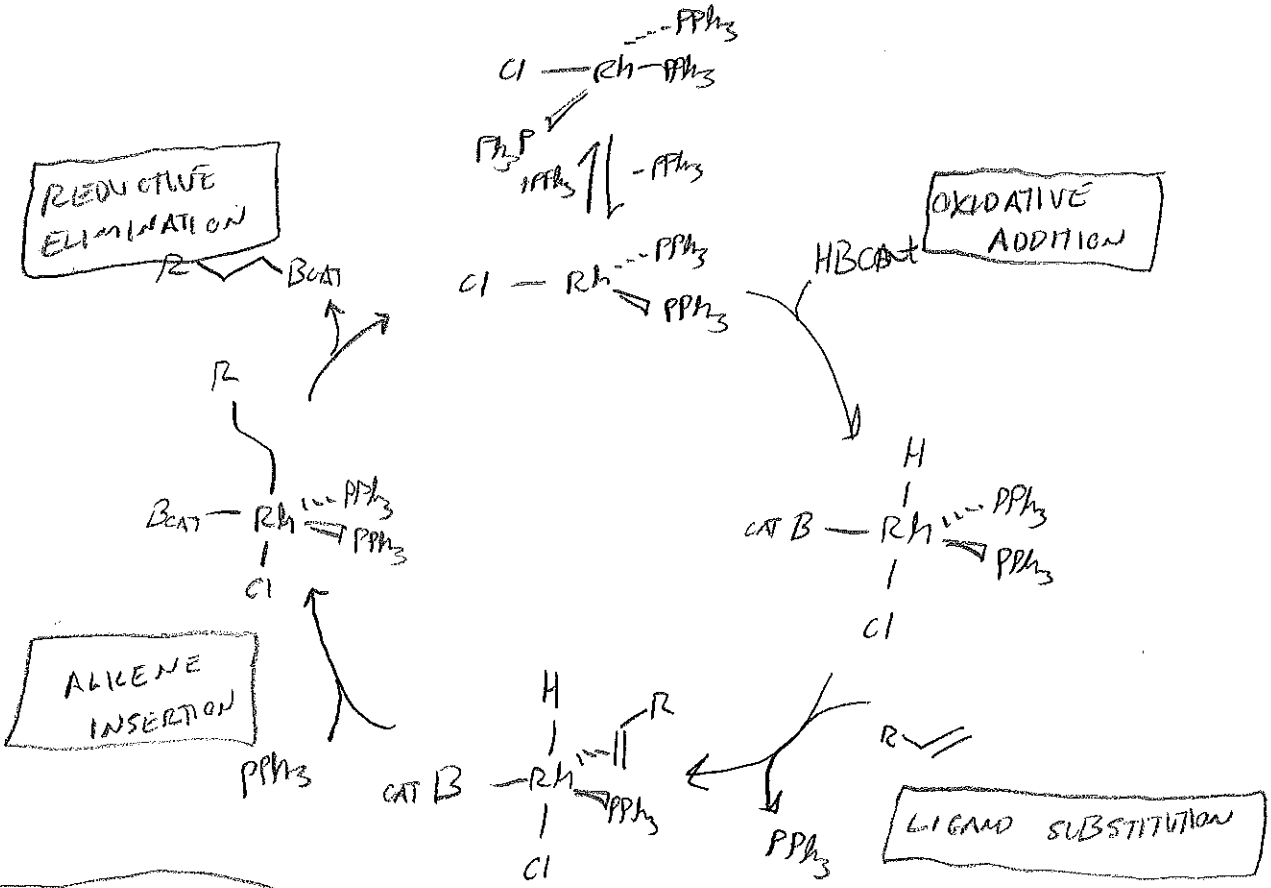
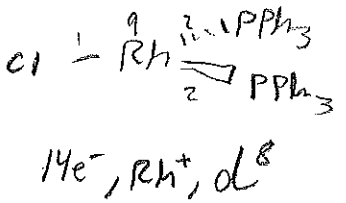
PS 8 AK

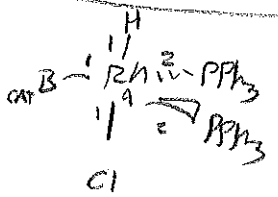
#1

a)

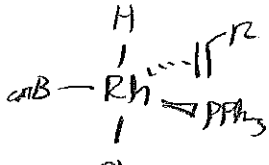




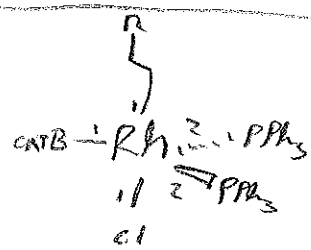
14e⁻, Rh⁺, d⁸



16e⁻, Rh³⁺, d⁶

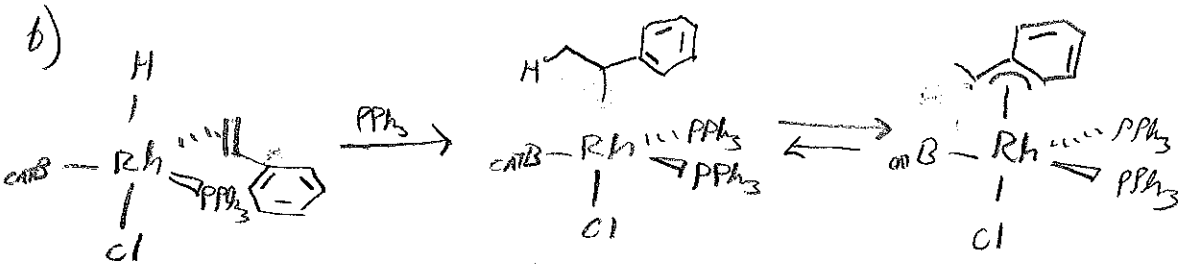


16e⁻, Rh³⁺, d⁶



16e⁻, Rh³⁺, d⁶

b)



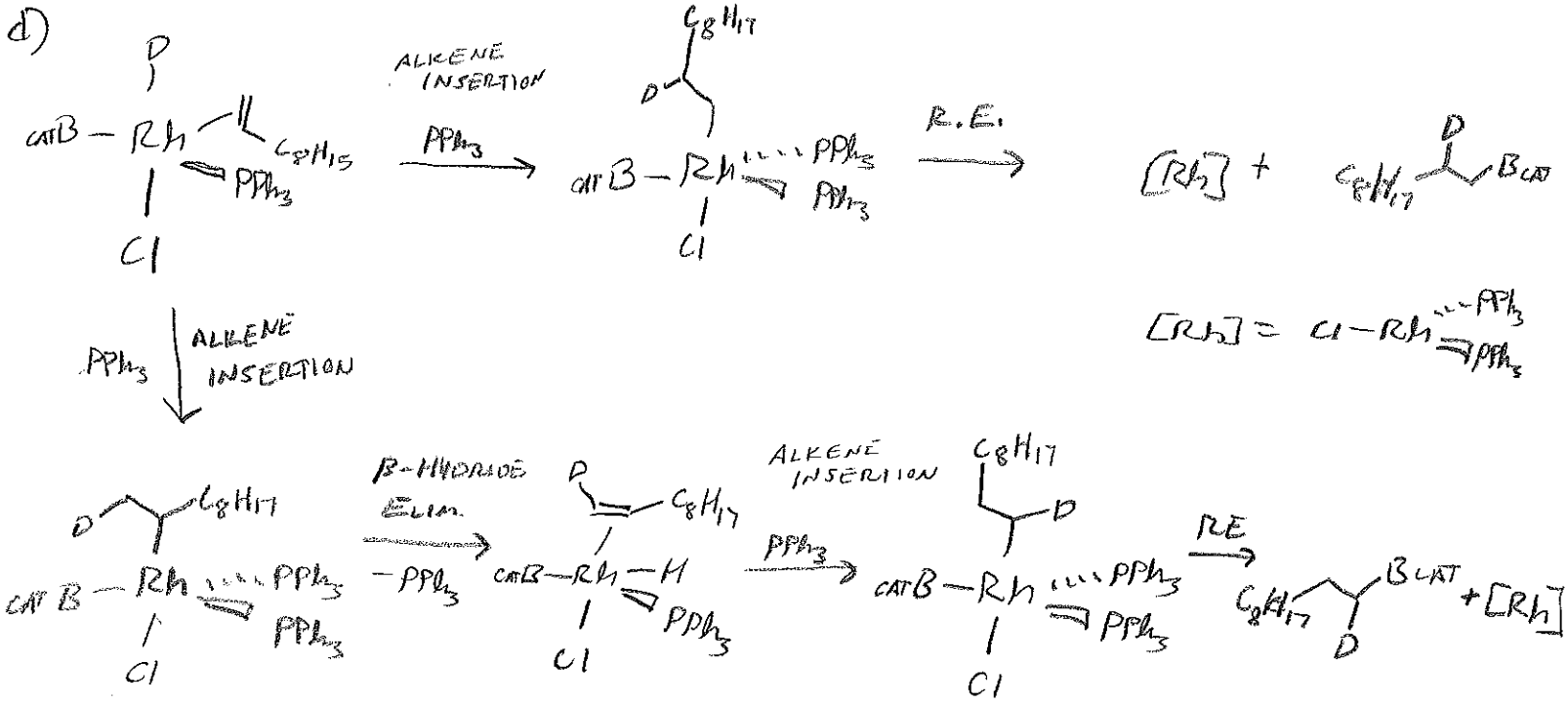
16e⁻

16e⁻

18e⁻

π-ALLYL INTERMEDIATE STABILIZES BINDING TO 2° CARBON, LEADING TO MARKOVNIKOV PRODUCT

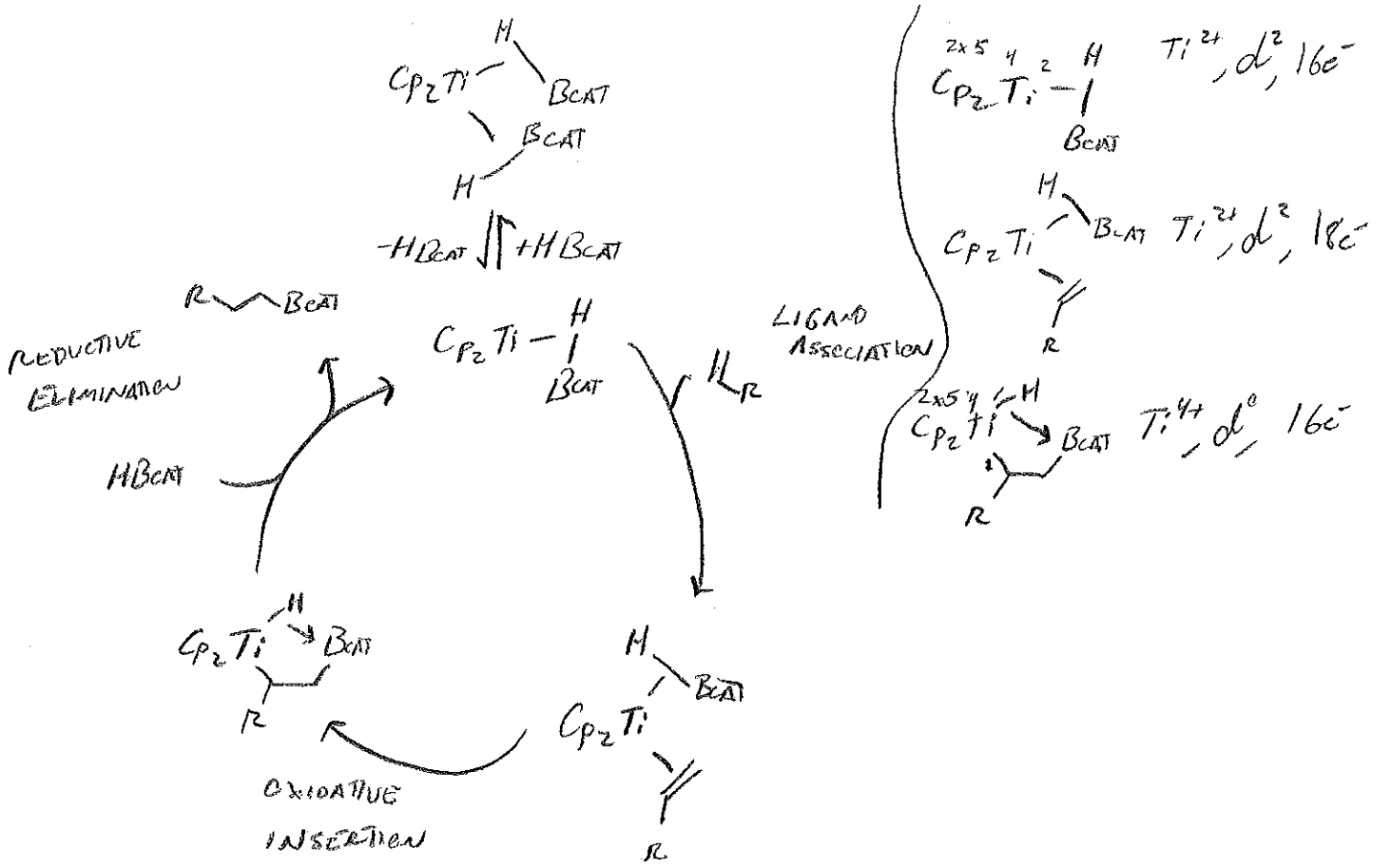
d)

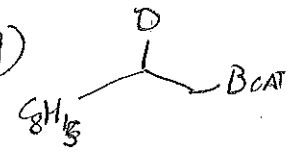


e) FOR 1-DECENE, STEP C IS REVERSIBLE AND NOT THE REGIOSELECTIVE DETERMINING STEP – LIKELY THE FOLLOWING REDUCTIVE ELIMINATION (STEP D)

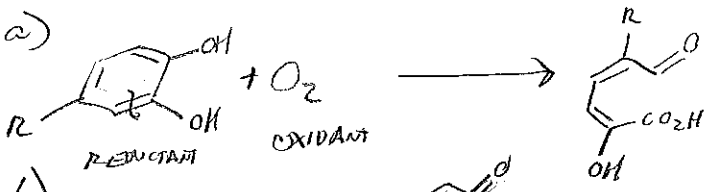
FOR STYRENE, STEP C IS IRREVERSIBLE AND DETERMINES THE REGIOSELECTIVITY FOR THE TRANSFORMATION

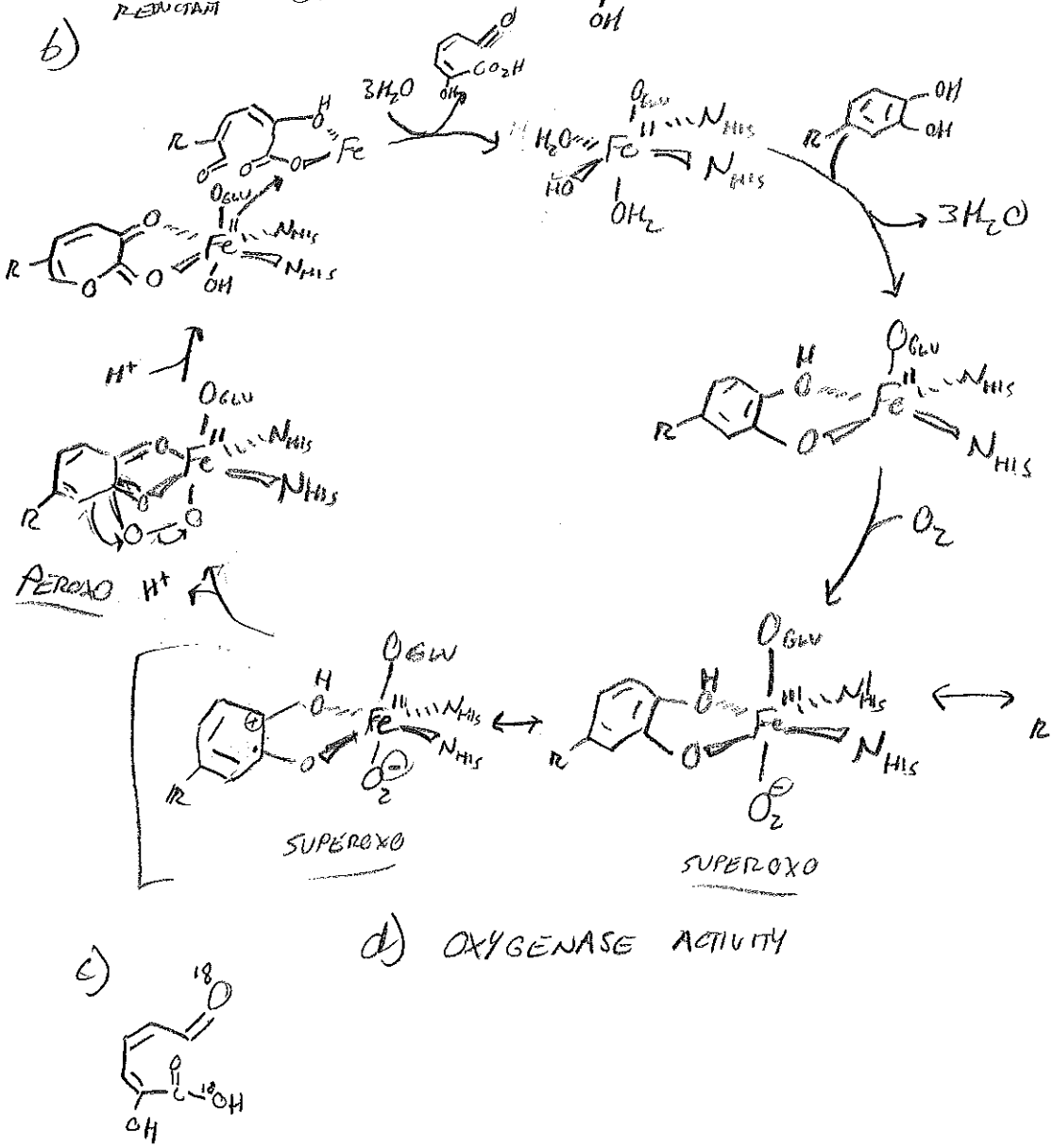
f)



9) 

2

a) 

b) 

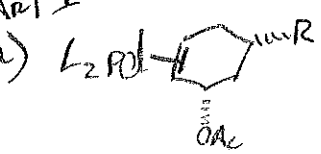
d) OXYGENASE ACTIVITY

e)

#3

PART I

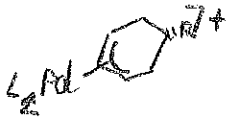
A

a) 

Pd	10
L_2	4
ll	2
	$16e^-$

Pd^0, d^{10}

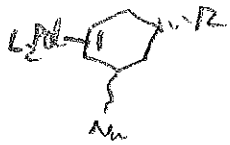
B



Pd	10
L_2	4
⌞	3
+	-1
	$16e^-$

Pd^{2+}, d^8

C



Pd	10
L_2	4
ll	2
	$16e^-$

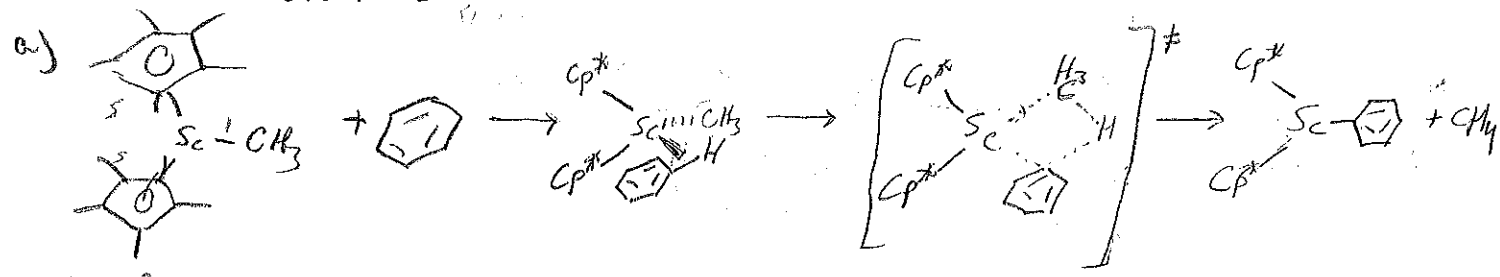
Pd^0, d^{10}

b) (a) REDUCTIVE ELIMINATION

(b) NUCLEOPHILIC ATTACK OF ALKYL (REDUCTIVE ELIMINATION)

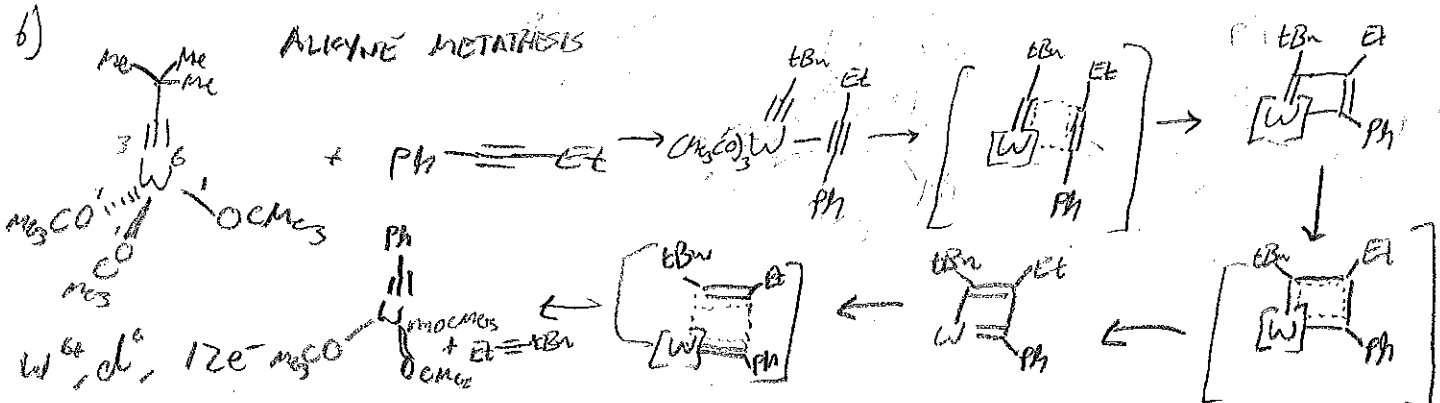
PART II

SIGMA BOND METATHESIS

a) 

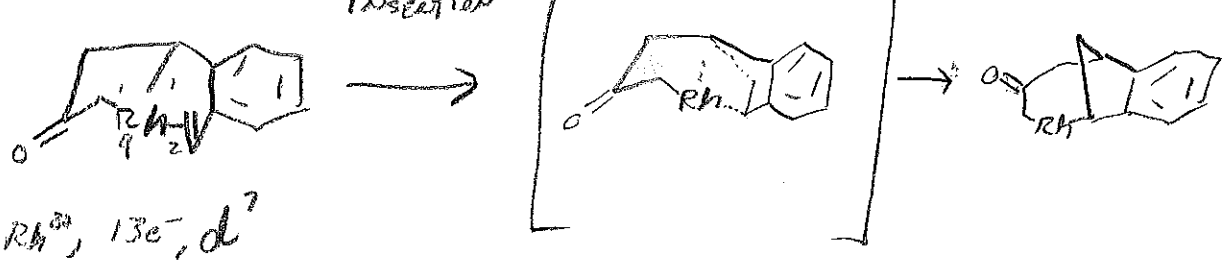
$Sc^{3+}, d^0, 14e^-$

b) ALKYNE METATHESIS



$W^{6+}, d^0, 12e^-$

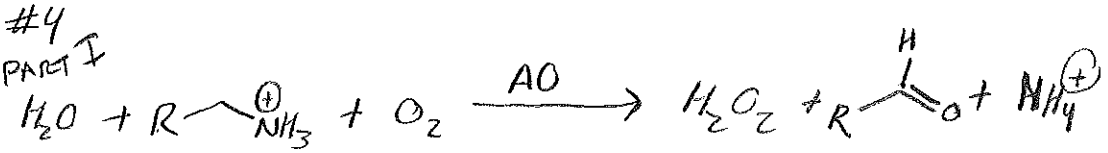
c) ALKENE INSERTION



$Rh^{3+}, 13e^-, d^7$

#4

PART I



$2e^-$, $2H^+$ TRANSFERRED

UP TO ALDEHYDE; AMINE IS REDUCTANT, TOPAQUINONE COFACTOR OXIDANT

REST OF MECHANISM; TOPAQUINONE COFACTOR REDUCTANT, O_2 OXIDANT

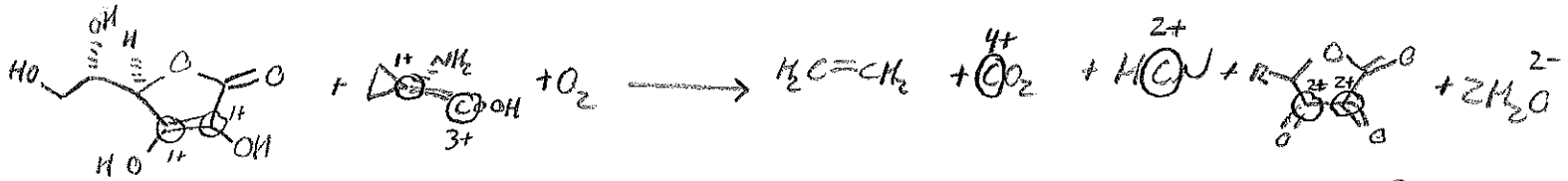
b+c) ON PAGE 6

d) OXIDASE

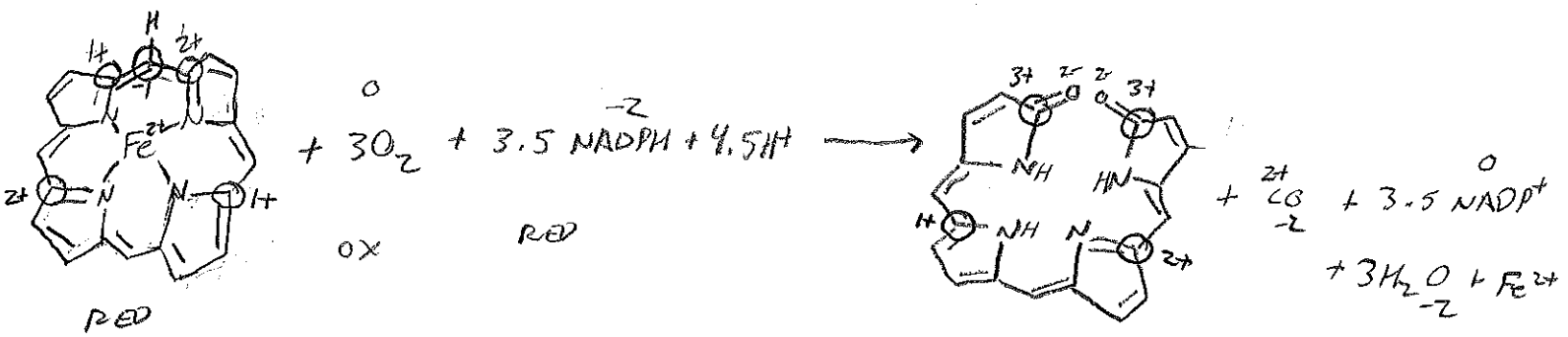
PART II

a)

RED. OX OXYGENASE

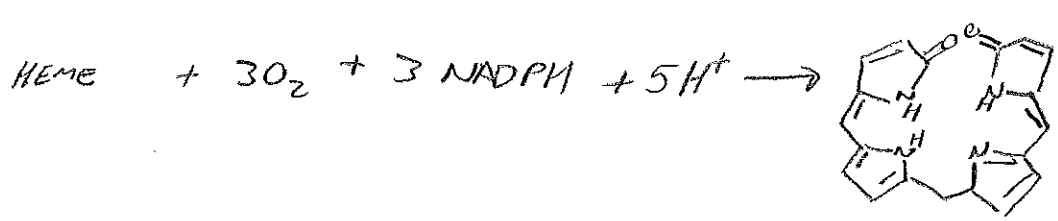


RED RED OX OXIDASE



RED OX RED OXYGENASE

WAS UNBALANCED IN P SET; CORRECT STOICHIOMETRY;



HEME + $3O_2$ + 3 NADPH + $5H^+$ → + CO + 3 $NADP^+$ + $3H_2O$ + Fe^{2+}

Problem 4 (2 points)

Part I

The copper-containing enzyme *AO* catalyzes the oxidation of primary amines to aldehydes, producing NH_4^+ and H_2O_2. The active site contains a unique cofactor covalently bound to the protein, topaquinone. This cofactor neighbors a Cu^{II} ion, which is bound to the protein in a square pyramidal geometry by three histidine residues, with two bound water molecules. The mechanism of this enzyme is shown below. *AO* enzymes have a variety of functions that are implicated in cell differentiation and growth, wound healing, detoxification, and signaling.