LEC (18) CHEM 30A Nov 14th

REACTIONS of ALKYNES READ 7.6-7.9, 9.1, 9.2

(1) ADDITION of X_2 PROBLEMS 7.4, 7.5

(2) ADDITION of HX 7.10-7.12, 7.16-7.18

(3) OXYMERCURATION ALKENE PROB SET

(4) HYDROBORATION

(5) REDUCTION

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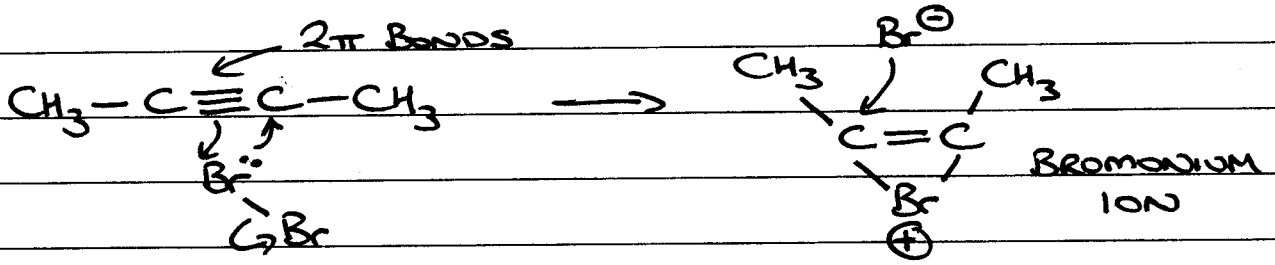
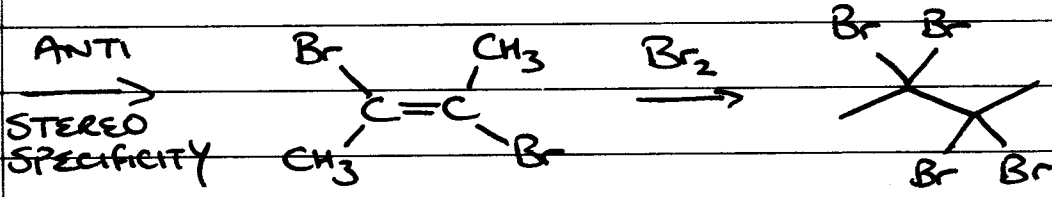
(1) ADDITION of X_2 (Br_2/Cl_2)



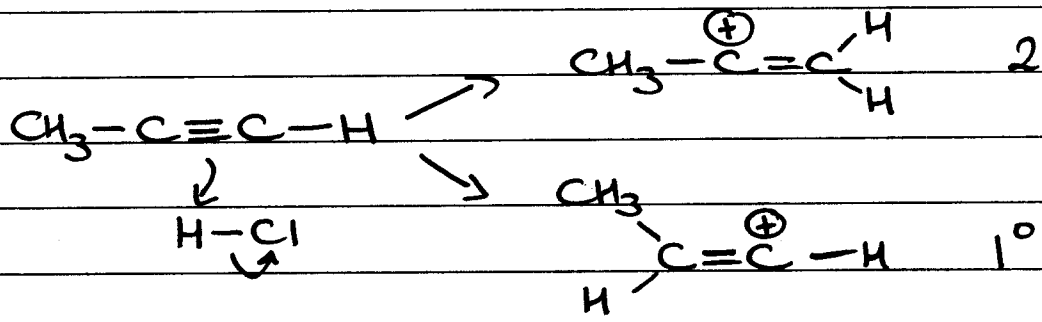


trans dibromide

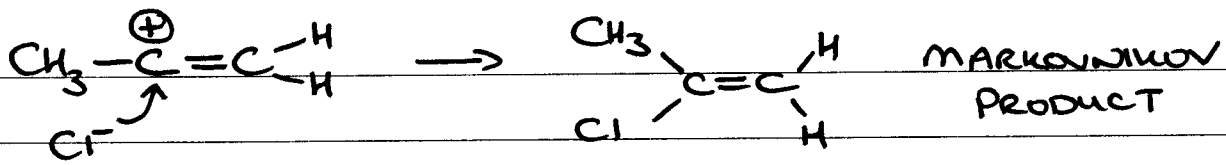
(DIFFICULT TO STOP HERE)

tetrabromoalkane

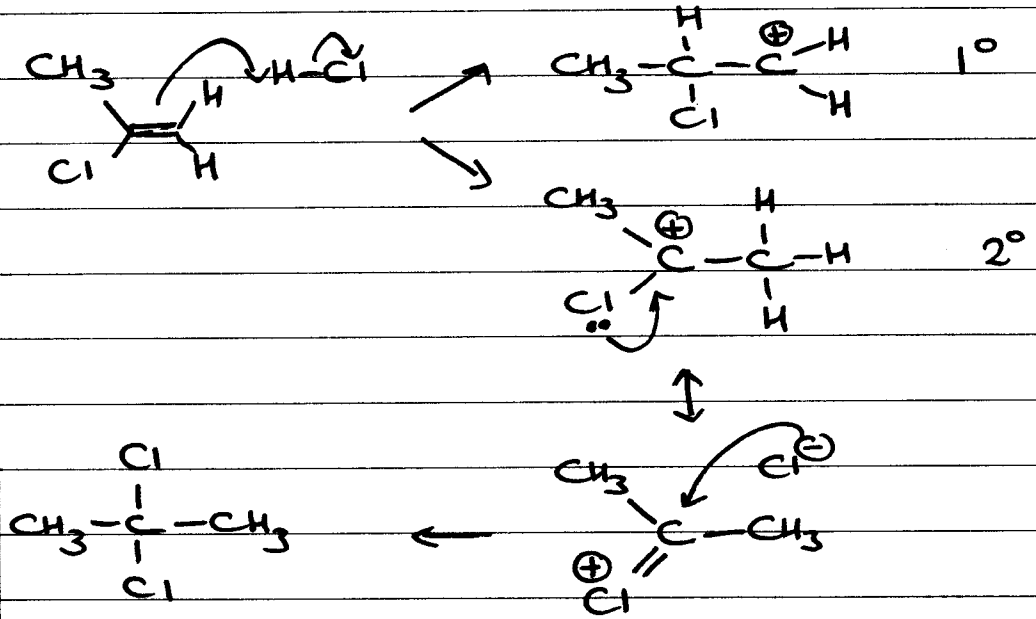
(2) HX (HCl, HBr, HI)



VINYL CARBOCATIONS (not very stable)



ALKENE PRODUCT COMPETES WITH ALKYNE FOR H-Cl IN THE REACTION (ALKENES MORE REACTIVE)

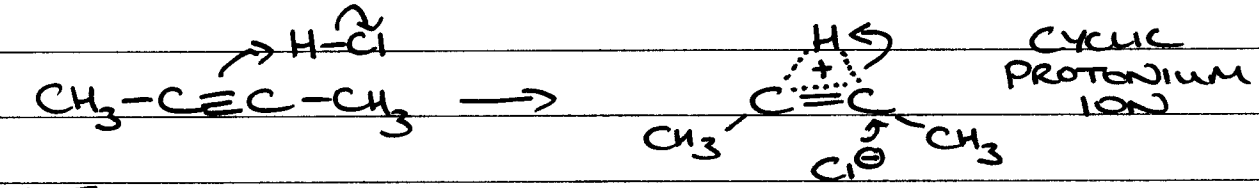


mechanisms actually more complicated, but this is not a bad model.

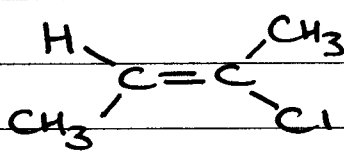
VINYLIC C^+ quite unstable

$2°$ VINYLIC $C^+ \cong 1° C^+$ not a viable reaction intermediate

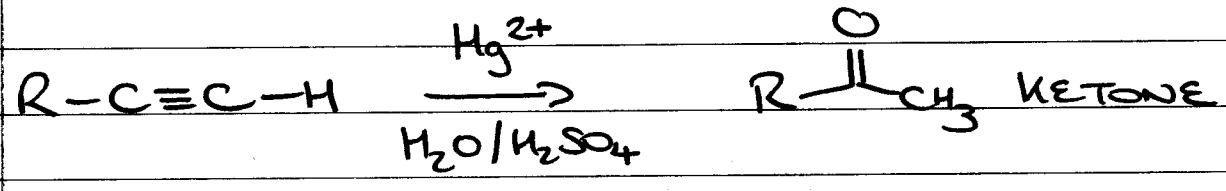
ALTERNATIVE:



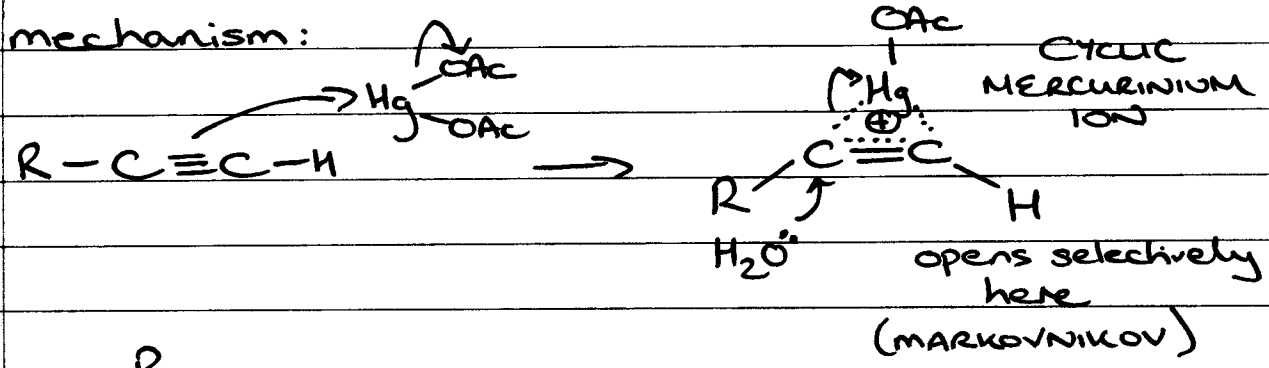
ACCOUNTS FOR OBSERVED TRANS SELECTIVITY

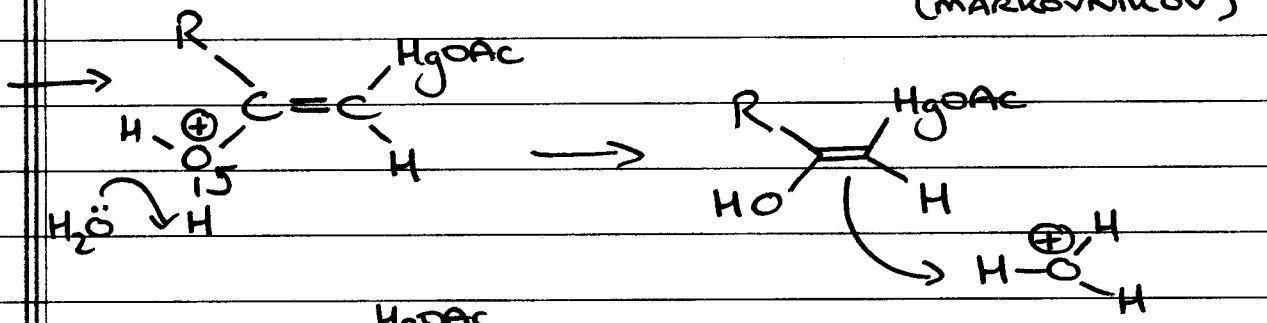


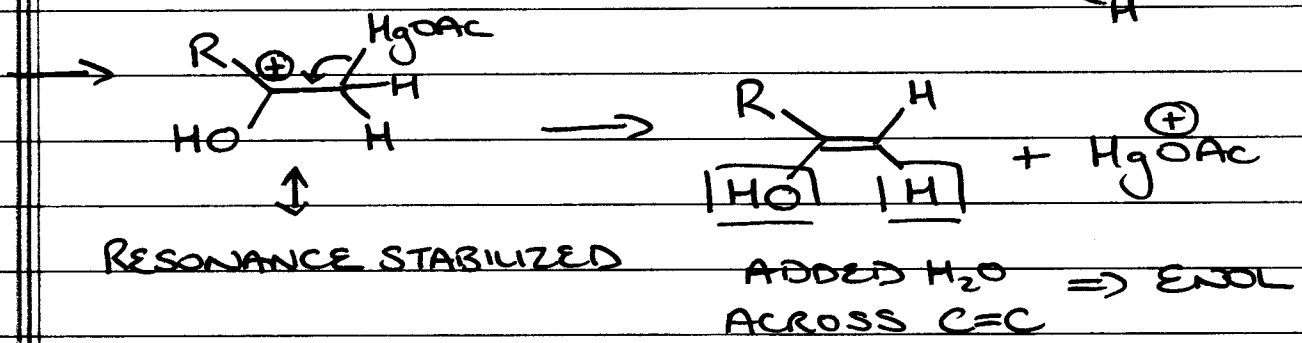
(3) OXYMERCURATION



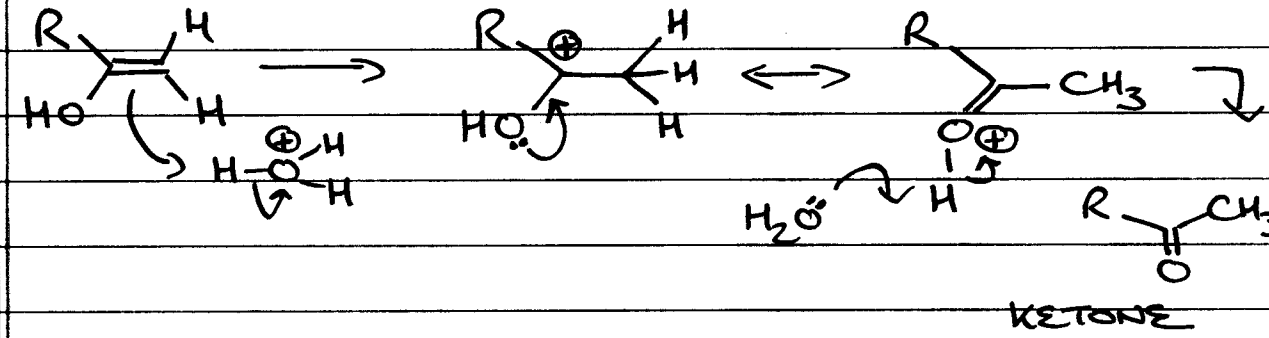
mechanism:

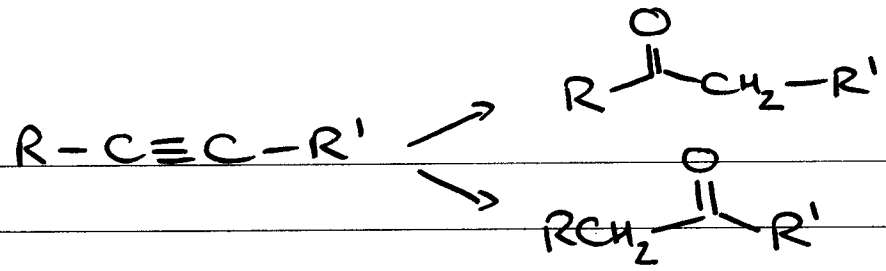






KETO-ENOL TAUTOMERISATION

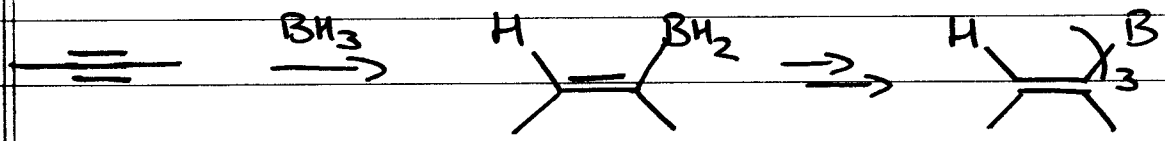




(4) HYDROBORATION

(R–C≡C–H, R–C≡C–R)

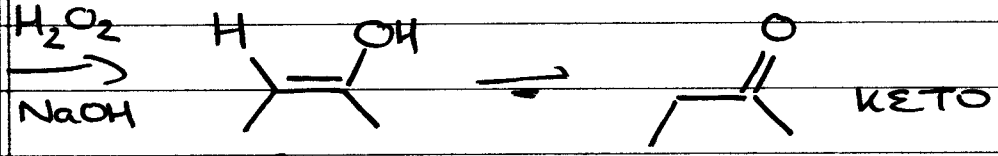
terminal non-terminal



cis

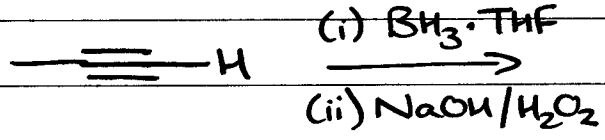
TRIALKENYL BORANE

(same mechanism as for alkenes)

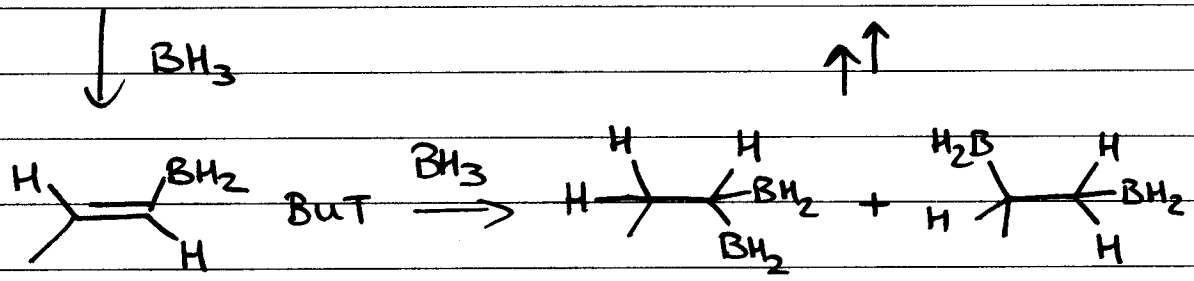


ENOL KETO

TERMINAL ALKYNES

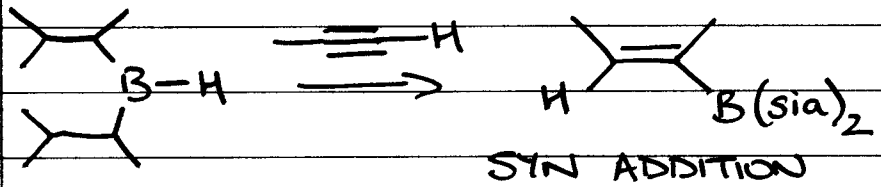


mixture of products



ANTI MARKOVNIKOV

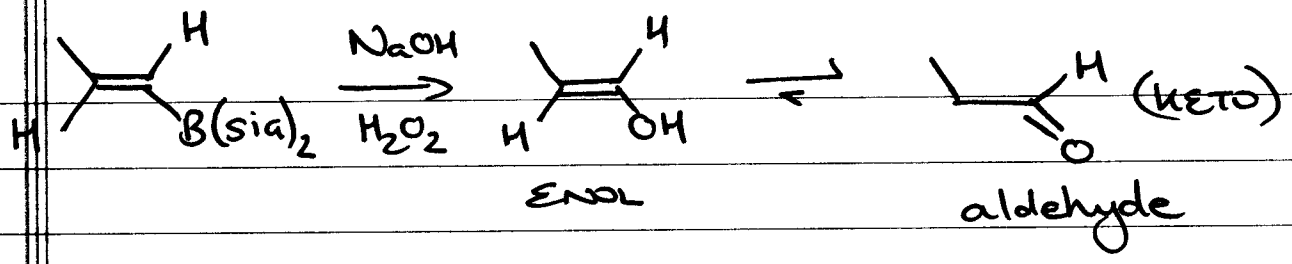
DISIAMYL BORANE $(sia)_2BH$



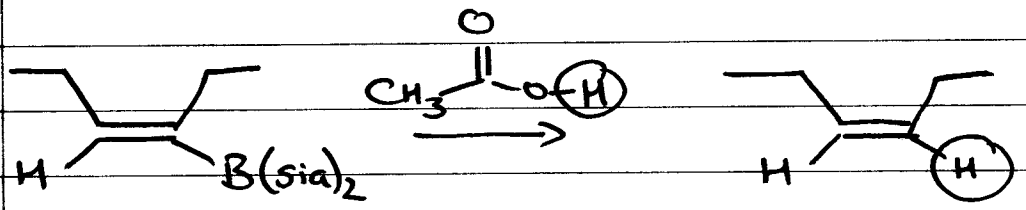
SYN ADDITION

STOPS HERE

– ONLY ONE B–H ADDITION (STERICS)



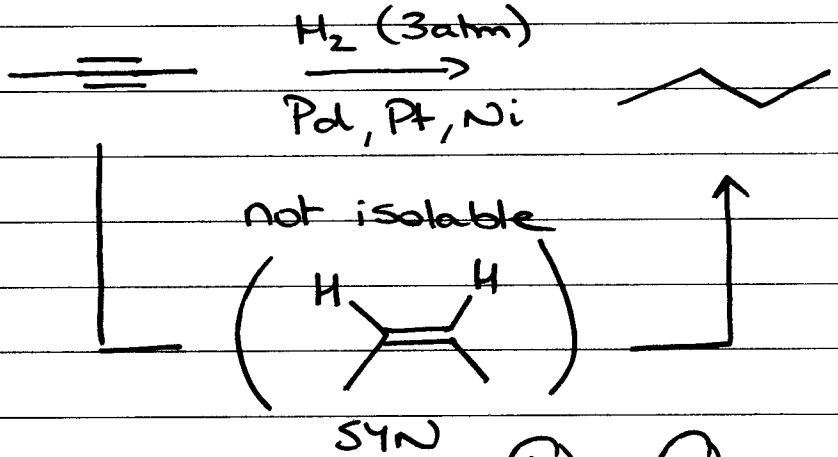
NOTE: RXN W/ ACETIC ACID

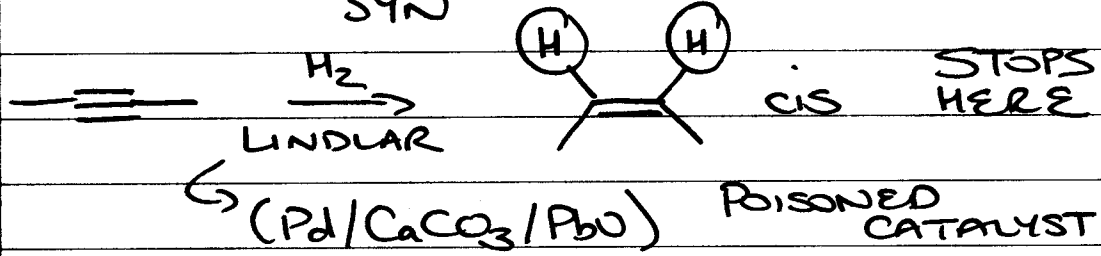


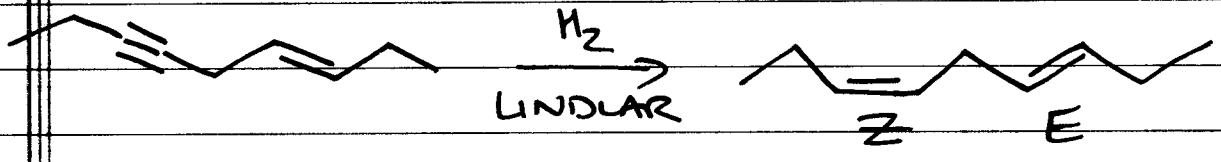
STEREOSPECIFIC
(HYDROBORATION / PROTONOLYSIS)

(5) REDUCTION

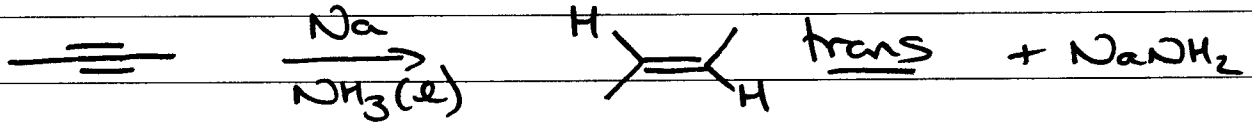
ALKYNE ⟶ [ALKENE] ⟶ ALKANE

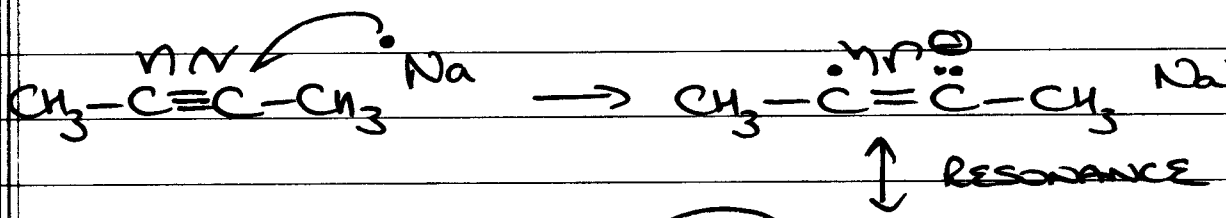
(i) 

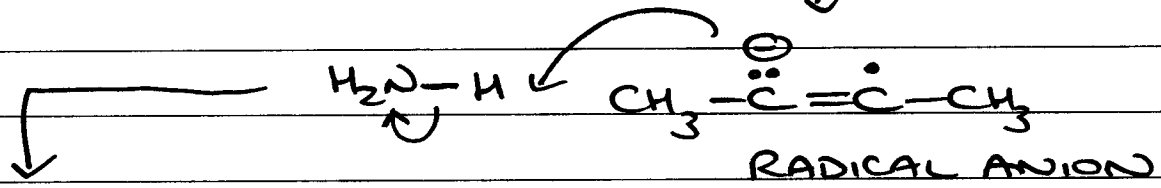
(ii) 

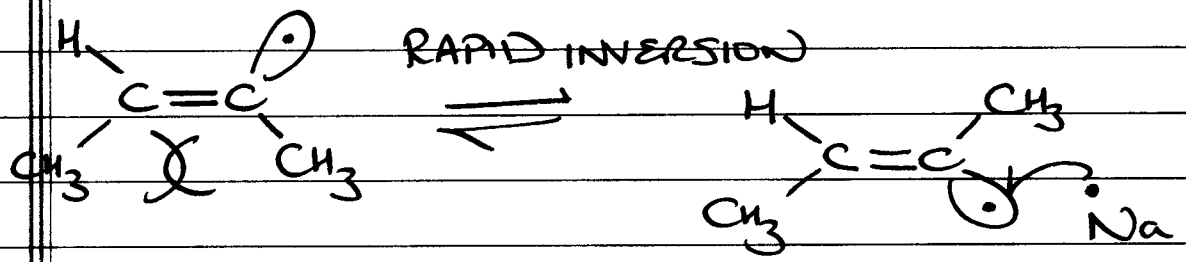


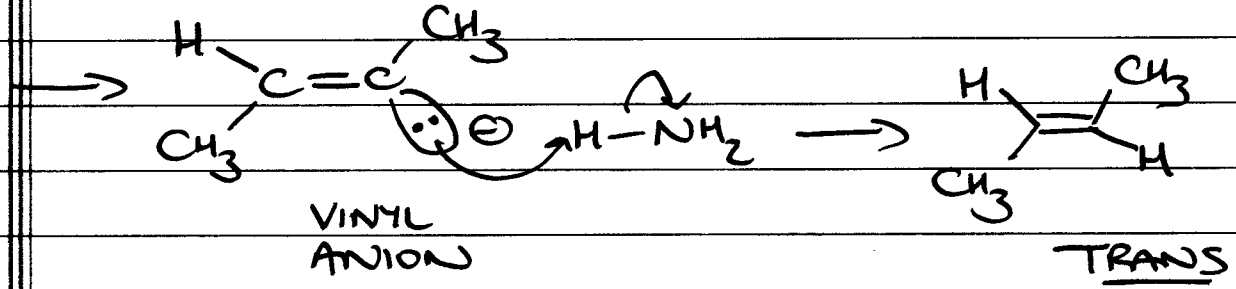
(iii) DISSOLVING METAL REDUCTION











DOES NOT WORK FOR TERMINAL ALKYNES