LEC (17) CHEM 30A Nov 10th

(1) OXIDATION
(2) REDUCTION
(3) STEREOCHEMISTRY REVISITED
(4) ADDITION TO ALKYNES

READ 6.6-6.7 & 10.9
PROBLEMS 10.5

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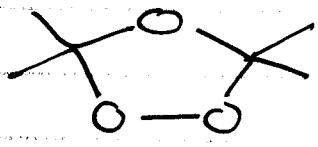
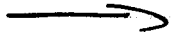
(1) OXIDATION

ozonolysis continued

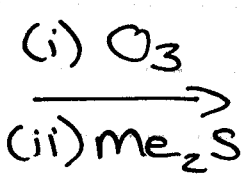


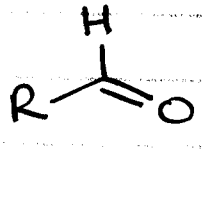
ozonide

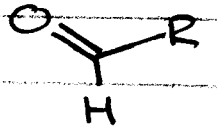


PRODUCTS

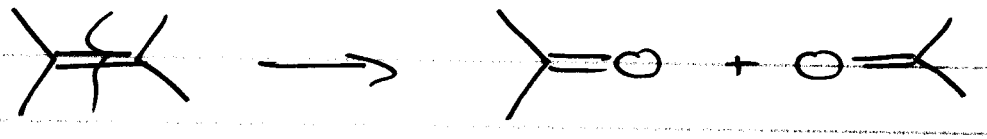
(i) Me_2S



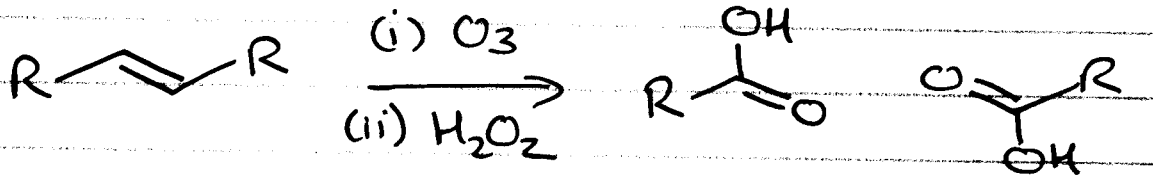




ALDEHYDES (OR KETONES)



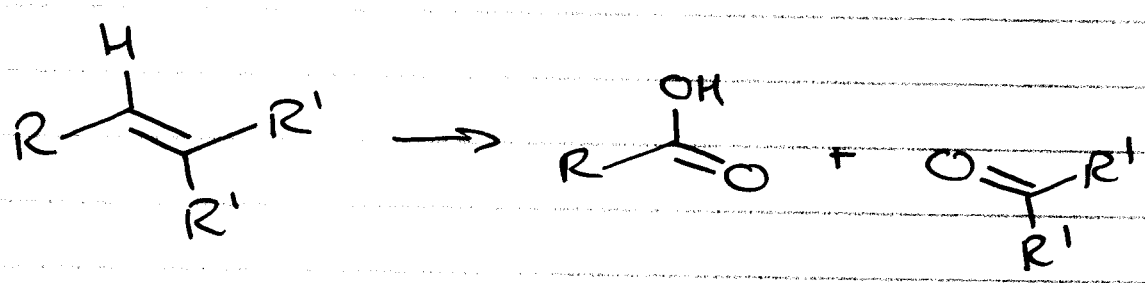
(ii) H_2O_2



CARBOXYLIC ACIDS (KETONES)

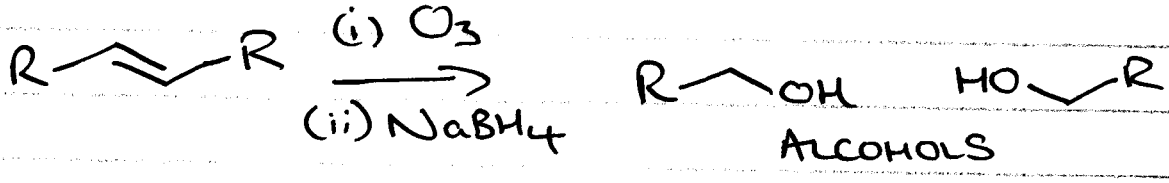
(MUST HAVE H ON C=C TO GET ACID)

i.e.



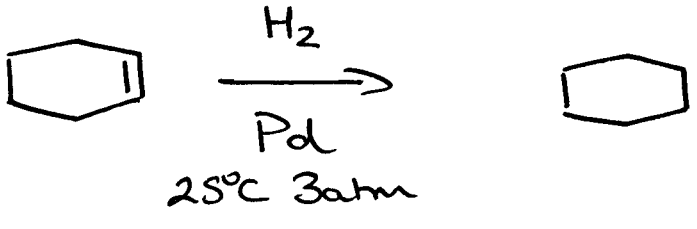
CARBOXYLIC ACID — KETONE

– $NaBH_4$



ALCOHOLS

(2) REDUCTION

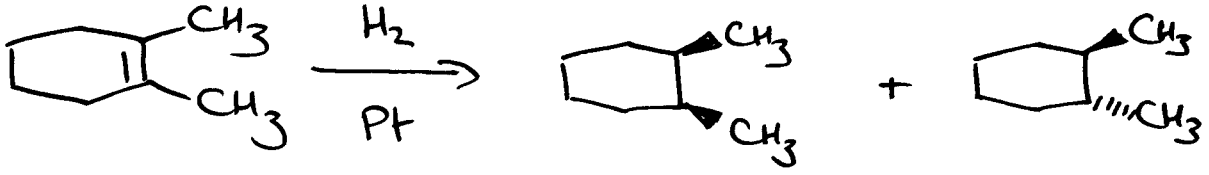


METAL CATALYST
Finely divided on an inert support (charcoal)

Transition metal catalyst Pt, Pd, Ru, Ni:

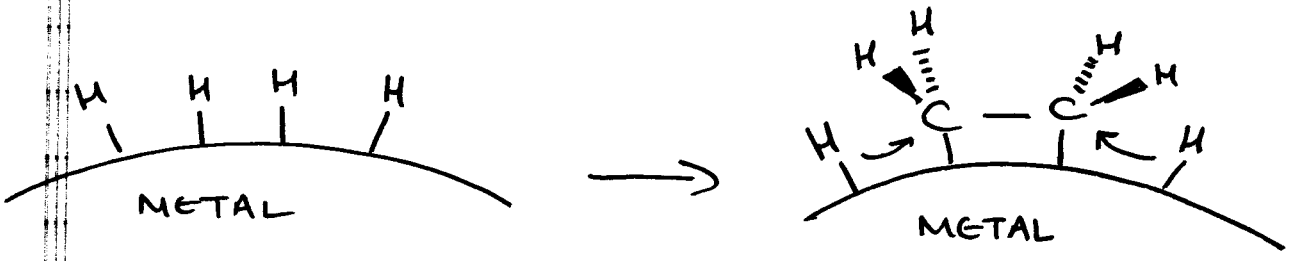
CATALYTIC REDUCTION / HYDROGENATION

- STEREOSELECTIVE



MAJOR MINOR

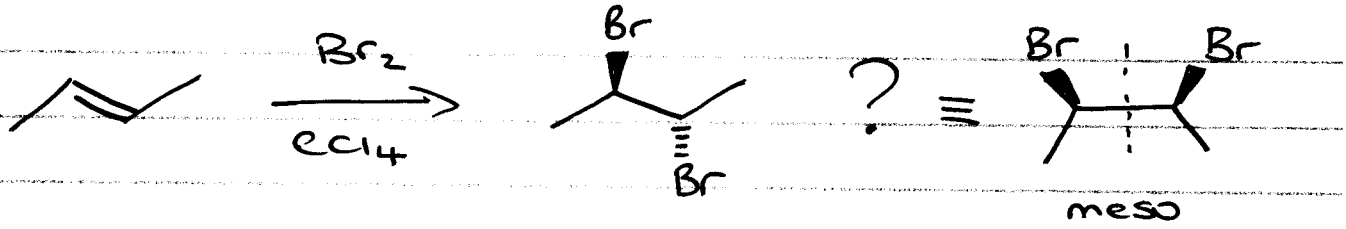
mechanism:

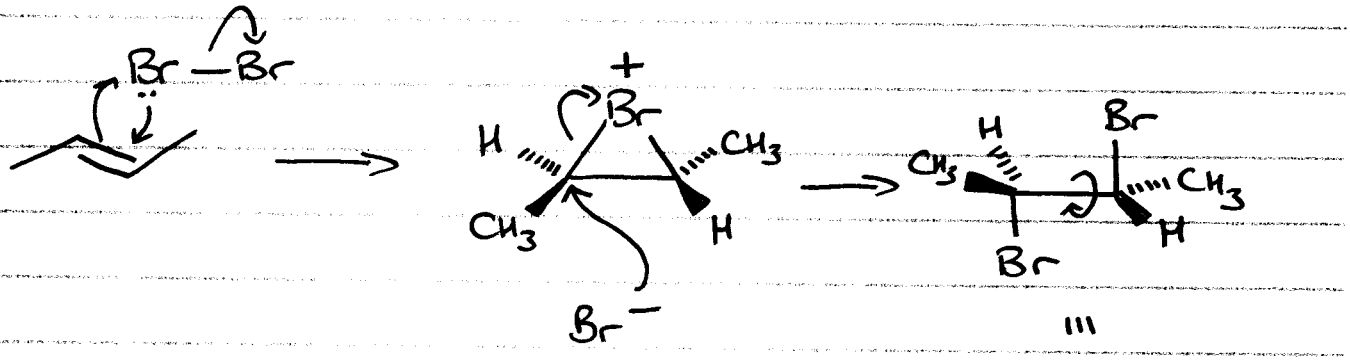


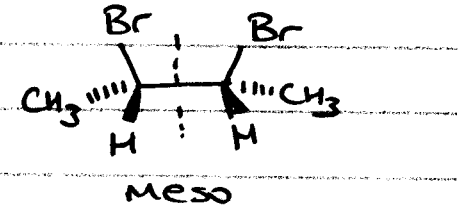
MINOR PRODUCTS RESULT FROM ISOMERIZATION OF THE ALKENE ON THE METAL CATALYST

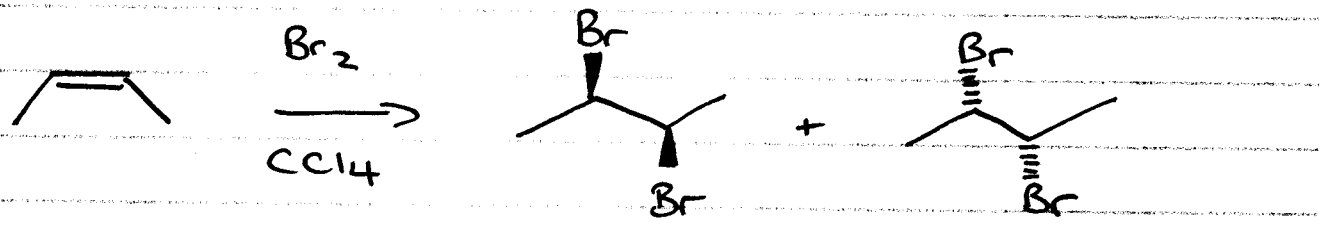
(3) STEREOCHEMISTRY REVISITED

consider

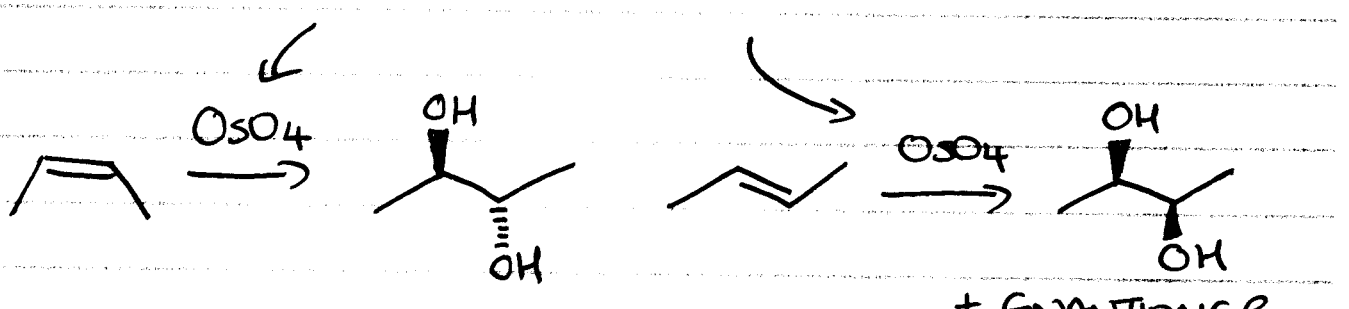






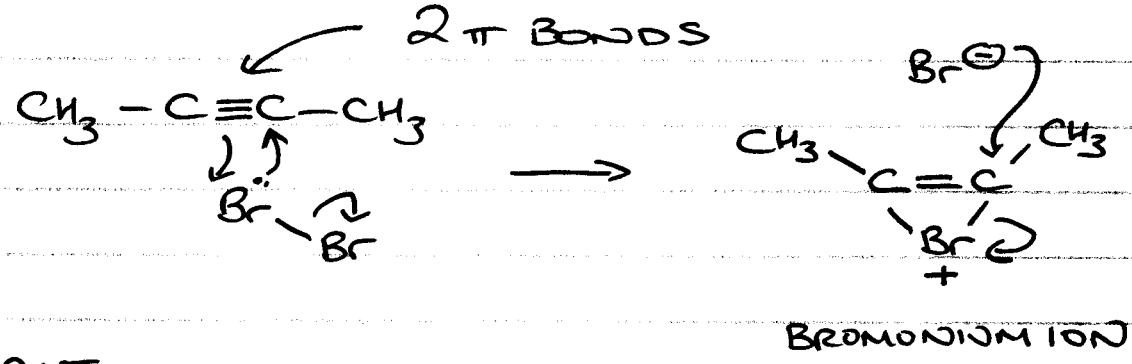


WORK THROUGH MECHANISM



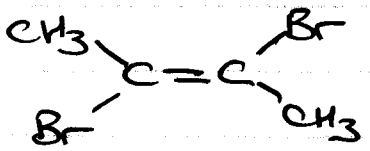
(4) ADDITION TO ALKYNES

(i) X_2 (Br_2 / Cl_2)



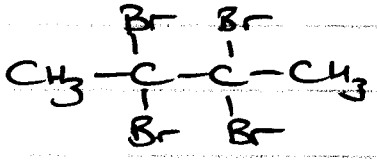
BROMONIUM ION

ANTI STEREO SPECIFICITY →



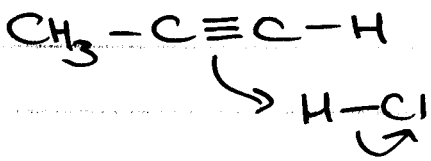
trans dibromide

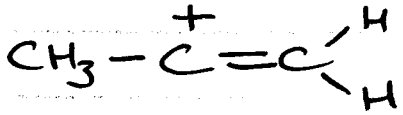
Br_2 →



tetrabromoalkane

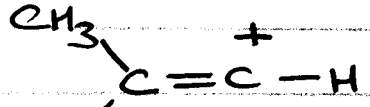
(ii) HX (HCl, HBr, HI)





2°

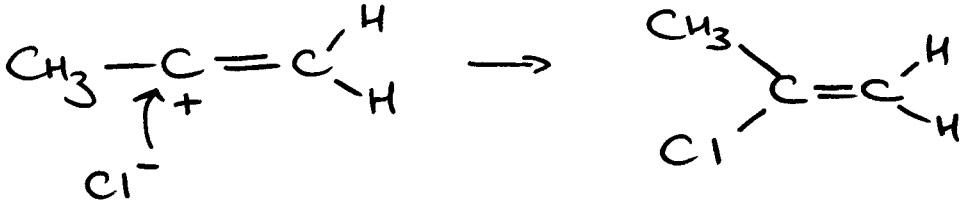
or



1°

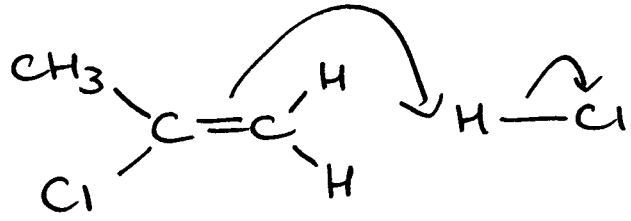
VINYL CARBOCATIONS

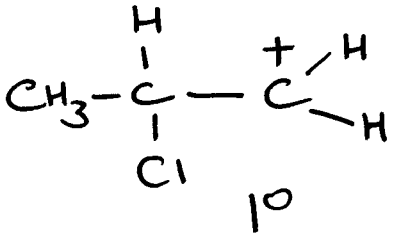
(MORE STABLE)



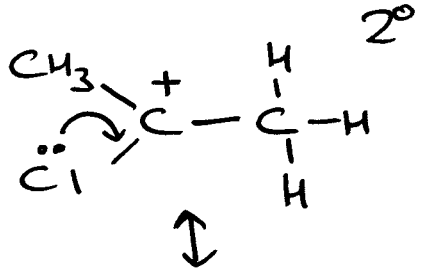
MARKOVNIKOV PRODUCT

ALKENE PRODUCT COMPETES WITH ALKYNE FOR H–Cl IN THE REACTION



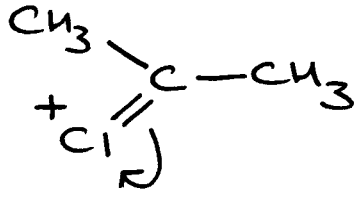


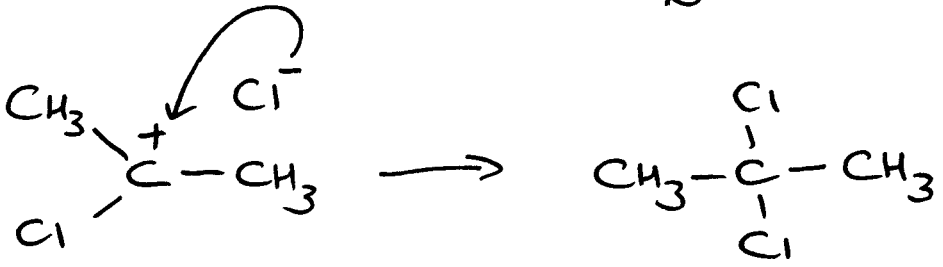
1°



2°

RESONANCE STABILIZED





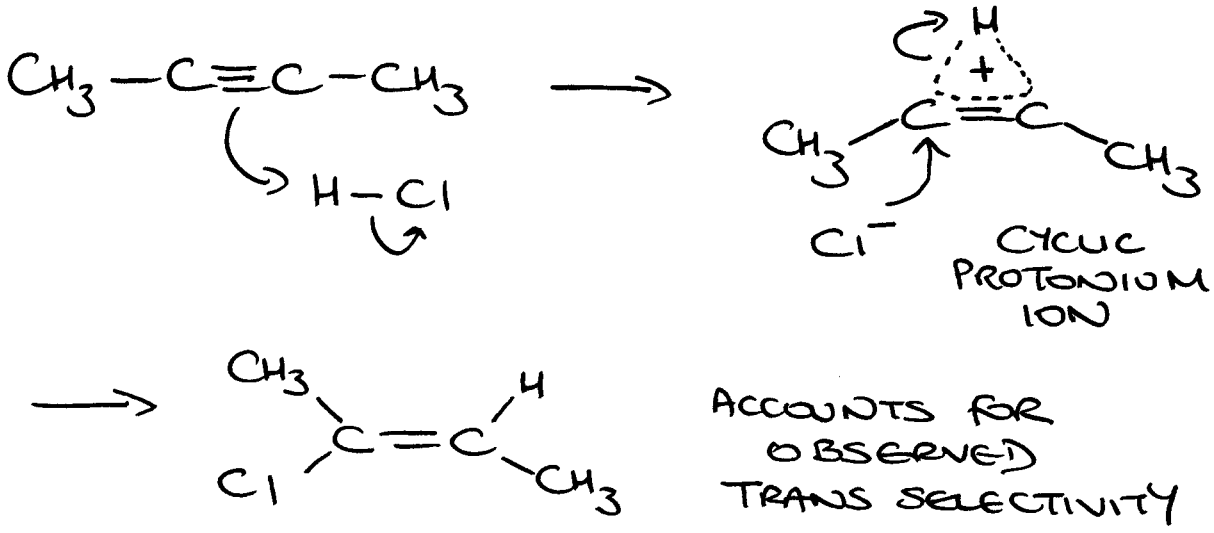
(Mechanisms actually more complicated than this, but these are good models)

VINYLIC C^+ VERY UNSTABLE

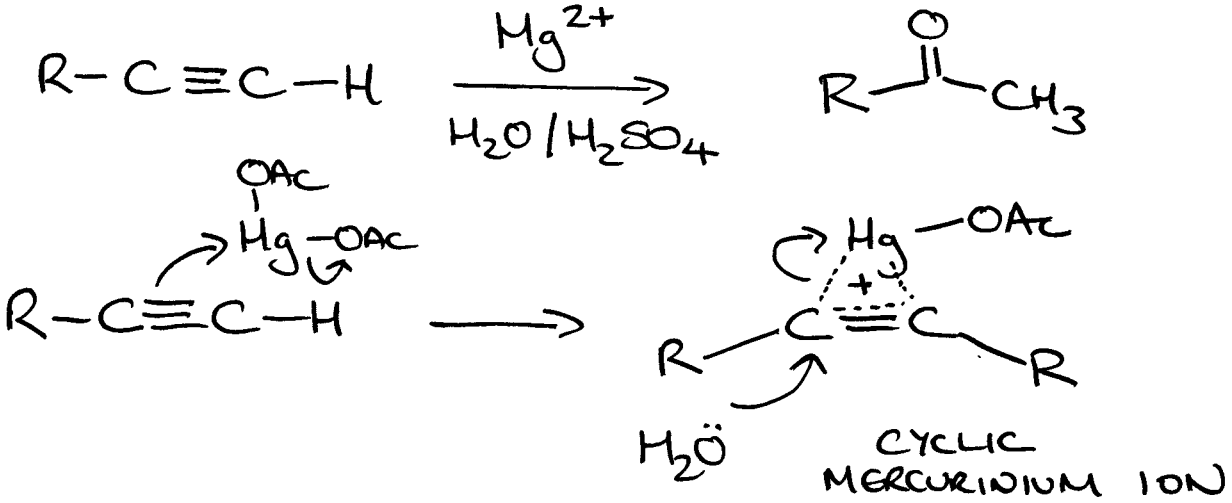
2° VINYLIC C^+ $\simeq$ 1° C^+

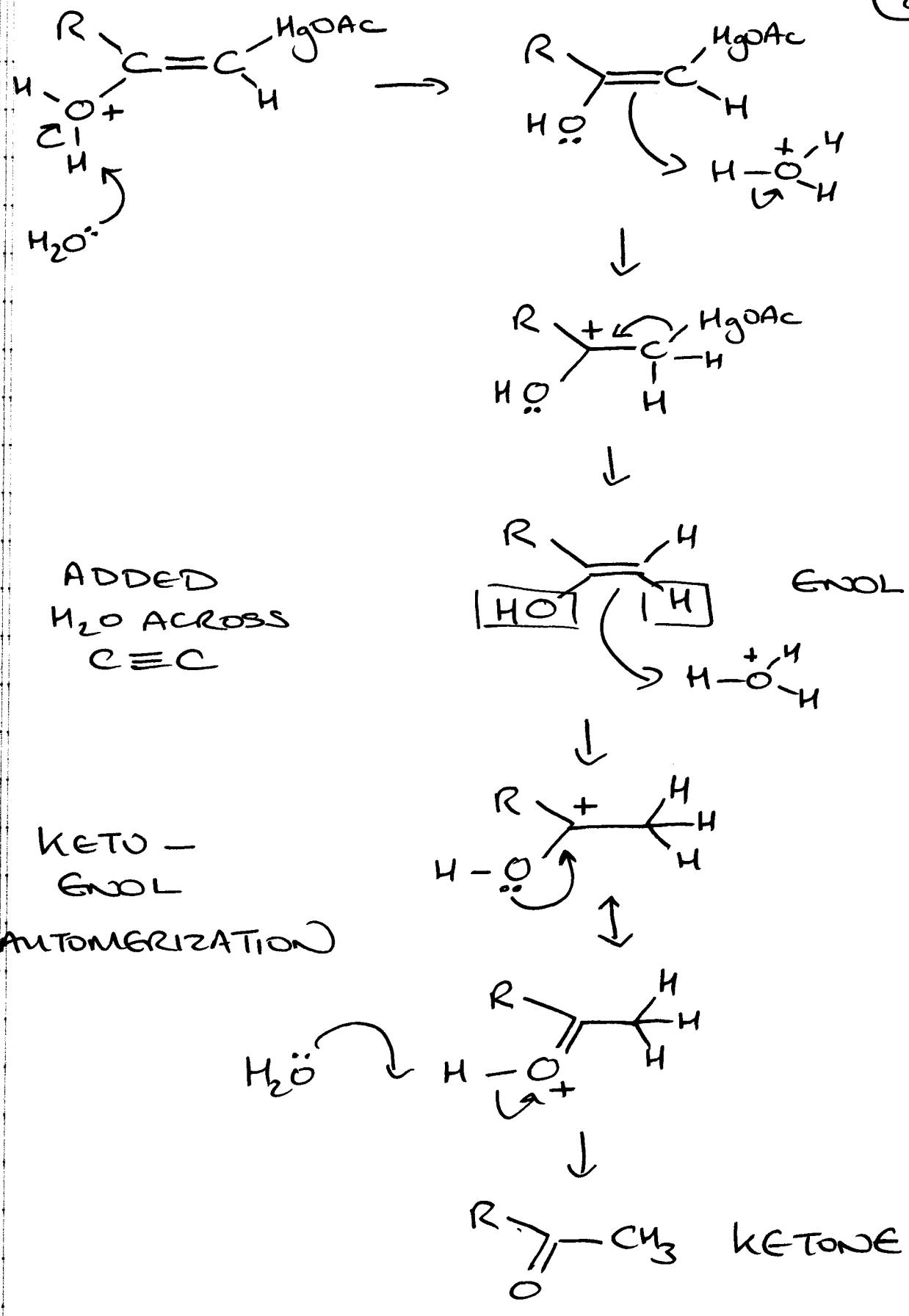
1° C^+ usually considered not to be a viable reaction intermediate

PROPOSED INTERMEDIATE



(iii) OXYMERCURATION




ADDED
H_2O ACROSS
C≡C
KETO –
ENOL
TAUTOMERIZATION
ENOL
KETONE