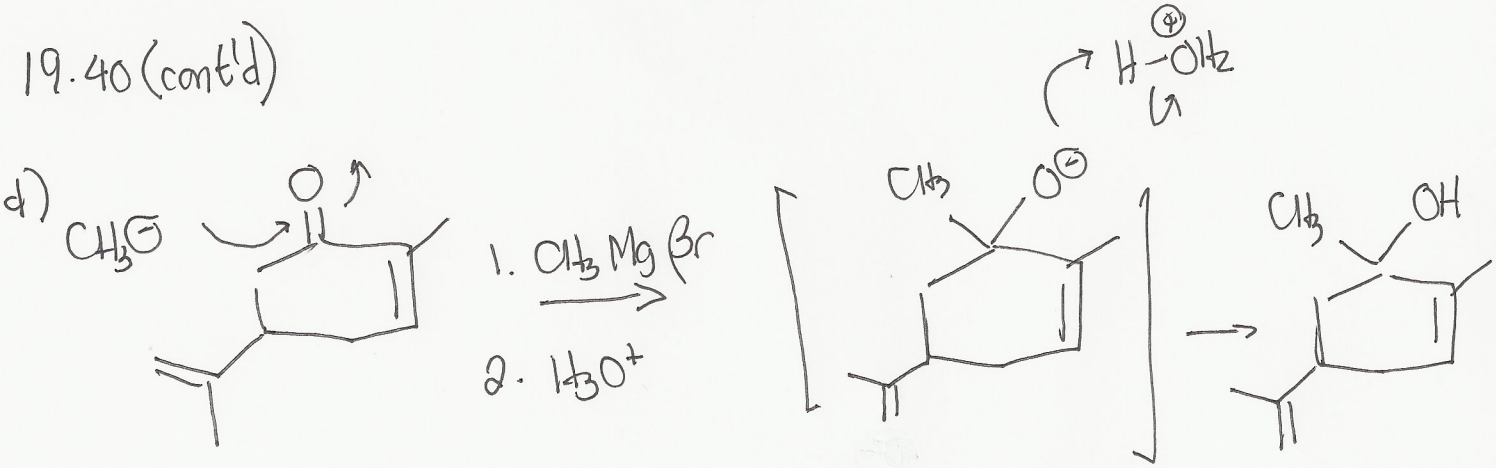


c)

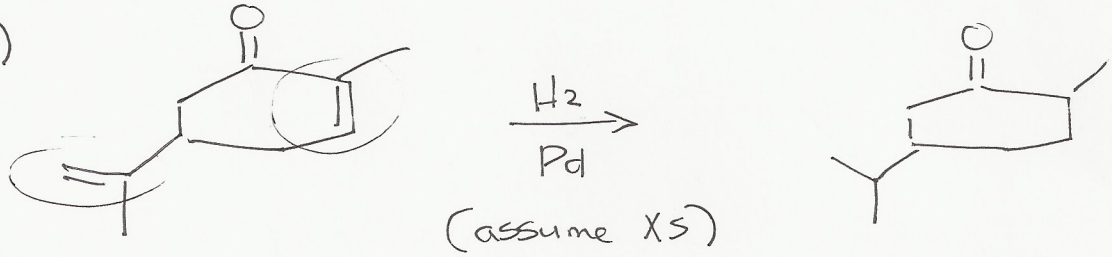


19.40 (cont'd)

d)

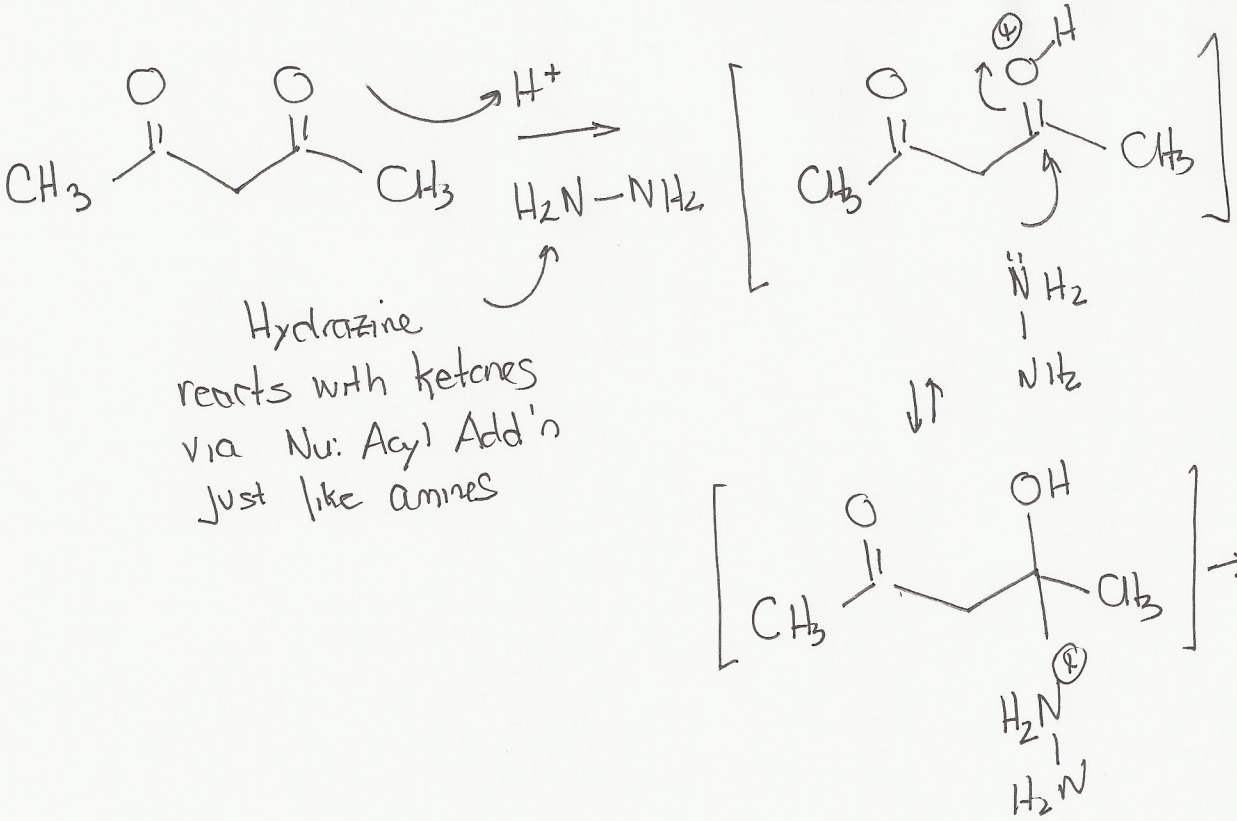


e)



Both alkenes reduce

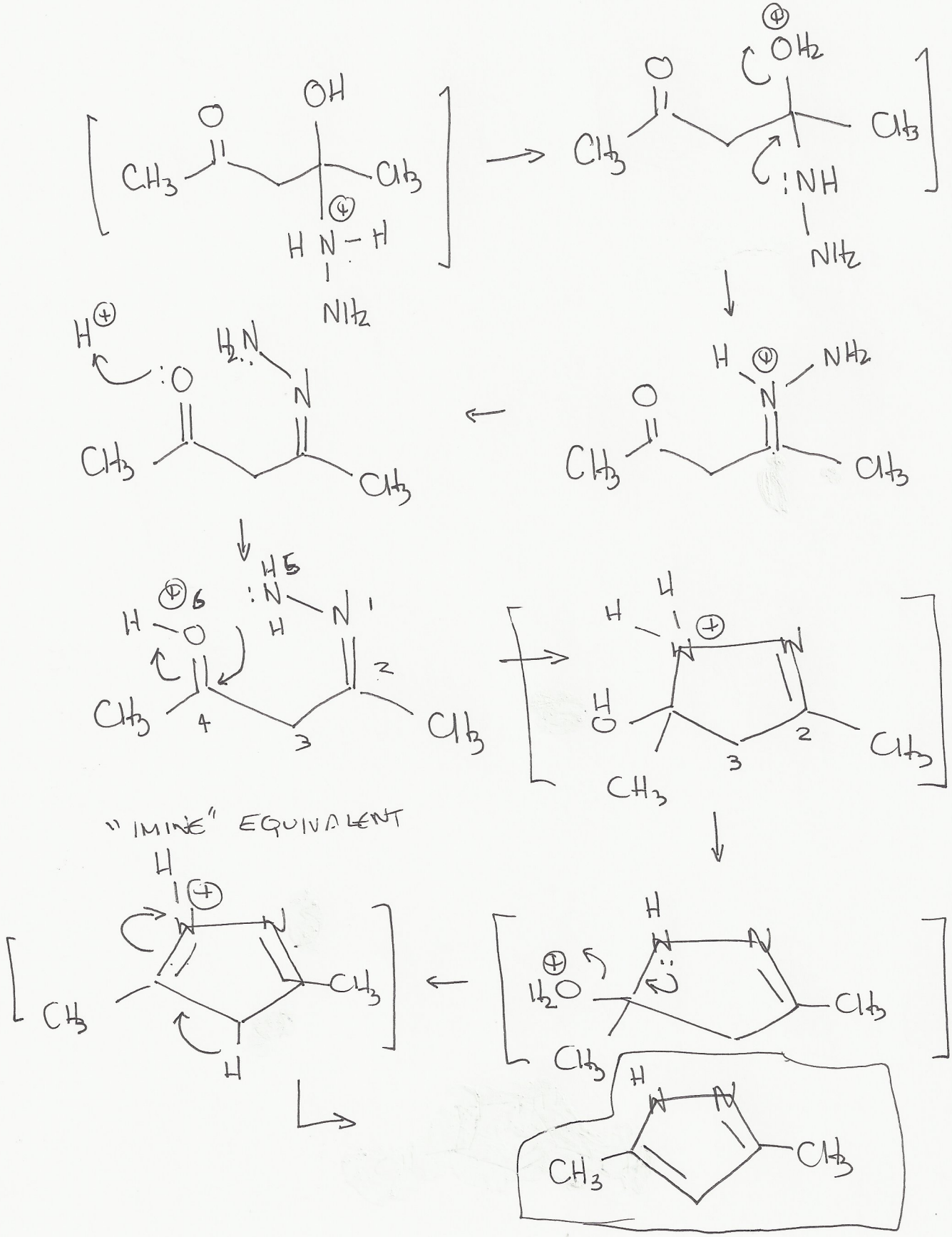
19.61



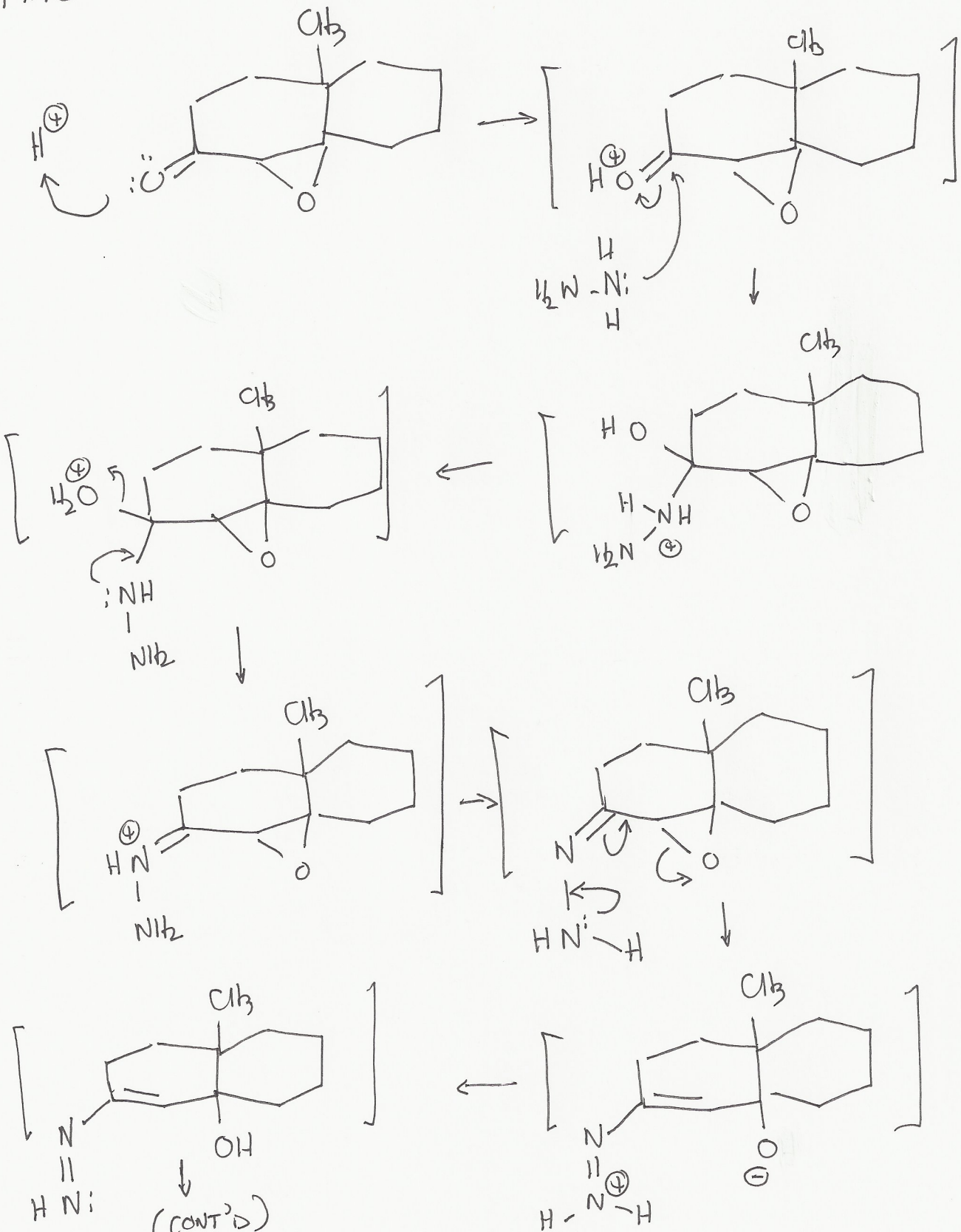
Hydrazine reacts with ketones via Nu: Acyl Add'n just like amines

→ cont'd

19.61 (cont'd)



19.75


CH3
H⊕
:O
O
H⊕O
H
H2N-N:
H
H O
H-NH
H2N ⊕
H2O⊕
:NH
NH2
HN⊕
NH2
N
O
HN:-H
N
OH
H N:
N
O⊖
N⊕
H-N-H

(CONT'D)

19.75