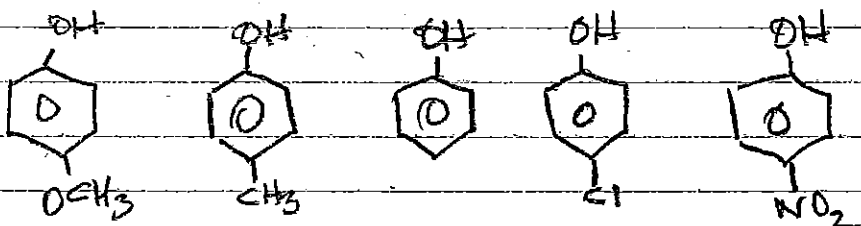


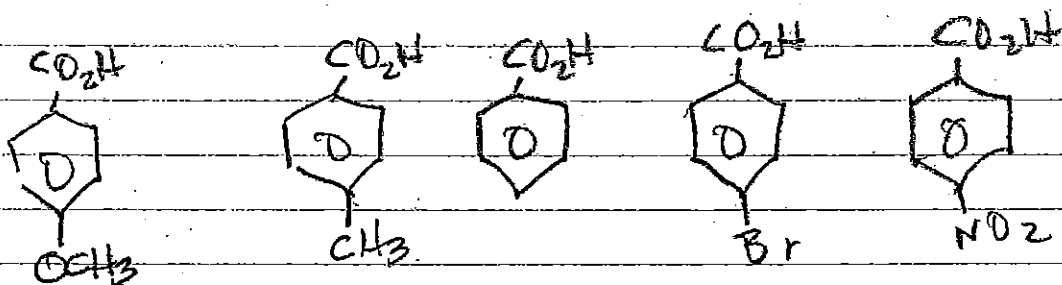
ORGANIC CHEMISTRY REVIEW OF SOME KEY TOPICS

1. EFFECT OF SUBSTITUENT GROUPS ON ACIDITY OF AROMATIC ACIDS

EW GROUPS IN PARA/ORTHO POSITIONS INCREASE ACIDITY BY STABILIZING CONJUGATE BASE.



pKa 10.20 10.19 9.95 9.38 7.14



pKa 4.47 4.34 4.20 4.00 3.44

EW GROUPS

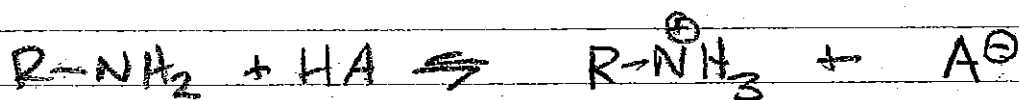
- CHO
- COR
- COOR
- COOH
- CN
- SO₃H
- NO₂
- NR₂⁺

ED GROUPS

- NH₂
- OH
- OR
- NHCOR
- R

EFFECT OF SUBSTITUENT GROUPS ON AMINE BASICITY

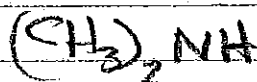
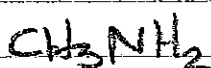
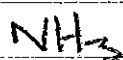
STRENGTH OF BASE COMMONLY MEASURED BY pK_a OF CONJUGATE ACID



STRONG BASE

WEAK ACID \equiv HIGH pK_a

\therefore HIGHER pK_a OF CONJUGATE AMINIUM ION \Rightarrow STRONGER AMINE BASE.

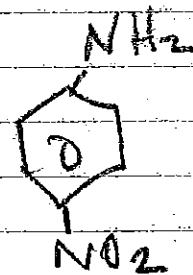
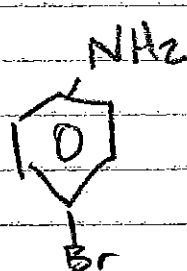
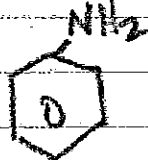
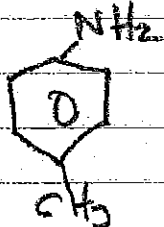
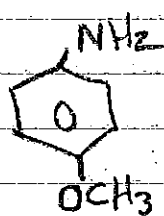


CONJUG ACID pK_a

9.26

10.64

10.72



CONJUG ACID pK_a

5.29

5.07

4.58

3.91

0.98

ALL ARYL AMINES ARE LESS BASIC THAN ALKYL AMINES BECAUSE e^- PAIR IS LESS AVAILABLE.

WADE 5TH CH 17

EAS ON SUBSTITUTED BENZENES



ED (ACTIVATE)

DIRECT ORTHO
PARA



EW (DEACTIVATE)

DIRECT META

AROMATICITY HUCKEL RULE: CYCLIC PLANAR, CONJUG
 $4n+2$ π ELECTRONS $n=0, 1, 2, 3, \dots$

AROMATIC # 2, 6, 10, 14, 18

ANTIAROMATIC # 4, 8, 12, 16, 20

WADE 5TH
CH 16



$6\pi e$
AROM.

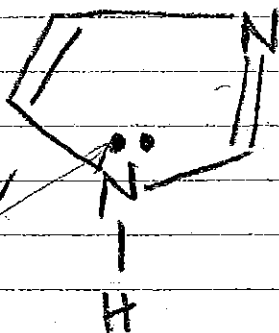


$4\pi e$
ANTIAROM

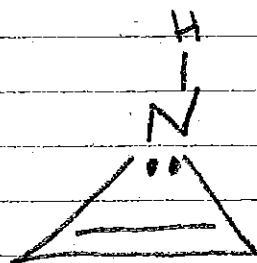


$5\pi e$
NONAROM.

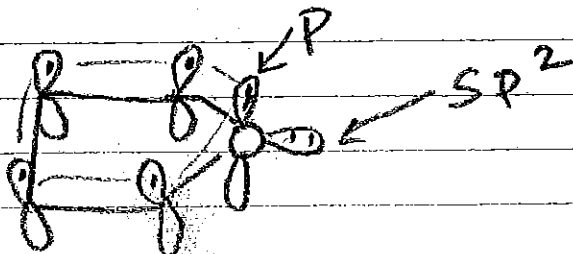
P
ORBITAL



AROMATIC
 $6\pi e$

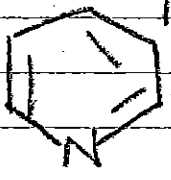


ANTIAROMATIC
 $4\pi e$



RE: WADE 5TH ed pg 698

PYRIDINE



↑
SP² ORBITAL

MORE AVAILABLE
MORE BASIC

PYRROLE

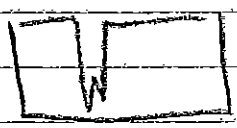


H
P ORBITAL

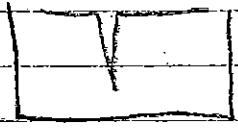
PROTONATION
CONVERTS TO SP³
BREAKS AROMATICITY
LESS BASIC

IR SPECTROSCOPY

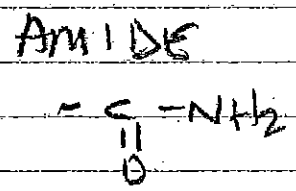
1^o AMINE
R-NH₂



2^o AMINE
R-NRH

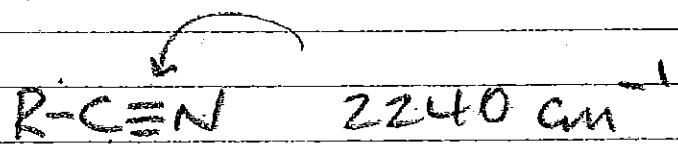


3^o AMINE
R₃N



ALSO HAS C=O AT 1680 cm⁻¹

NITRILE



MASS SPEC.

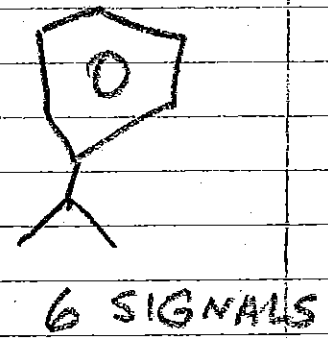
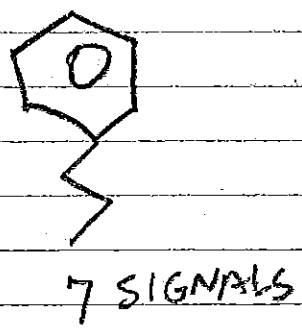
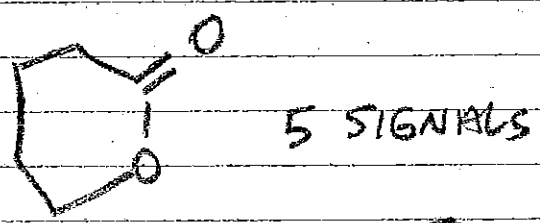
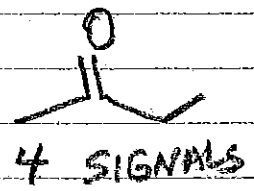
RE: WADE 5TH PG 523

ATOM	RELATIVE ABUNDANCE		
	<u>M+</u>	<u>M+1</u>	<u>M+2</u>
³⁵ Cl	75%	—	25%
⁷⁹ Br	50%	—	50%
¹²⁷ I	100%	—	—

¹³C NMR

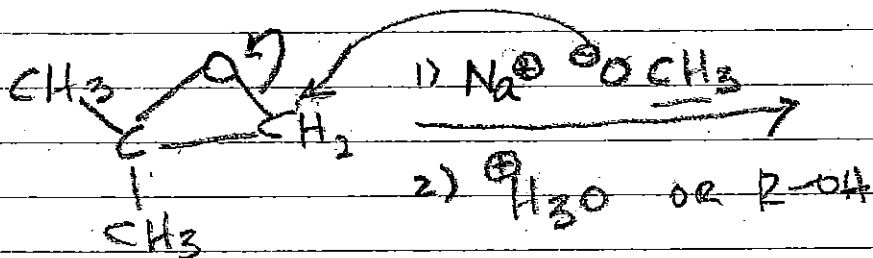
WADE 5TH PG 585

¹H PROTON DECOUPLED SPECTRA GIVES NUMBER OF CARBON TYPES (ALL SINGLET)

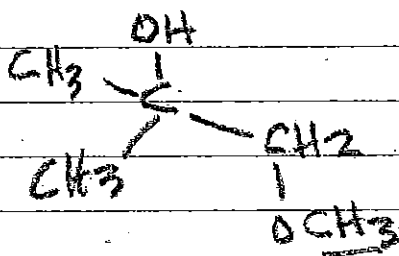


EPOXIDES AP; WADE 5th pg 627-629

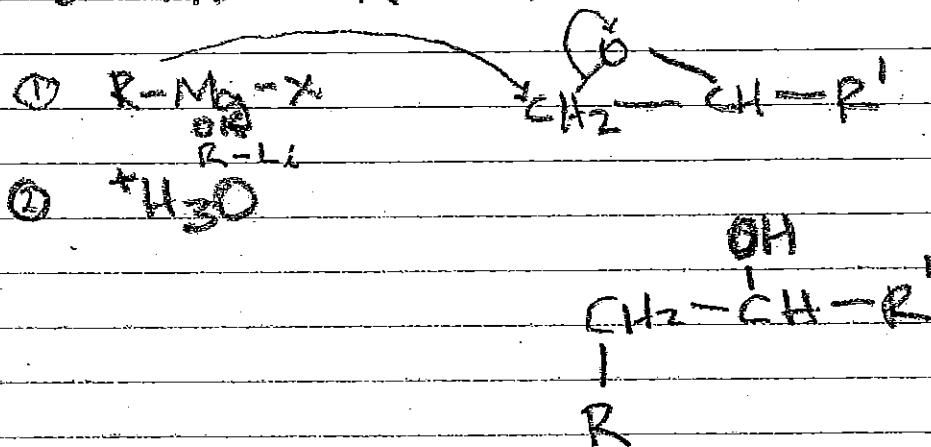
S_N2 WITH STRONG BASE



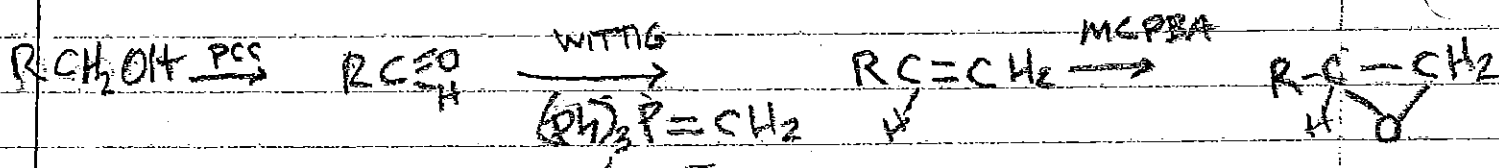
ALKOXIDE ION ATTACKS LESS HINDERED CARBON



WITH GRIGNARD OR ALKYL LITHIUM



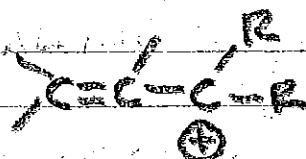
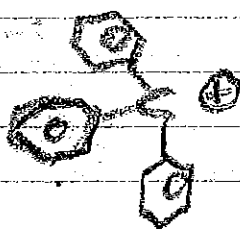
EPOXIDES MADE FROM ALKENE WITH MCPBA



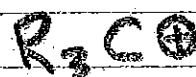
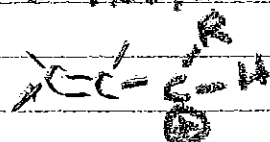
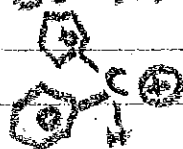
CARBODATION STABILITY RE: BRUCE 4th pg 410

MOST STABLE

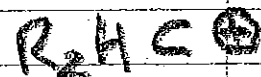
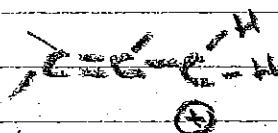
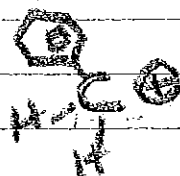
↑ 3° BENZYLIC ≈ 3° ALLYLIC



2° BENZYLIC ≈ 2° ALLYLIC ≈ 3° ALKYL



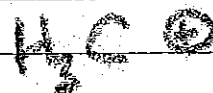
1° BENZYLIC ≈ 1° ALLYLIC ≈ 2° ALKYL



1° ALKYL



LEAST STABLE METHYL



STABILITY OF FREE RADICALS IS SIMILAR

CONJUGATED DIENES RE: WADE 5TH pg 647

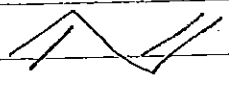
KINETIC
FORMS FAST

vs.

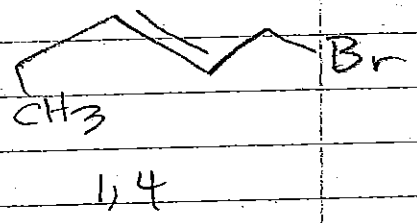
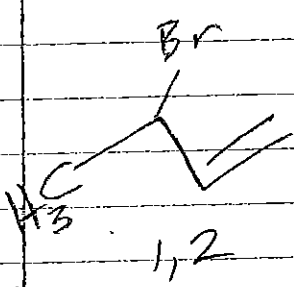
THERMODYNAMIC
MORE STABLE

LOW TEMP
-80 °C

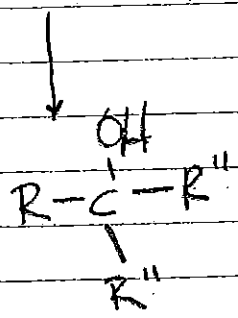
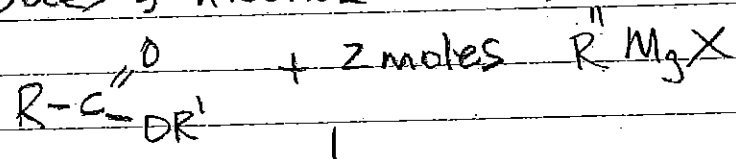
HIGH TEMP 40 °C



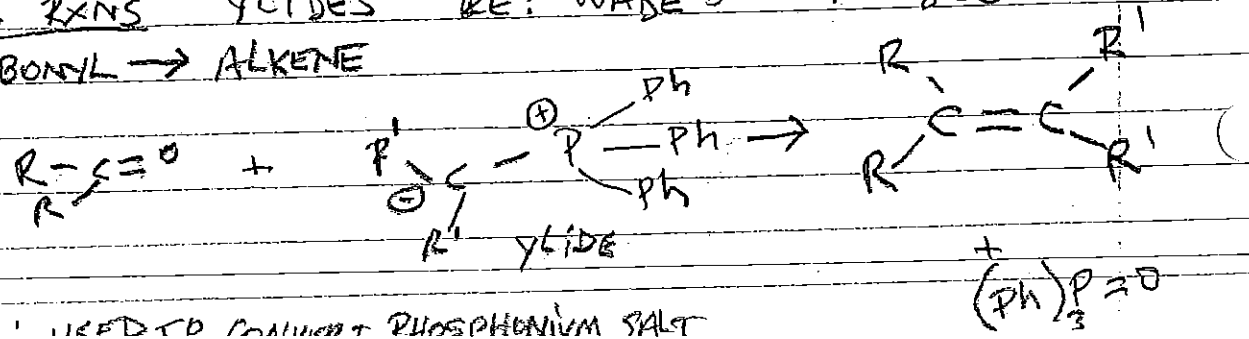
+ HBr



GRIGNARD RXNS ON ESTERS RE: CHE 243 EXPT 12
PRODUCES 3° ALCOHOL WITH SYMMETRY



WITTIG RXNS YLIDES RE: WADE 5TH PG-800
CARBONYL → ALKENE

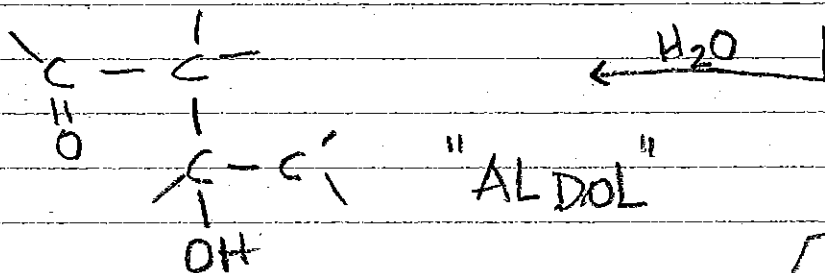
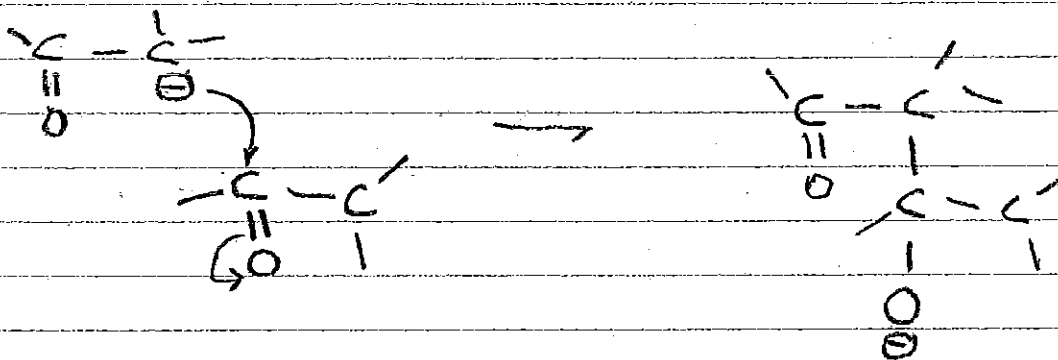
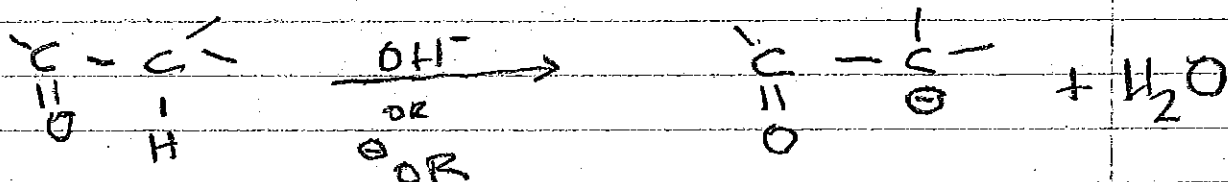


USED TO PREPARE + PHOSPHONIUM SALT

ENOLS / ENOLATES / ALDOL CONDENSATION

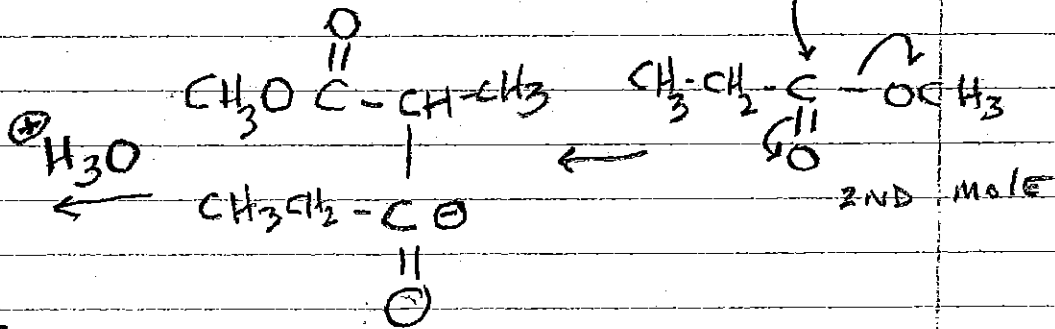
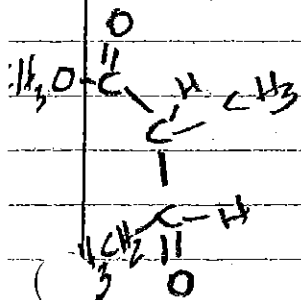
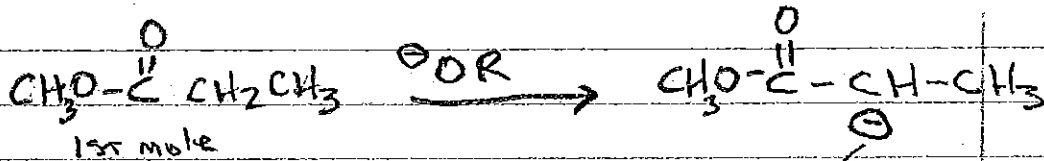
RE WADE 5TH PG 1003/1004, 1018

α H ARE ACIDIC



WADE PG 1028

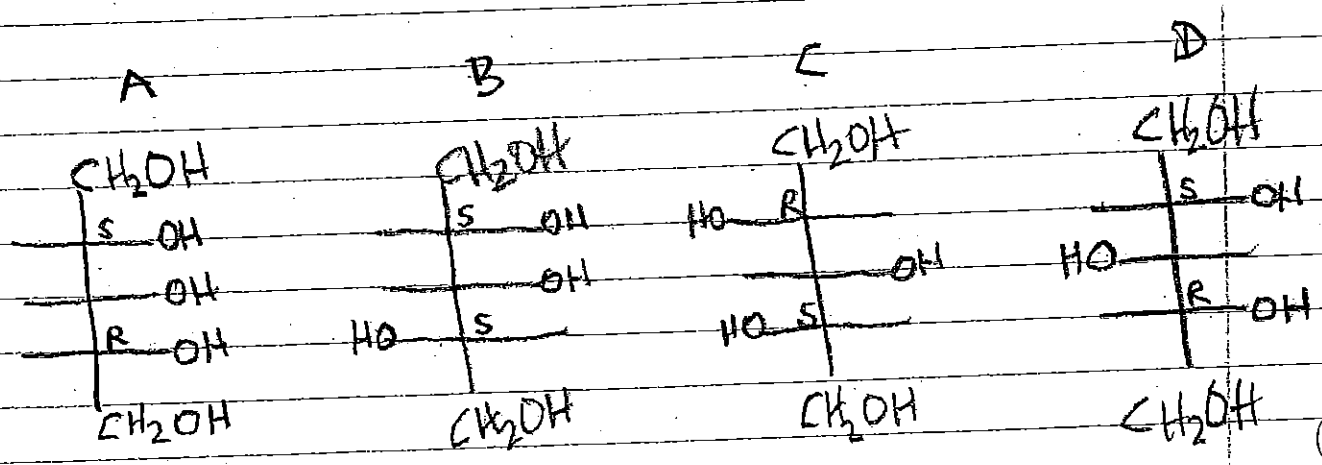
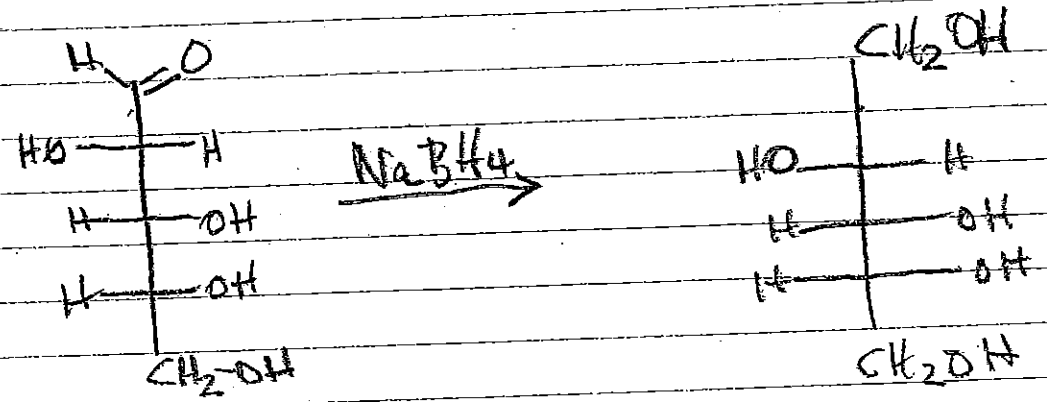
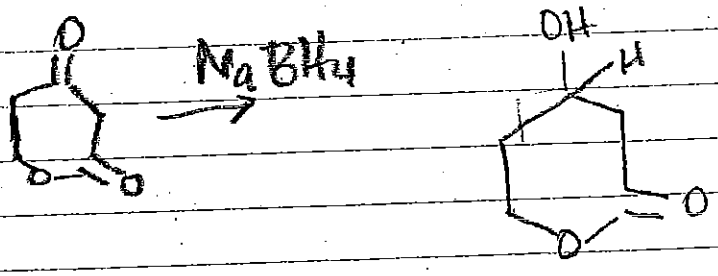
FOR ESTER



β KETOESTER

NaBH_4 SELECTIVE REDUCING AGENT WADE PG 43?

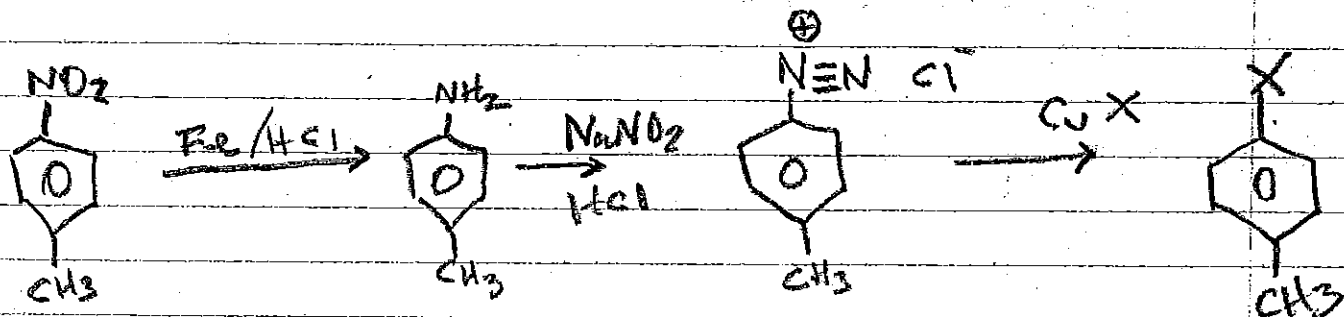
REDUCES ALDEHYDES
KETONES NOT ESTERS
ACIDS LACTONES



(B) OPTICALLY ACTIVE ENANTIOMER IS R R
CAN BE SUPERIMPOSED ON MIRROR IMAGE

IN PLANE

ARENE DIAZONIUM SALT RXNS WADE PG 870

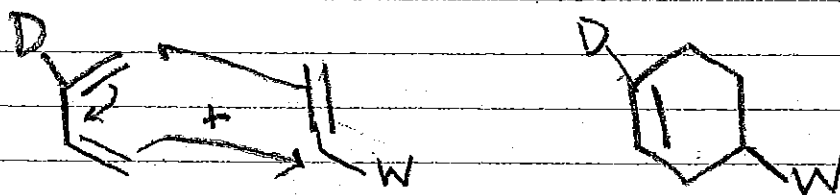


DIELS ALDER WADE 5TH PG 655-

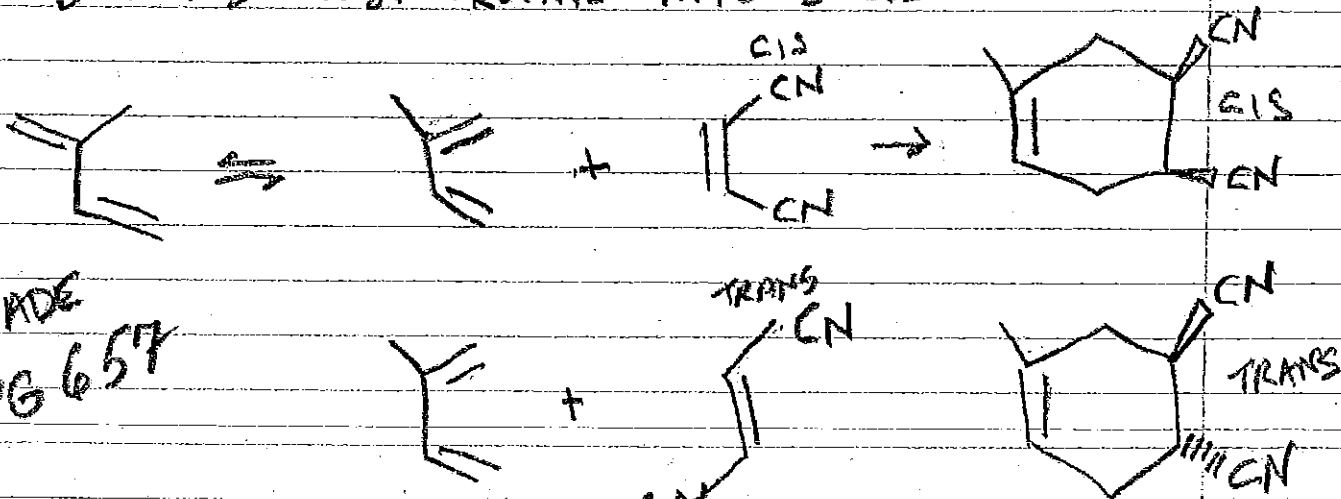
DIENE PLUS DIENOPHILE MAKES RING 4+2 CYCLOADDITION

SYN CHEMISTRY RETAINS REACTANT CONFIG. IN PRODUCT

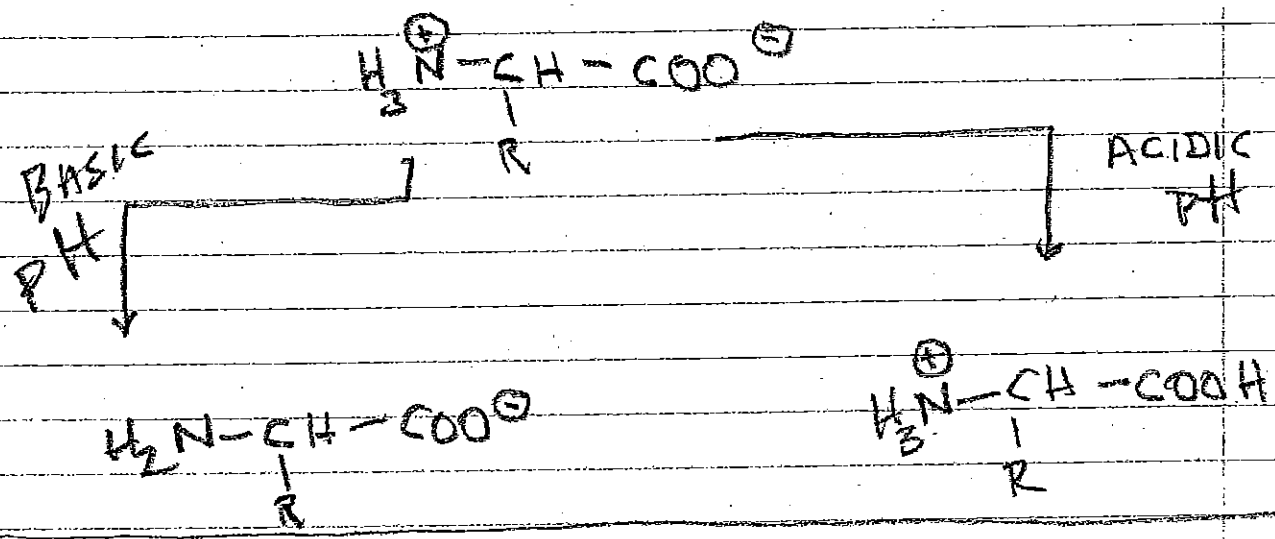
GENERAL



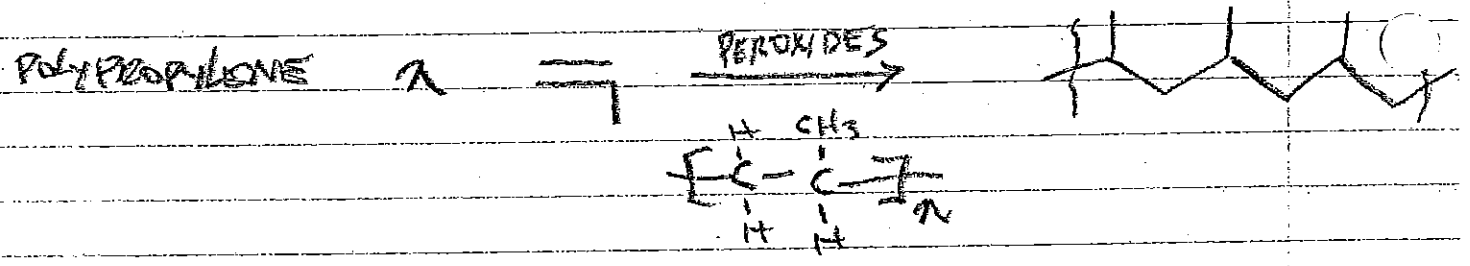
S-TRANS MUST ROTATE INTO S-CIS



AMINO ACIDS
ISOELECTRIC POINT



POLYMERS WADE PG 1185



WADE 1193 NYLON POLYAMIDES FROM DIACID AND DIAMINE

