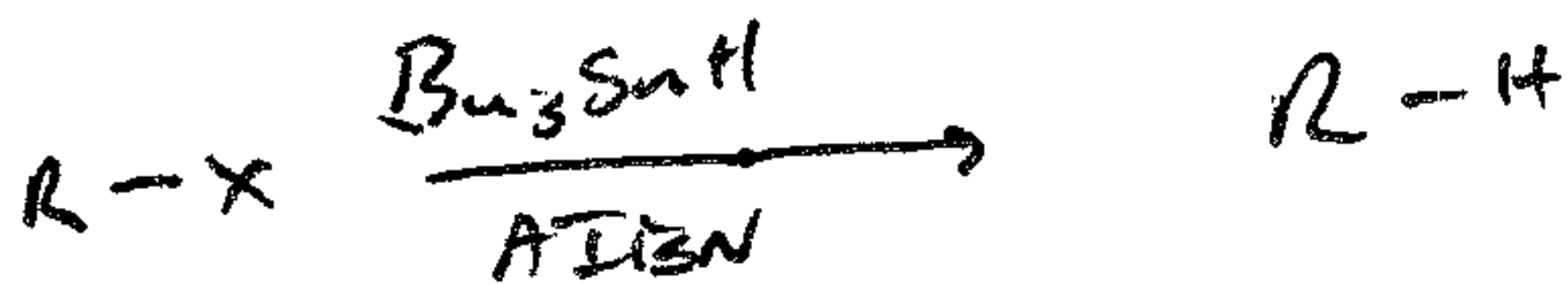
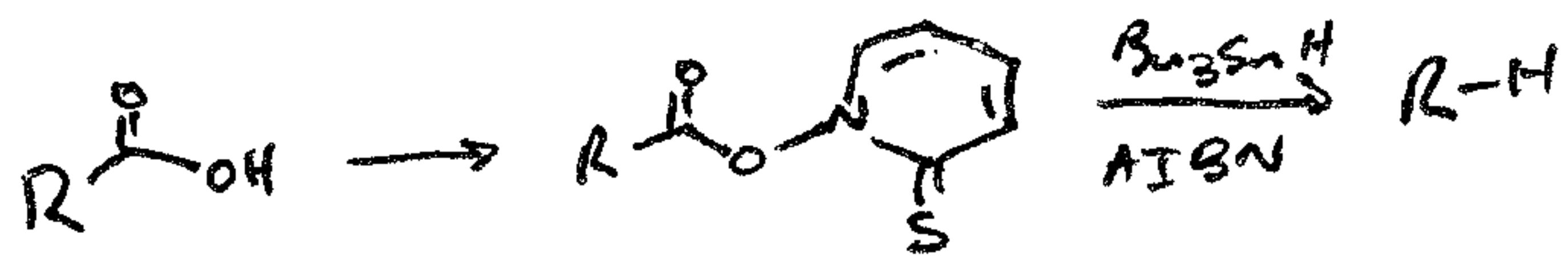
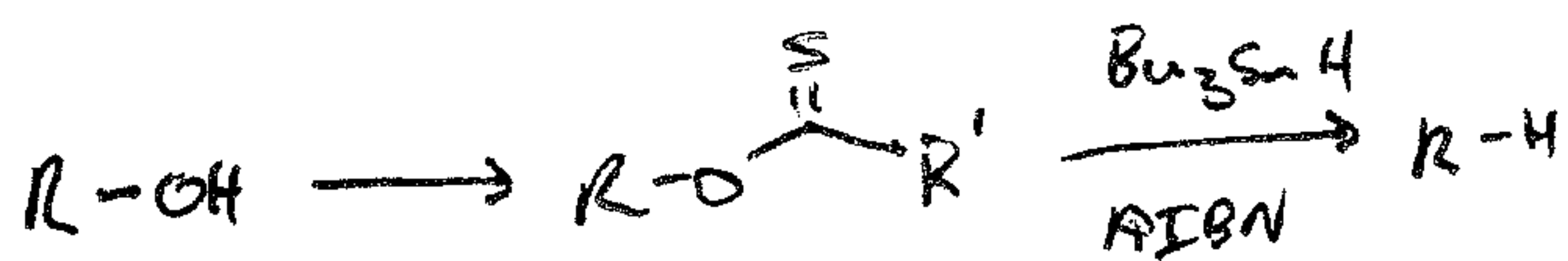


# Radical Chemistry C&EB 10.3

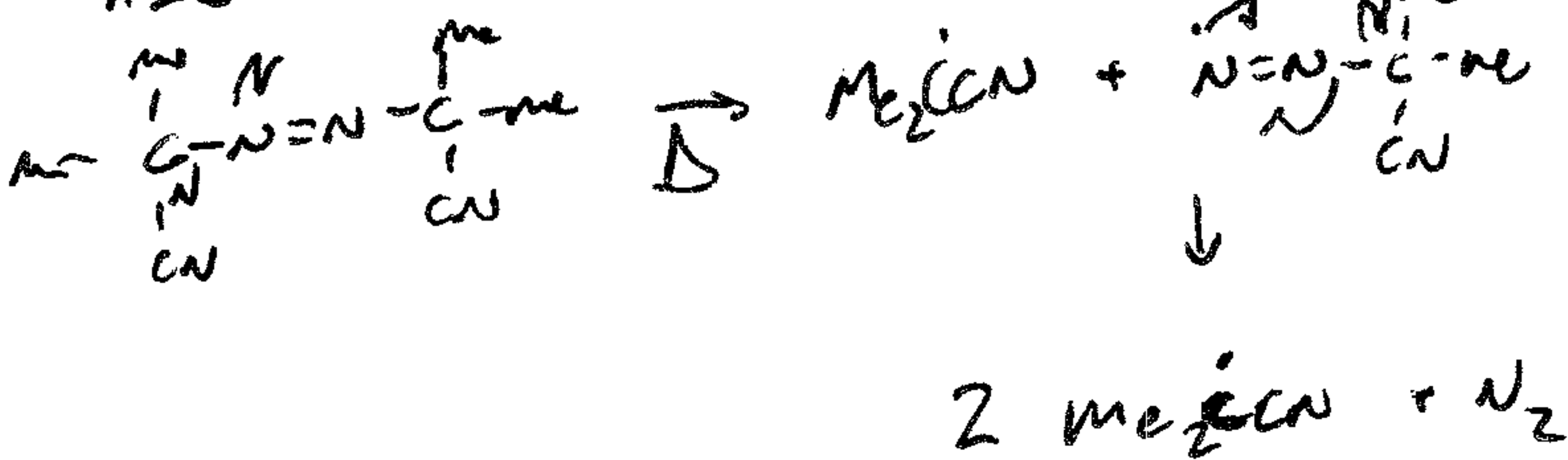
Recall <sup>Radical</sup> Reduction Rxns:



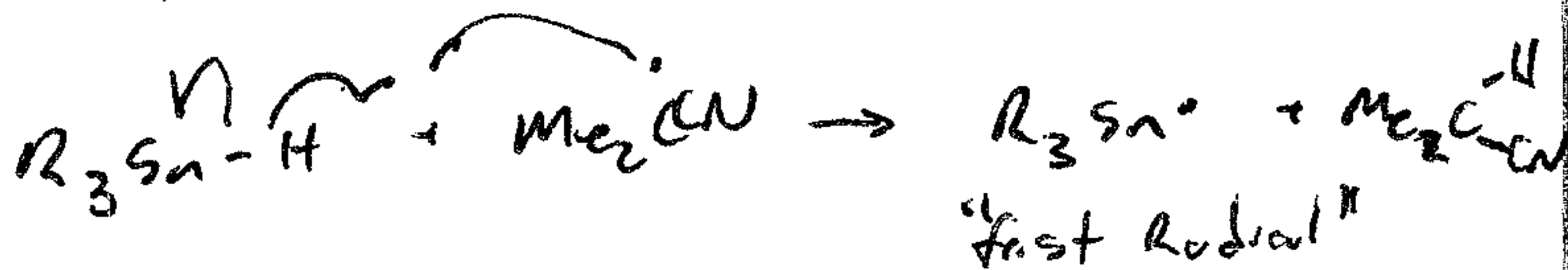
NOTE: Radical mech = single headed arrows!

Initiation - make a radical

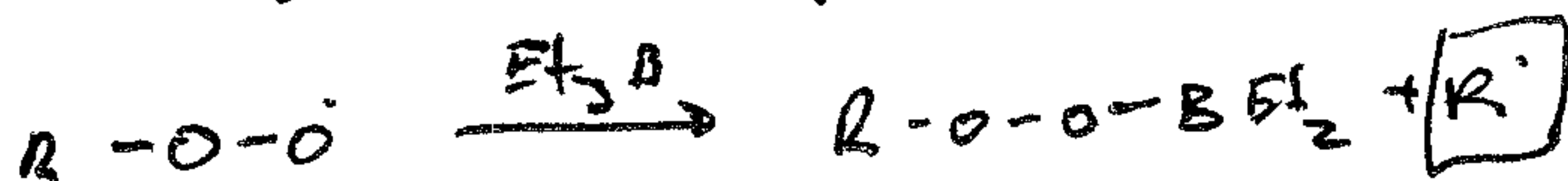
AIBN:



w/  $\text{R}_3\text{Sn-H}$



4) Boron / O<sub>2</sub>



In General these (& many) Radical Rxns proceed via 3 part mechs. (Called Radical Chain Rxn)

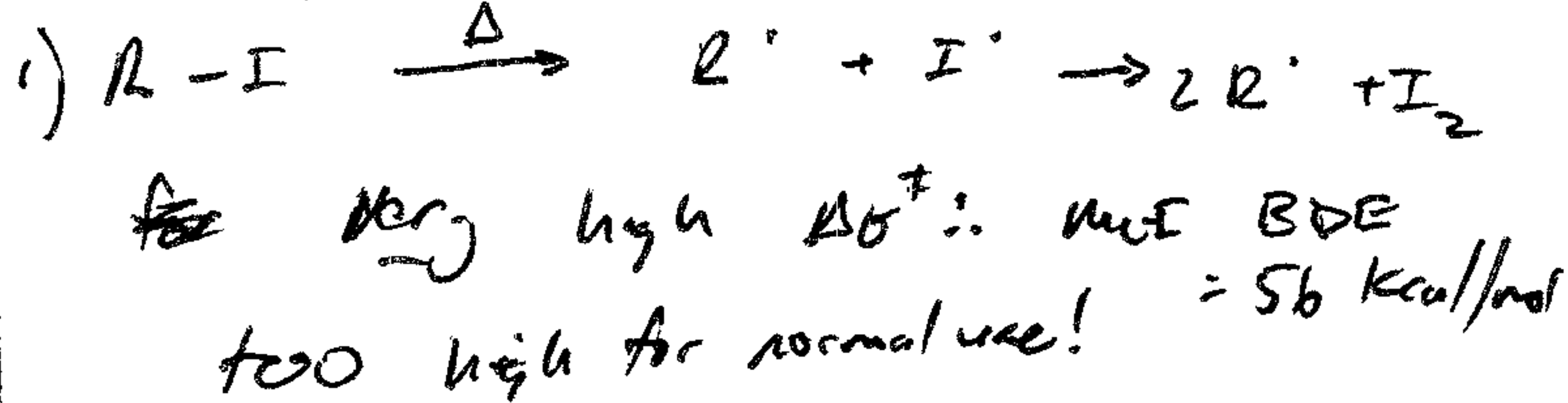
Initiation - make a radical

Propagation - radical does stuff - usually making another radical

Termination - "quench" radical (normally bad)

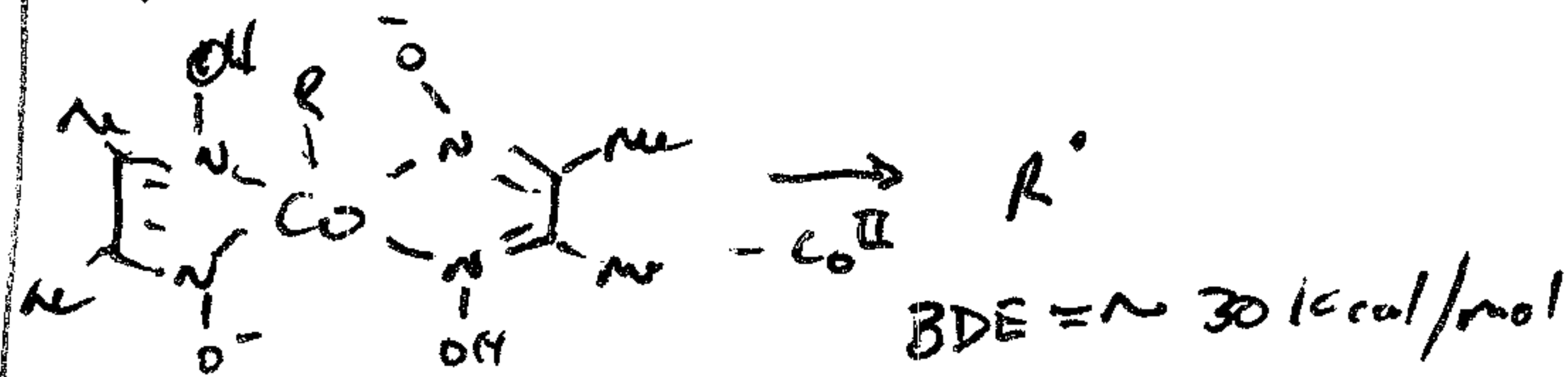
will discuss Prop. below

Other Radical Int. homolytic bond cleavage:



R = Ph "Benzoyl peroxide"  $\text{BDE} = 37 \text{ kcal/mol}$   
still high for activation!

3) water:



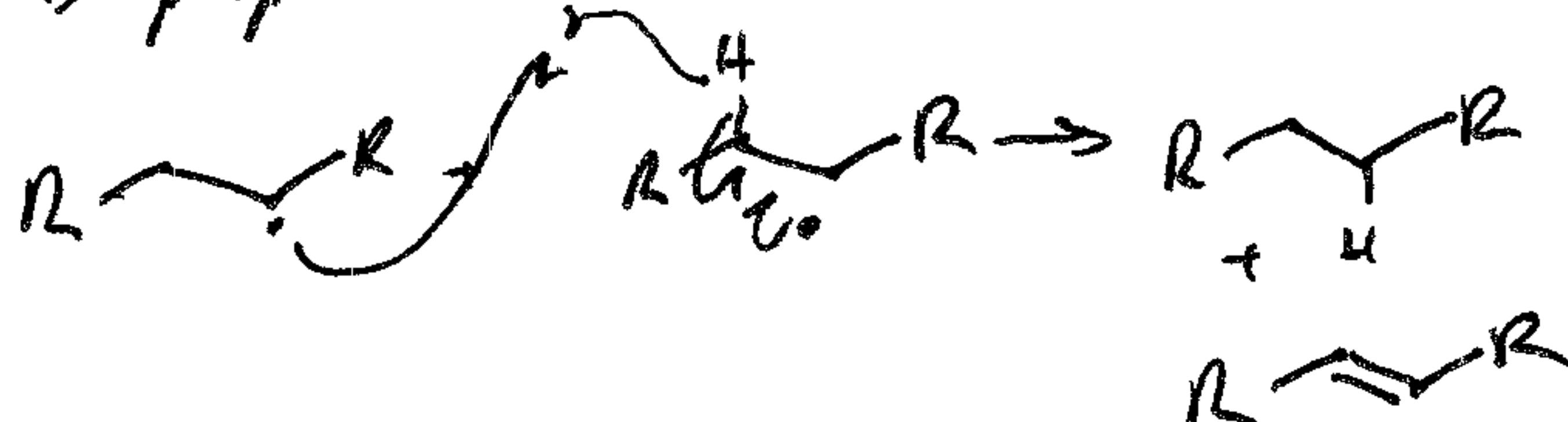
Termination - loss a radical!

1) Dimerization



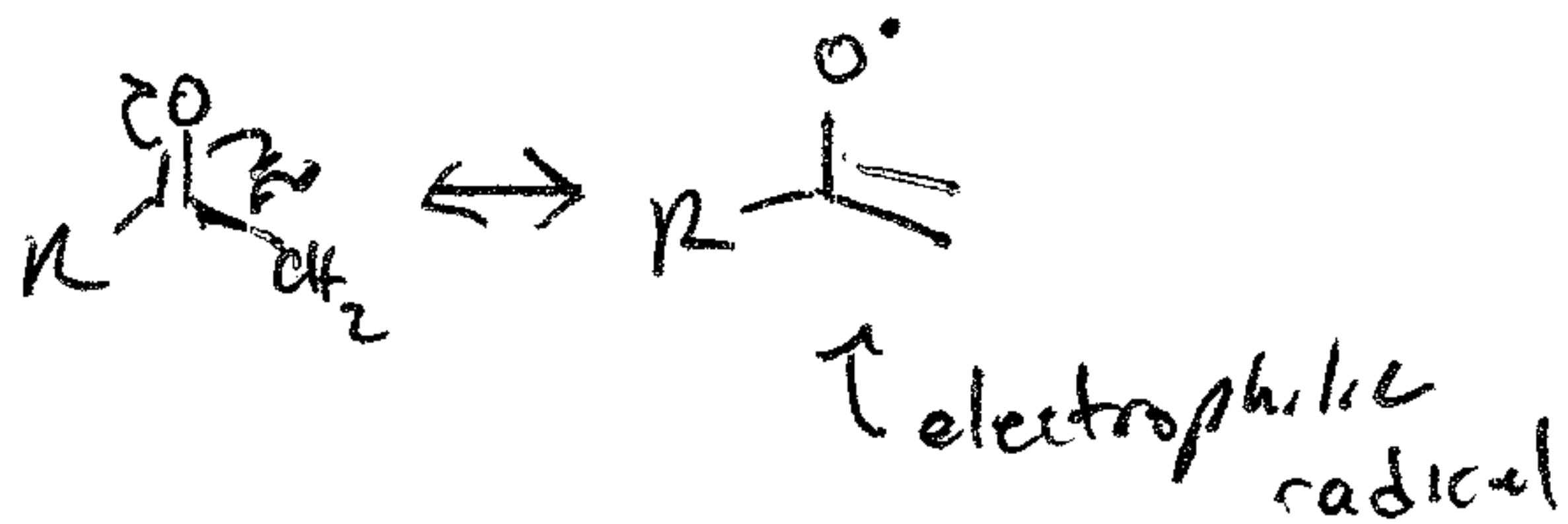
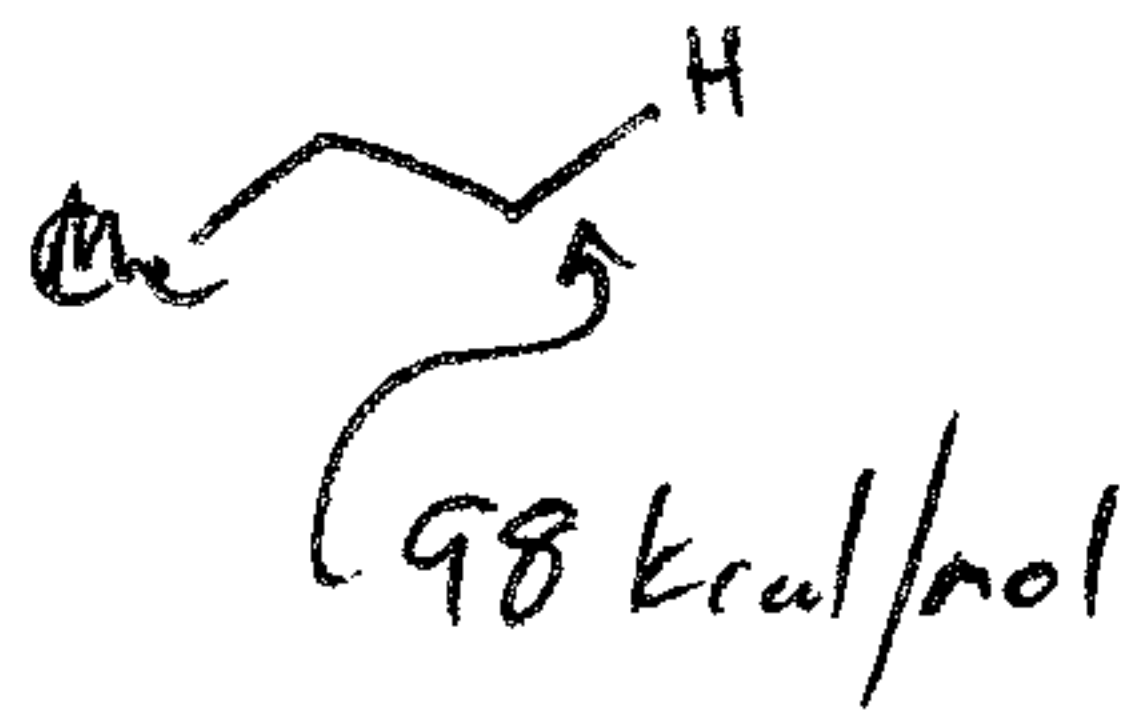
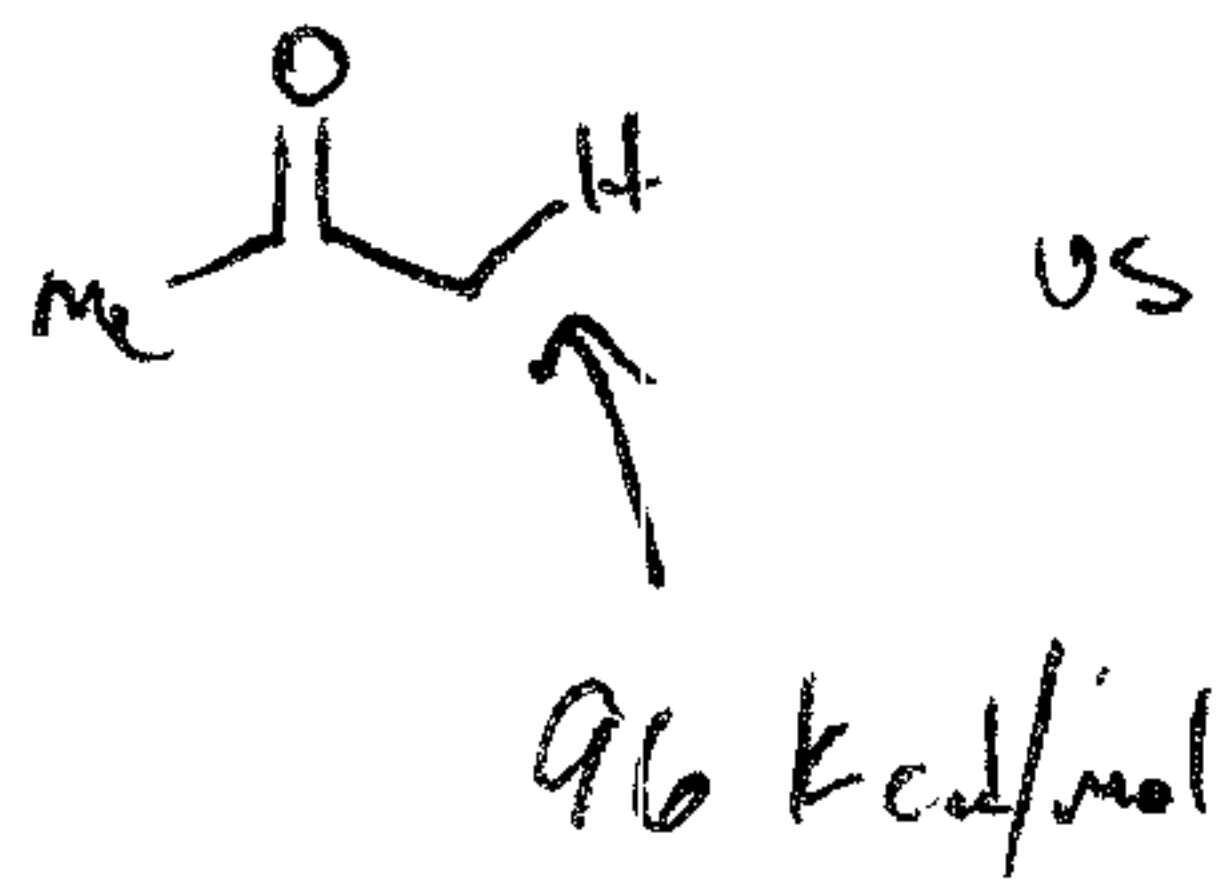
~ diffusion control rxn:  $k \sim 10^9 \text{ /ms}$   
keep [radical] low!

2) Disproportionation





$\alpha$  - EWG



cup to dative radical - (Push-Pull)



~~Other Important BDE's~~



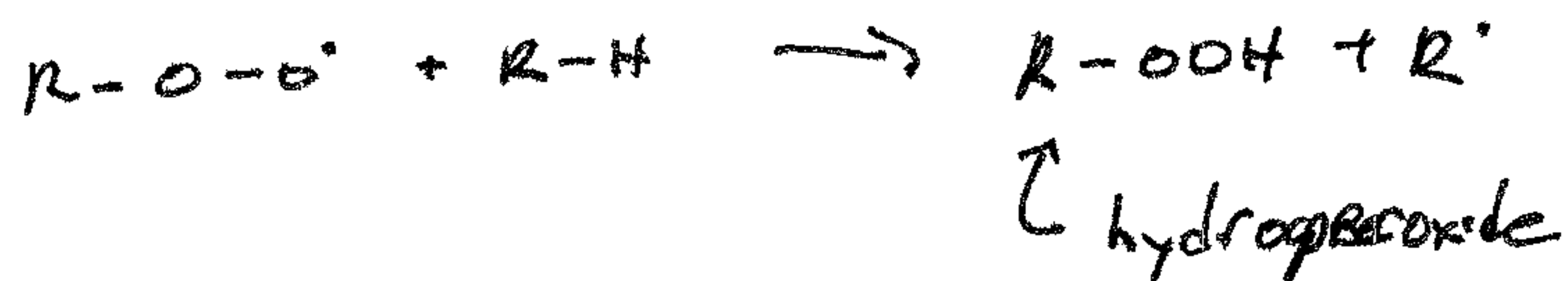
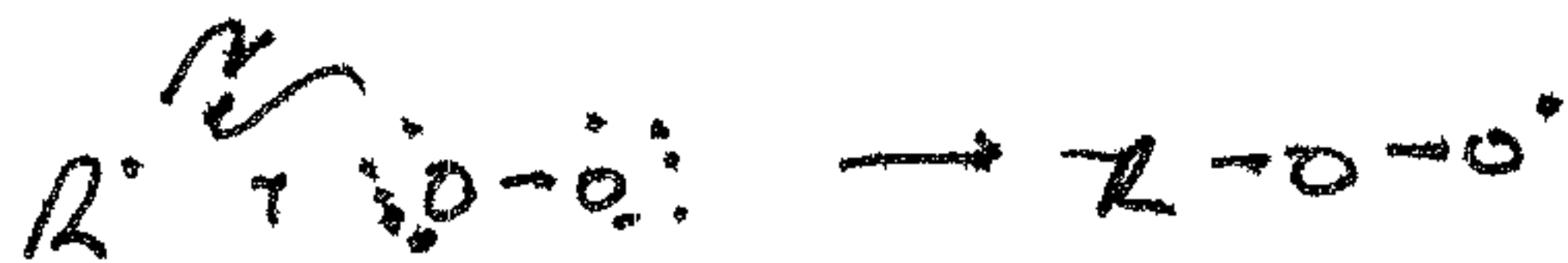
~~Notes 86+60=146~~

Other Important BDE's (kcal/mol)

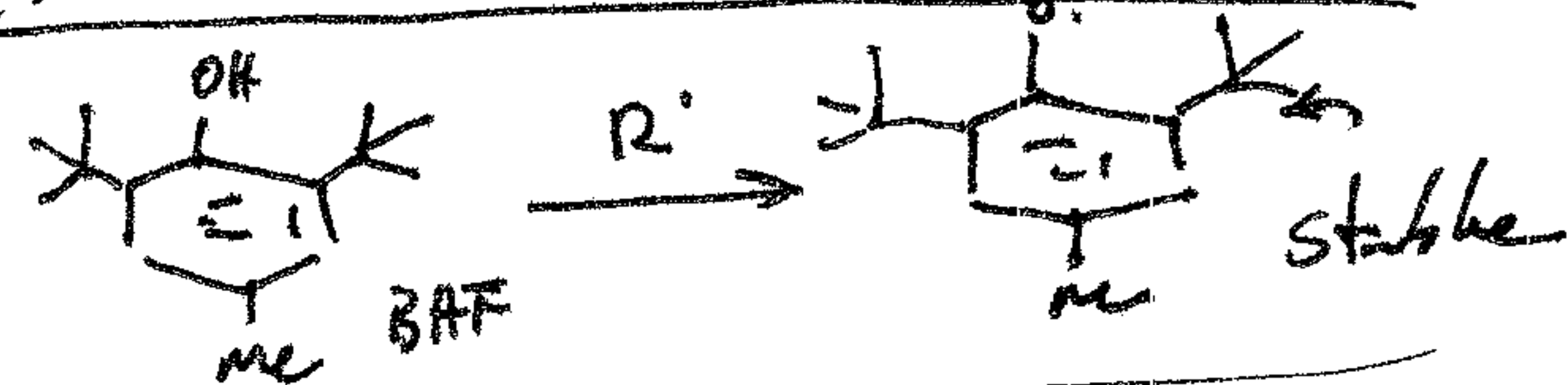
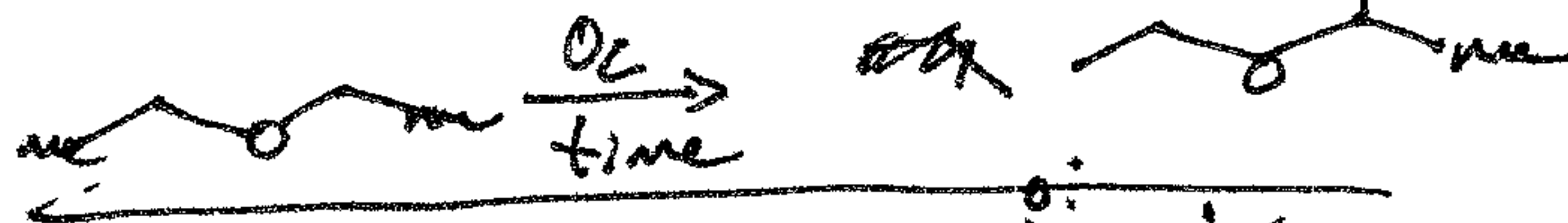
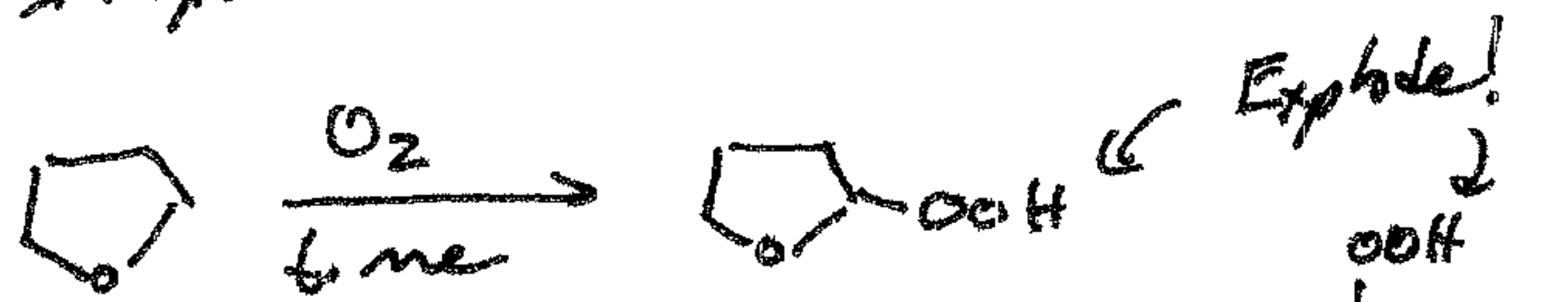
MeS-H	87
Et-I	56
Et-Br	70
Et-Cl	84
Et-F	113
Br-Br	
I-I	

Propagation Reactions

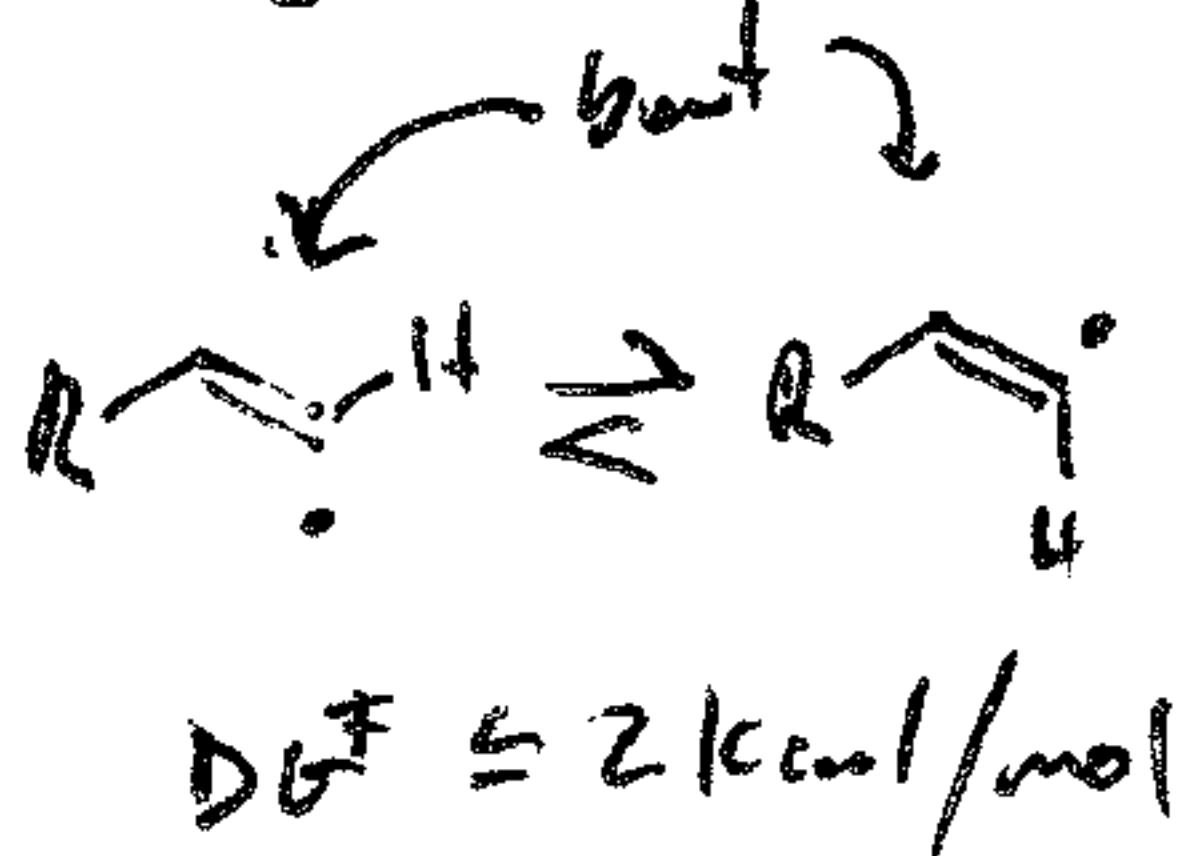
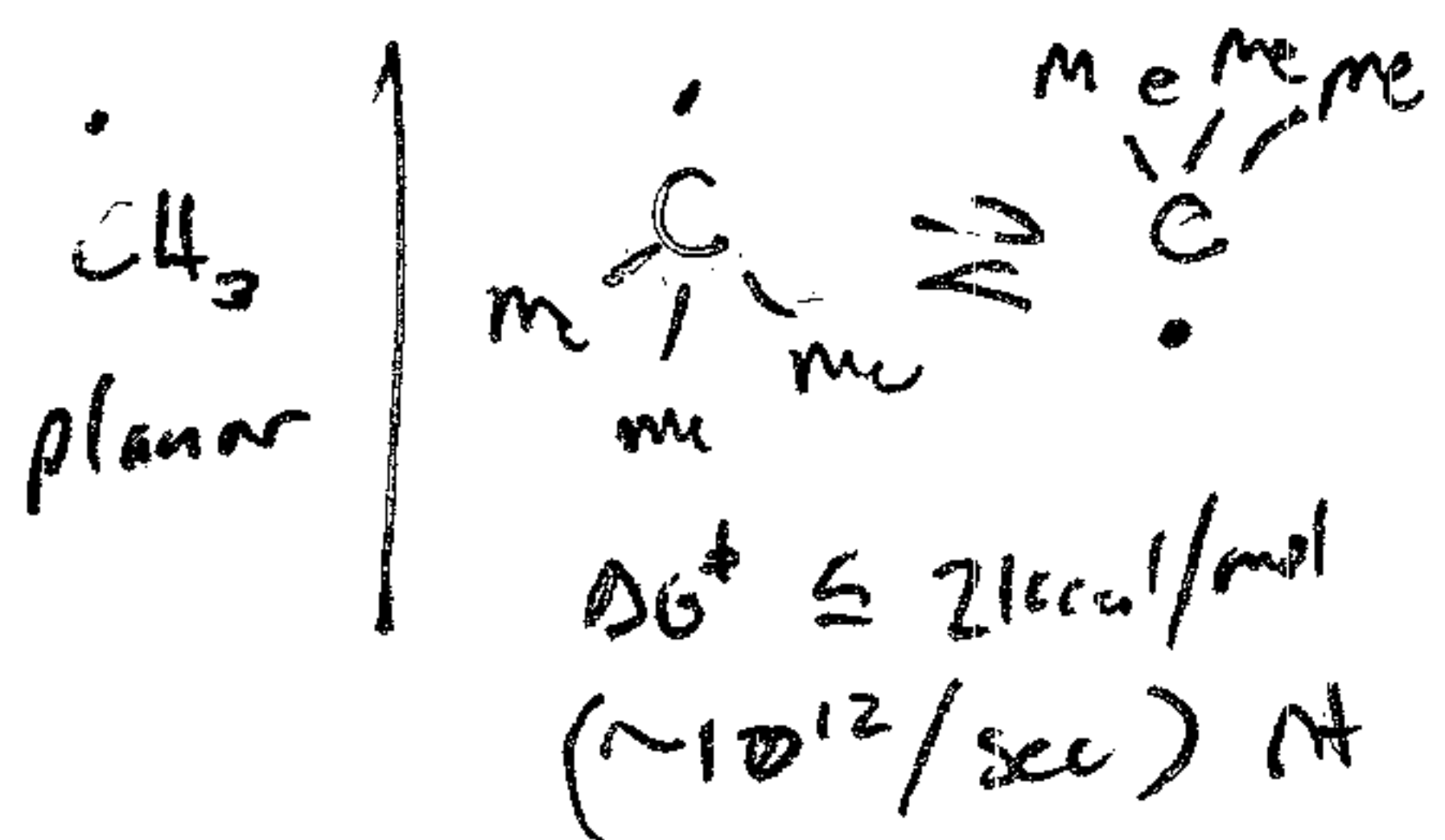
Reaction w/ O<sub>2</sub>



Important in lab!



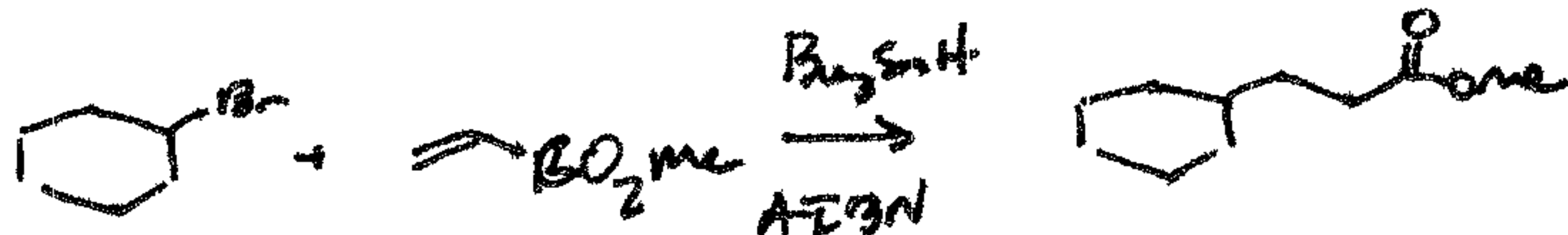
Radicals are not ~~not~~ conformationally stable!



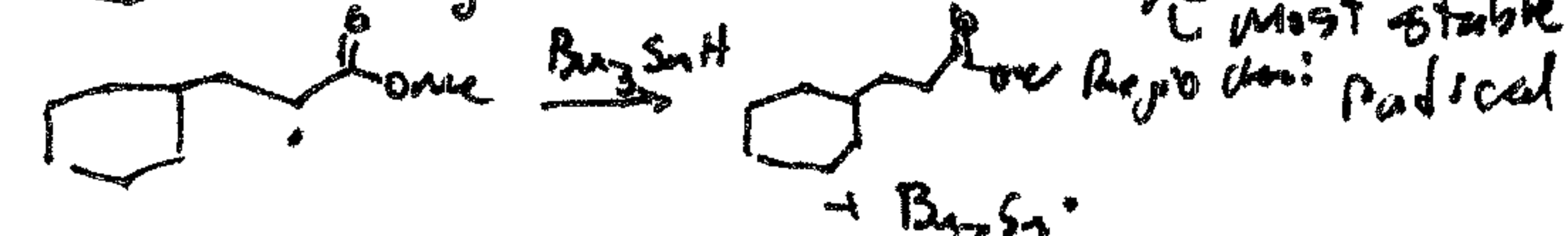
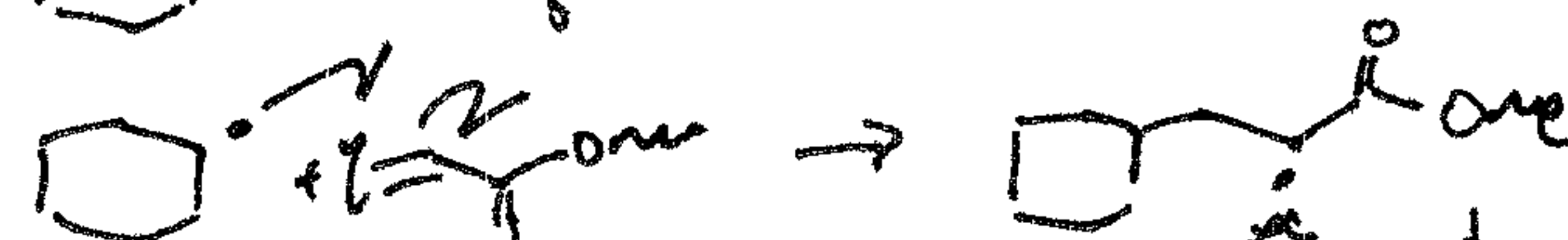
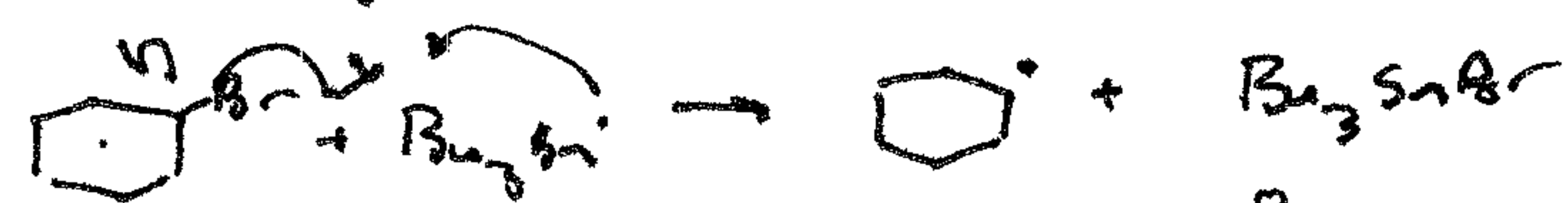
Reduction Reactions

- see nearby earlier notes.

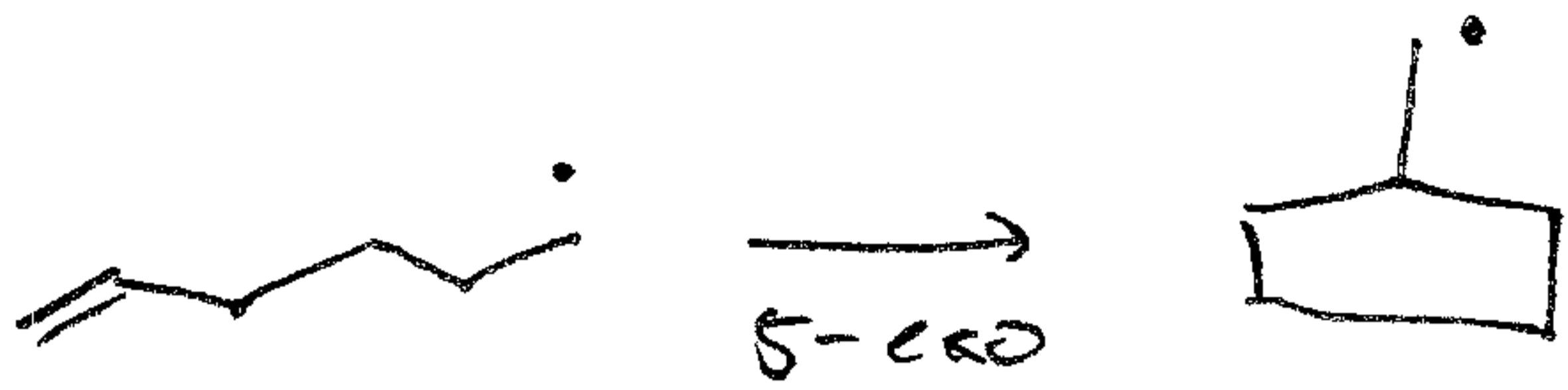
Reactions w/ C=C



Int. Bu<sub>3</sub>Sn<sup>•</sup>



intra mol rxn



$$\Delta G^\ddagger \sim 6 \text{ kcal/mol}$$

compare to  $\Delta G^\ddagger \sim 3 \text{ kcal/mol}$   
5-exo generally preferred. - FMO control

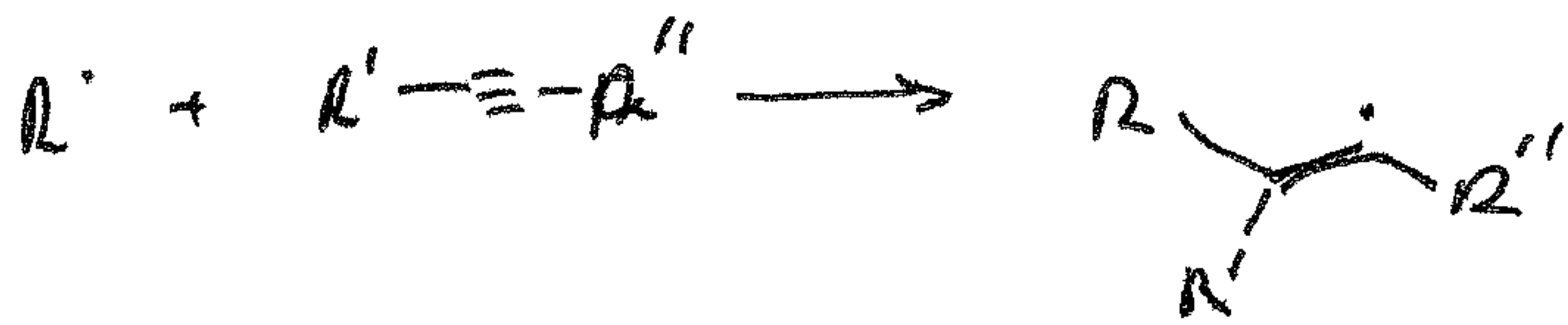
Thermochem:

BDE	C=C	145 kcal/mol
	C- $\sigma$	85 kcal/mol
	C- $\pi$	60 kcal/mol

Rxn trades 60 kcal/mol bond for 85 kcal/mol bond

$\therefore$  favorable by  $\sim 25$  kcal/mol!

Alkynes

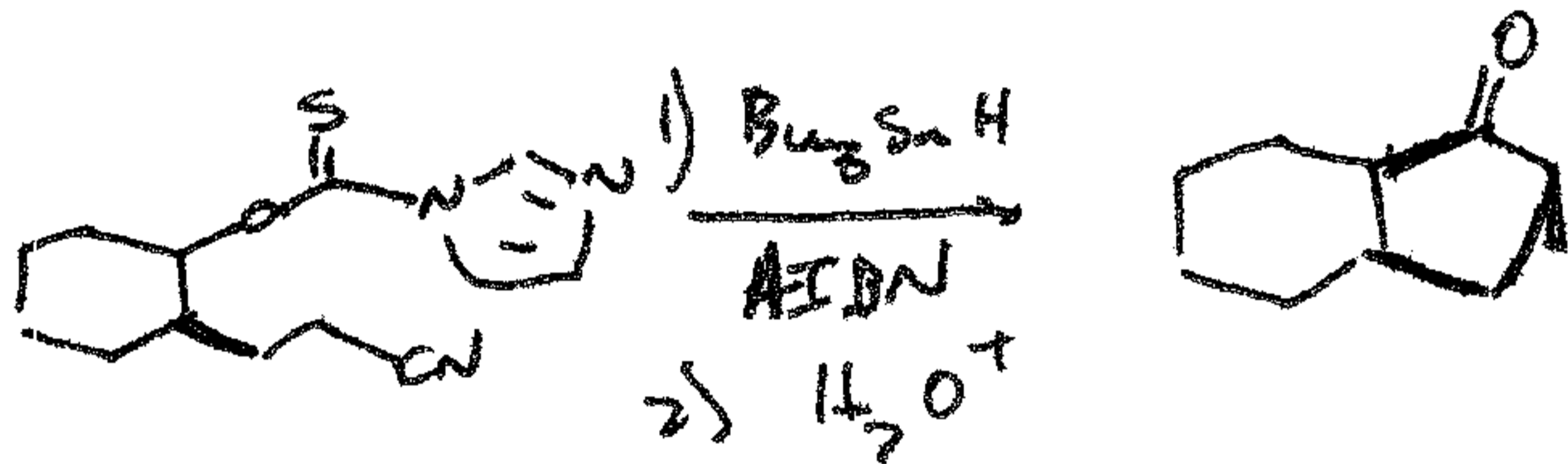


C $\equiv$ C	198 kcal/mol	] 2 $\pi$ $\sim$ 53 kcal/mol
C=C	145 kcal/mol	
C-C( $\sigma$ )	> 85 kcal/mol	

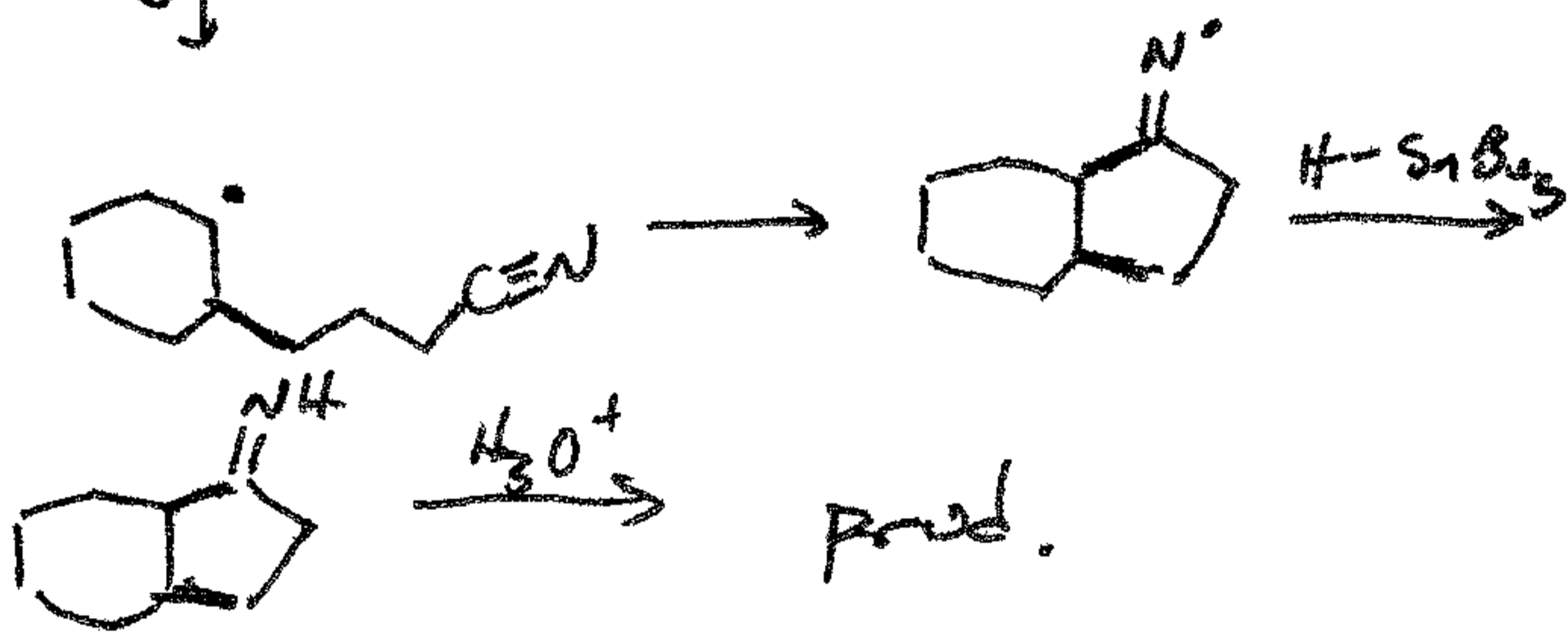
$$\Delta G^\ddagger = 85 - 53 = \sim 32 \text{ kcal/mol}$$

C=N  $\pi$  systems also okay

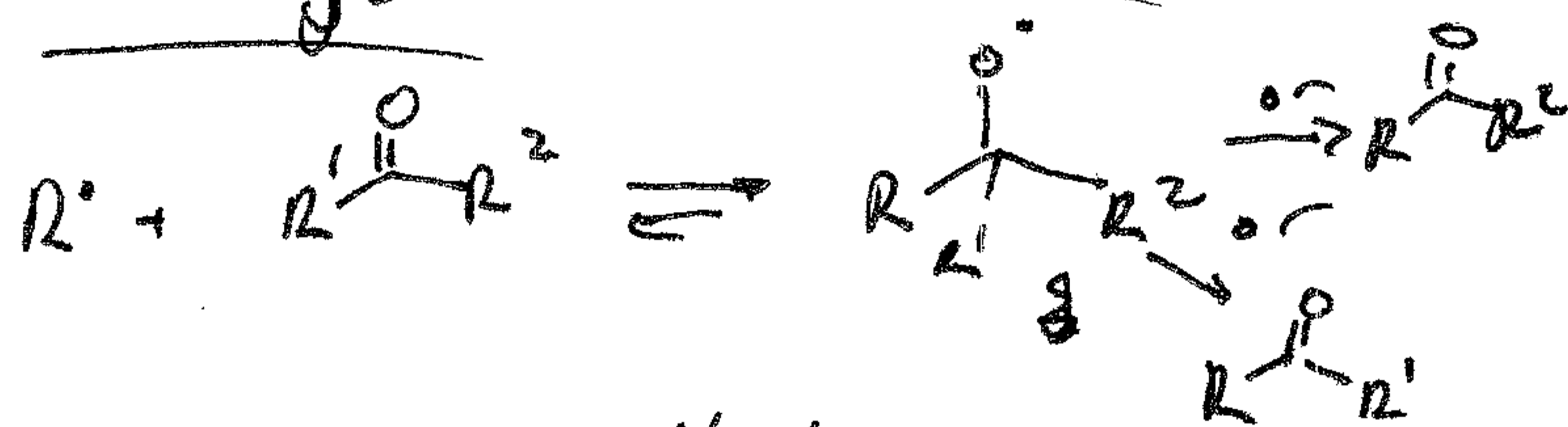
N $\cdot$   $\approx$  C $\cdot$



$\downarrow$



Carbonyls



C=O 175 kcal/mol

C-O( $\sigma$ ) 80

$\therefore$  C-O( $\pi$ ) 95 kcal/mol

C-C( $\sigma$ ) 85 kcal/mol

$\therefore \sim 10$  kcal/mol, endothermic!

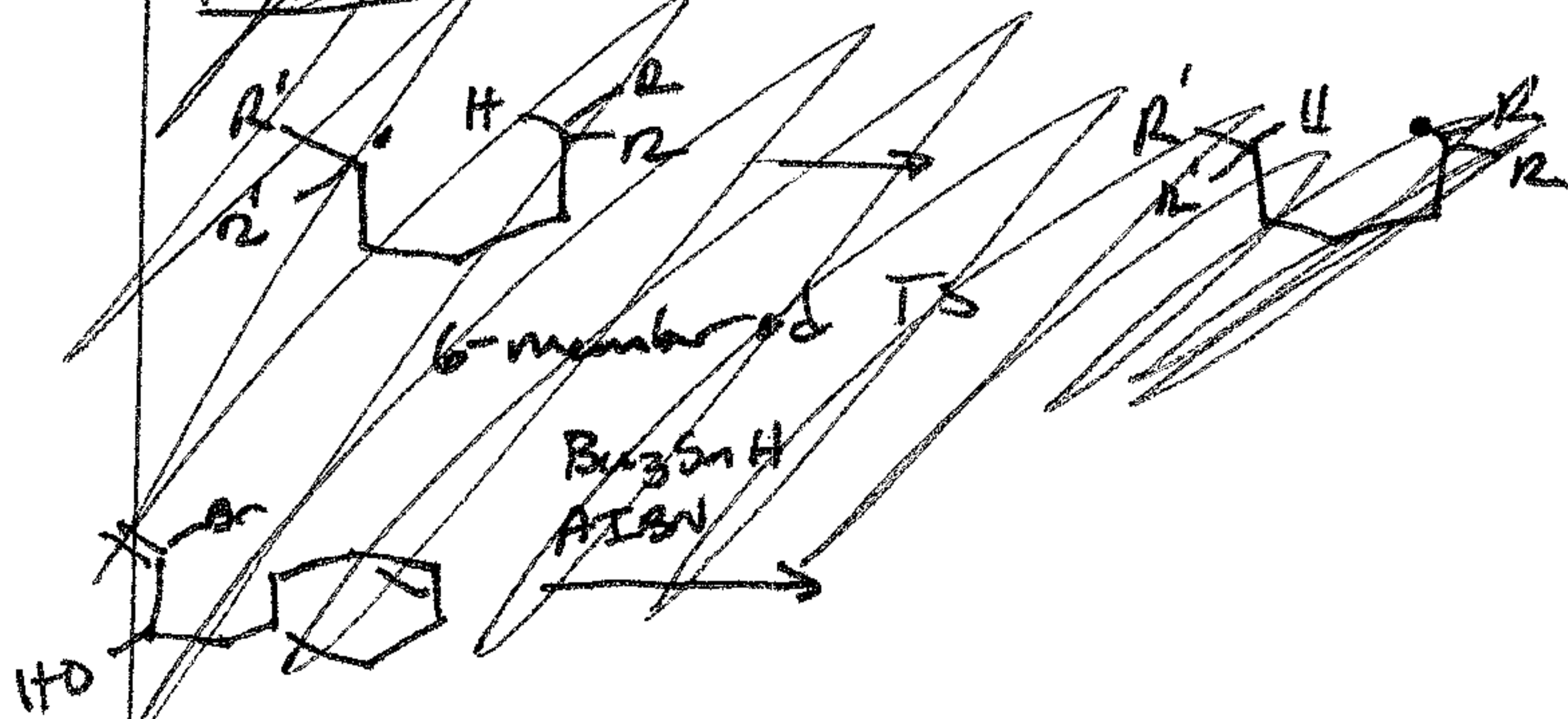
Fragmentations



X = Bu3Sn or SPh etc

C stable radicals

~~1,5-H-atom abstraction~~

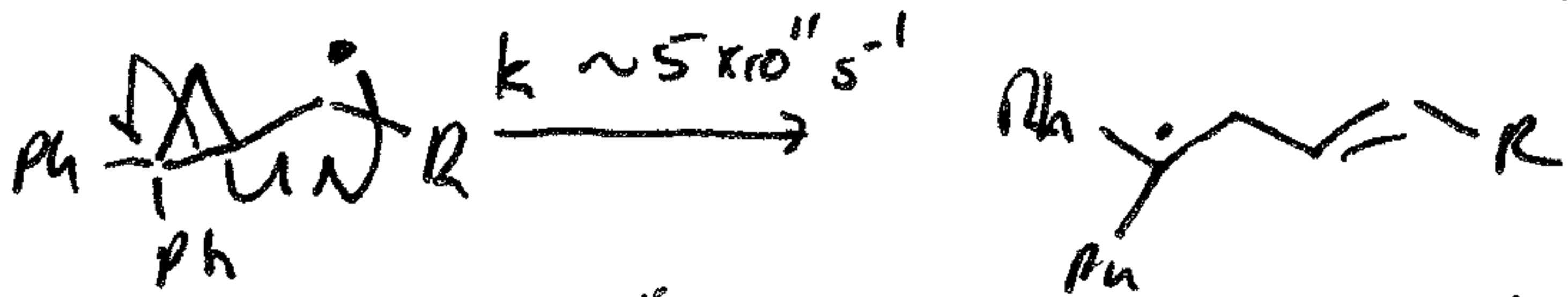


# Fragmentations as Radical Clock (Cyclopropyl carbonyl radicals)



fast rxns controlled by diffusion

Bimol rxn max  $k \sim 10^9 \text{ m}^{-1} \text{ s}^{-1}$

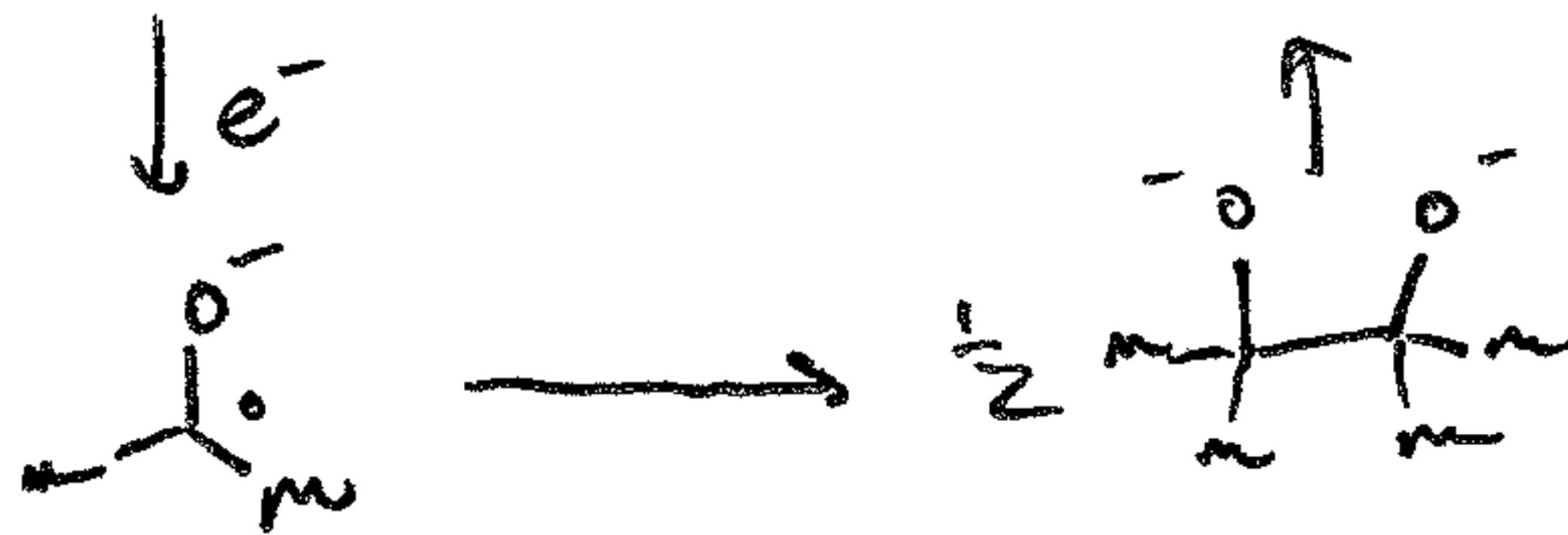
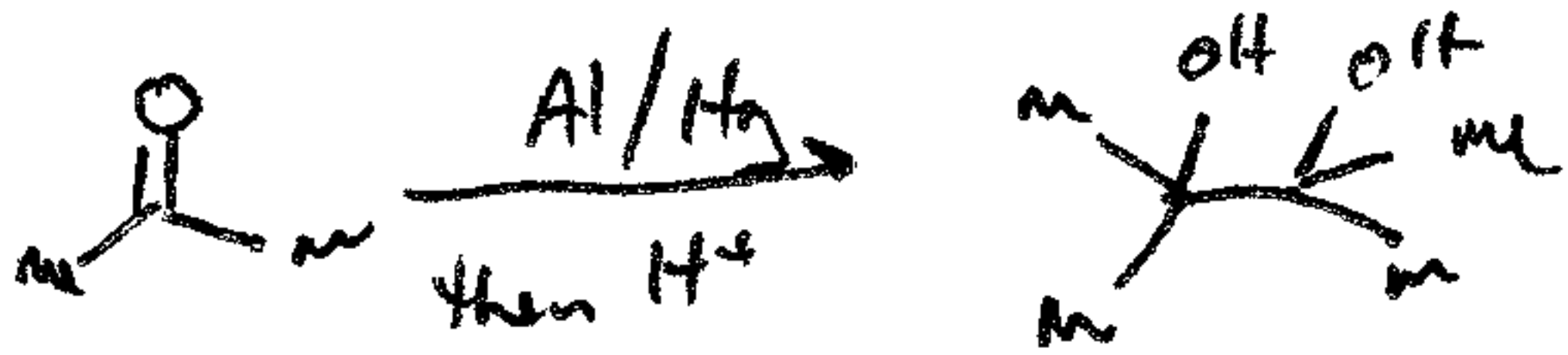


Approaches "vibrational control", faster than bimol rxn! used a kinetic tool & as test for radicals!

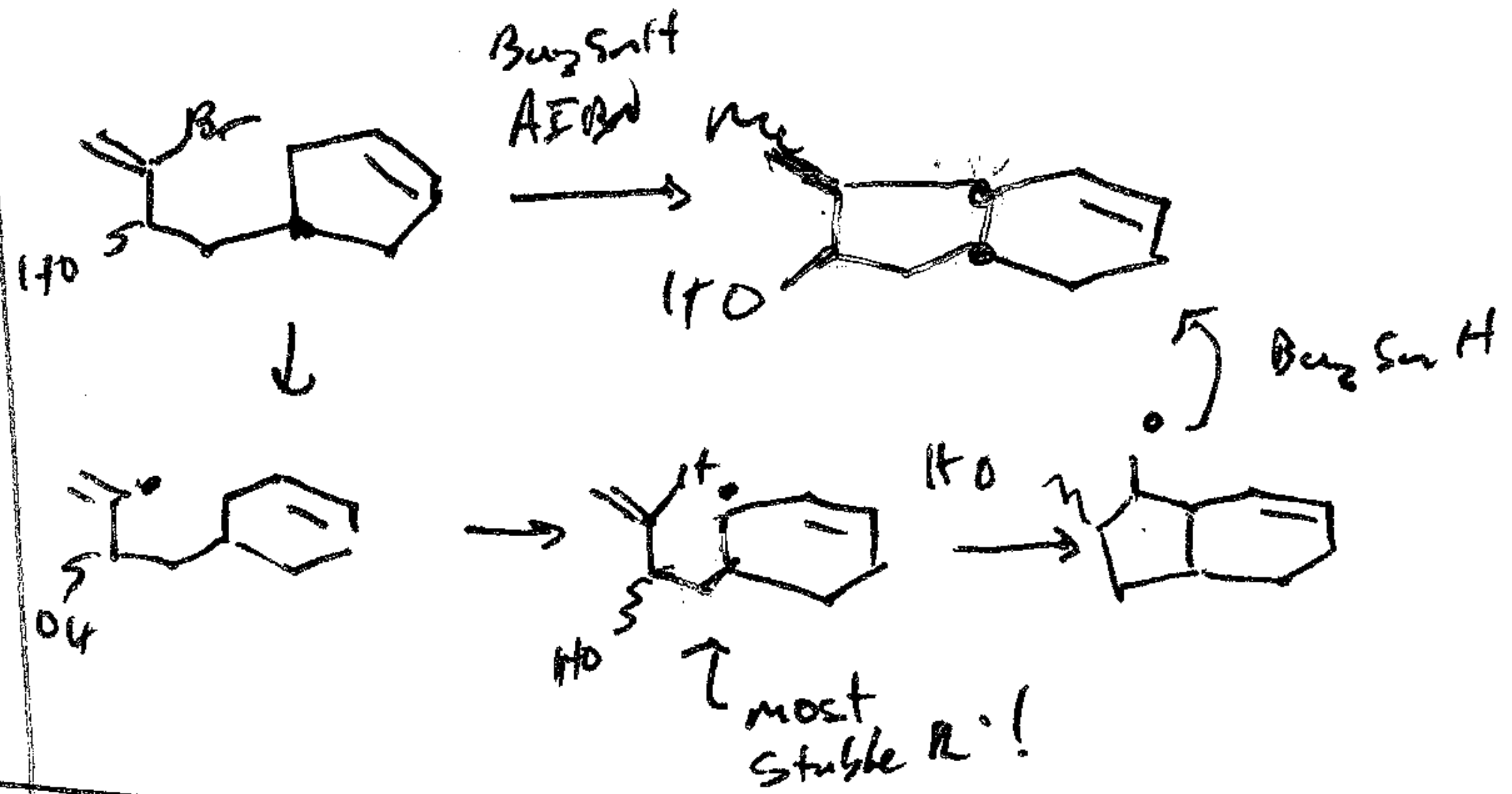
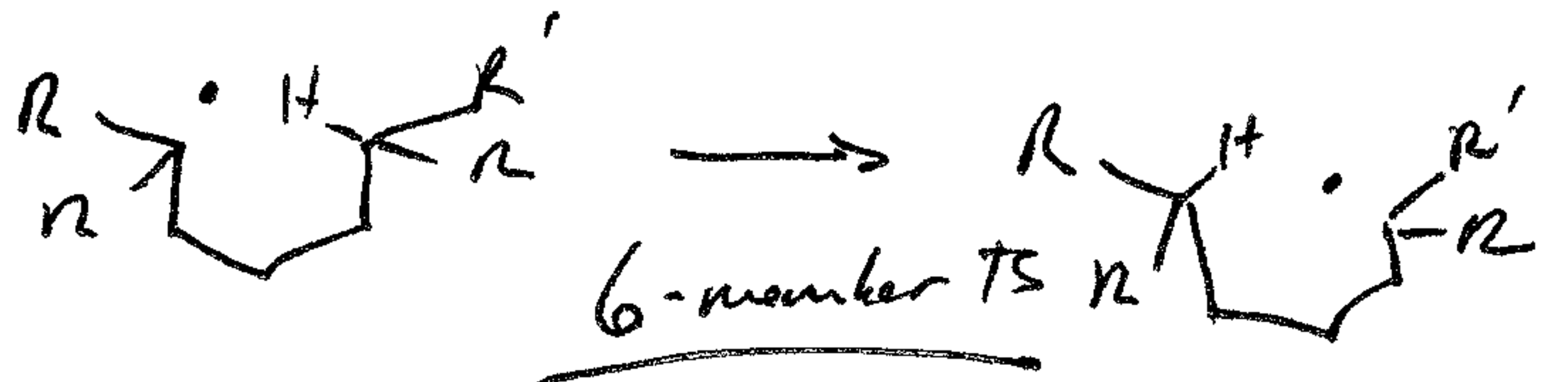
## Reductive Radical coupling of carbonyls

~~Pinnacol~~

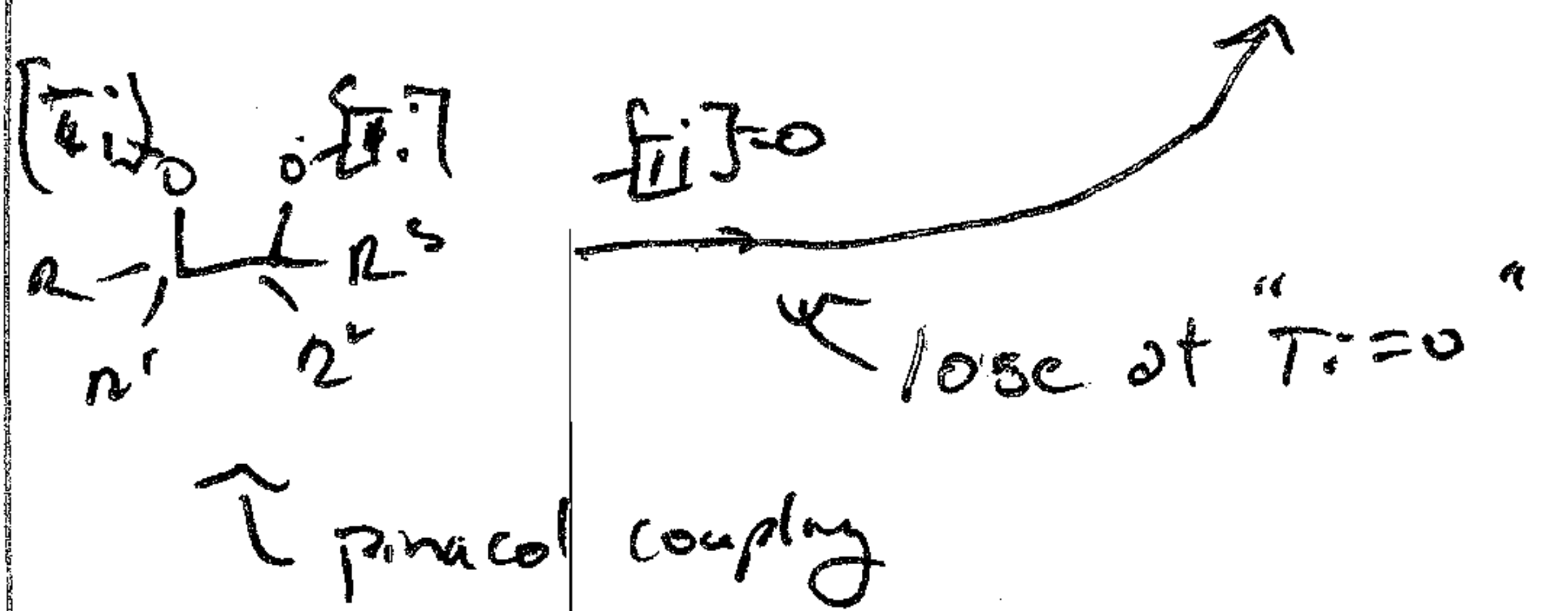
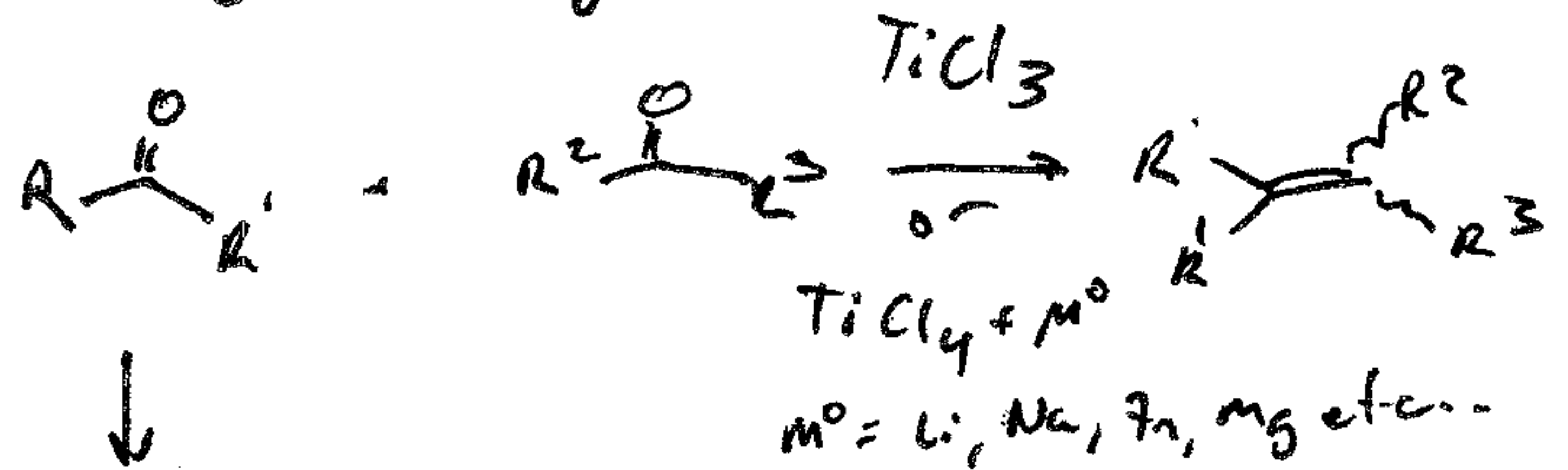
Pinnacol coupling



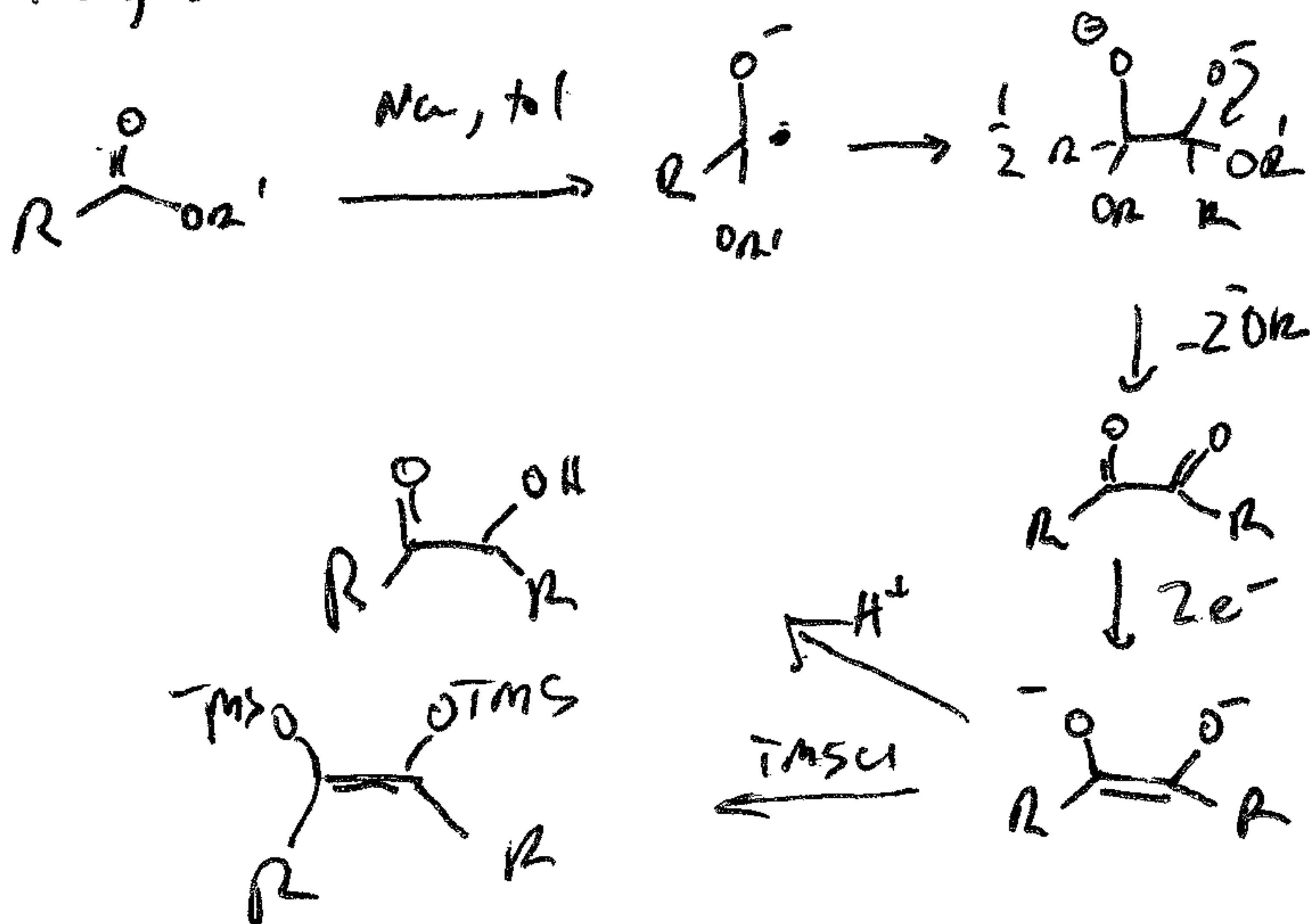
## H-atom Abstraction



## McMurry Coupling



## Acylouin condensation



example:

