LEC (19) CHEM 30A NOV 16th

(1) ALKYNES cont... READ 9.1-9.5

– NUCLEOPHILIC SUBSTITUTION PROBLEMS 9.1-9.30

(1) INTRODUCTION

(2) MECHANISMS MIDTERM on MONDAY

(3) ELECTROPHILE LAST NAME A-J CS76 K-Z CS50

(4) NUCLEOPHILE

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(1) ALKYNES - DISSOLVING METAL REDUCTION

See last page of LEC (18)

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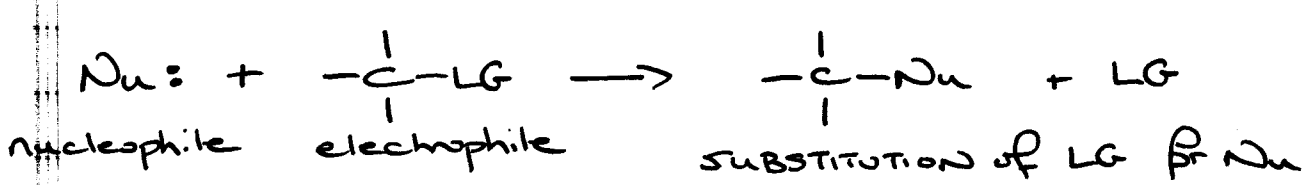
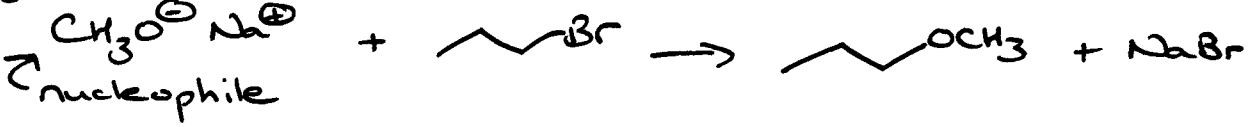
(1) INTRODUCTION TO NUCLEOPHILIC SUBSTITUTION

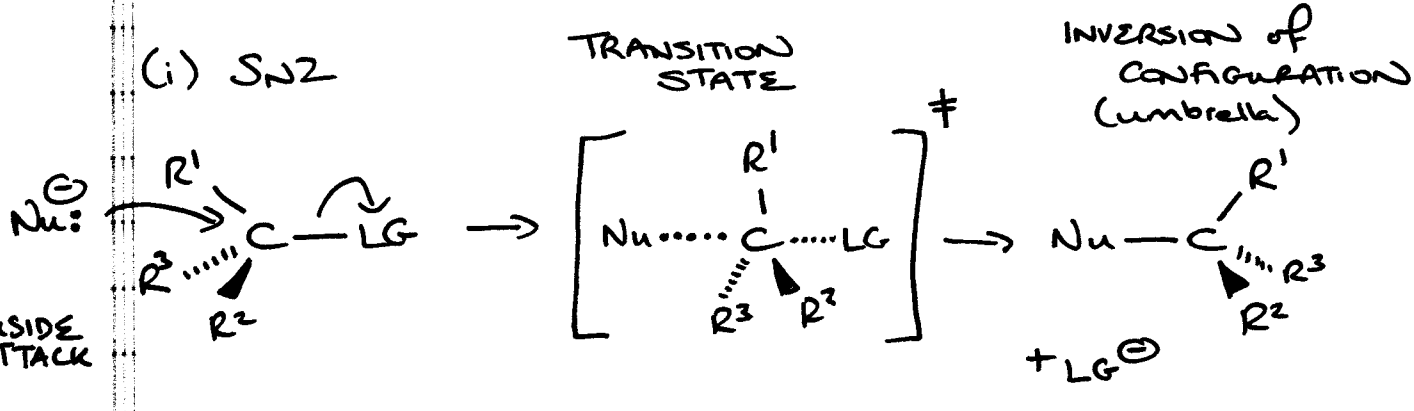


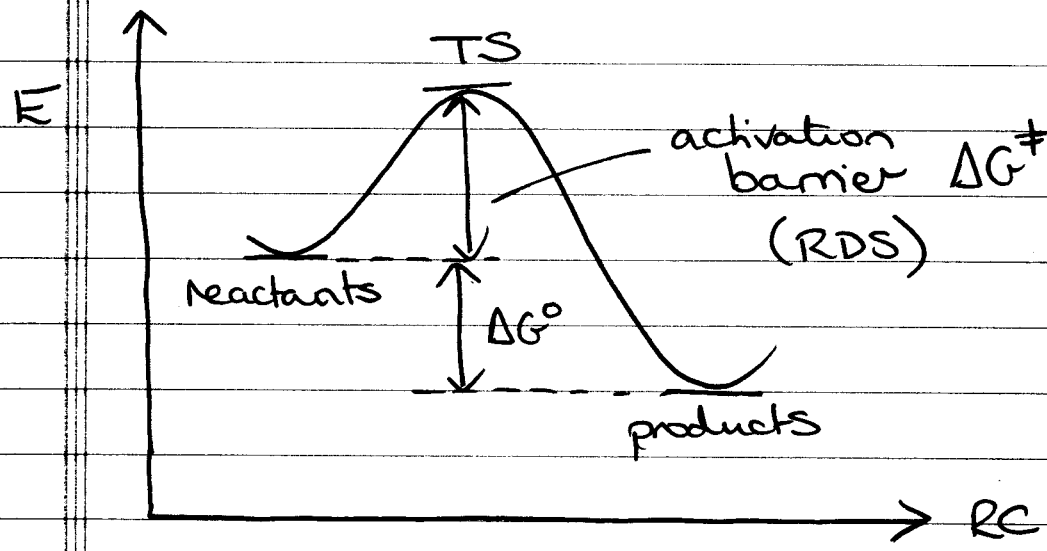
e.g.



(2) MECHANISMS (TWO LIMITING ONES)

(i) SN2





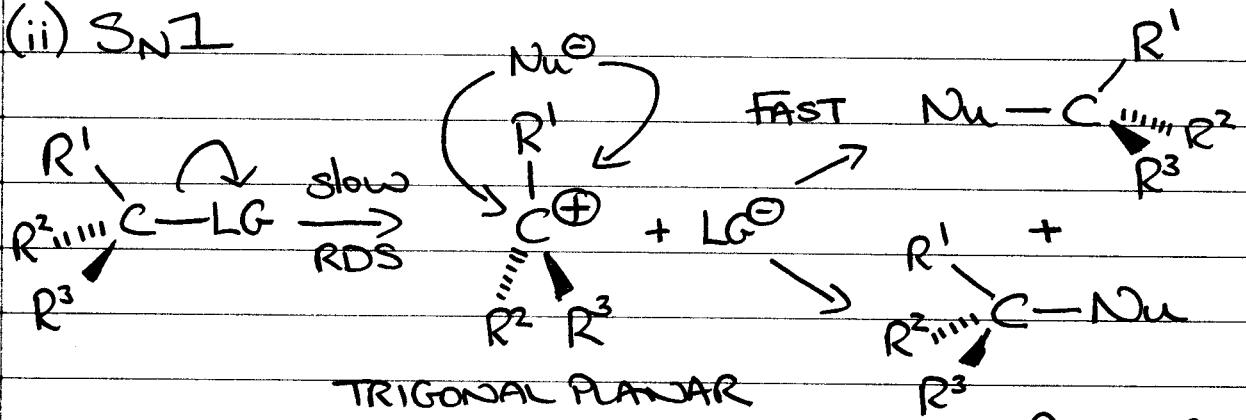
S_N2 = SUBSTITUTION, NUCLEOPHILIC, BIMOLECULAR

BIMOLECULAR – Rate of reaction is dependant upon the concentrations of <u>both</u> the NUCLEOPHILE and the ELECTROPHILE

$$\text{rate} = k_2[Nu][E]$$

k_2 ← 2nd order rate constant

(ii) S_N1



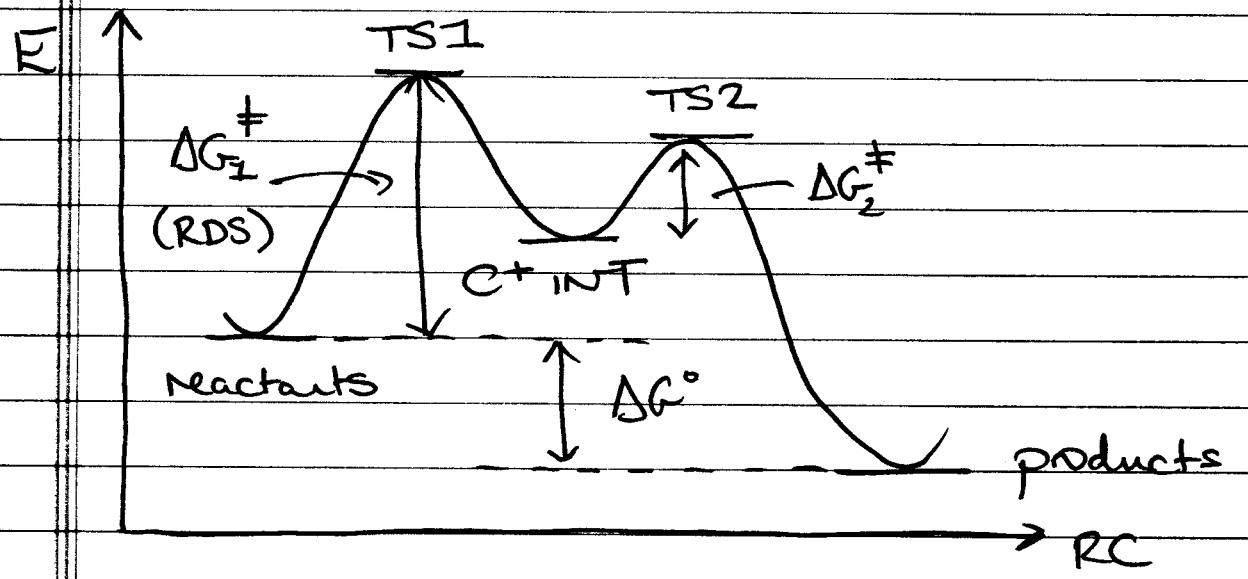
REARRANGEMENT ⇐

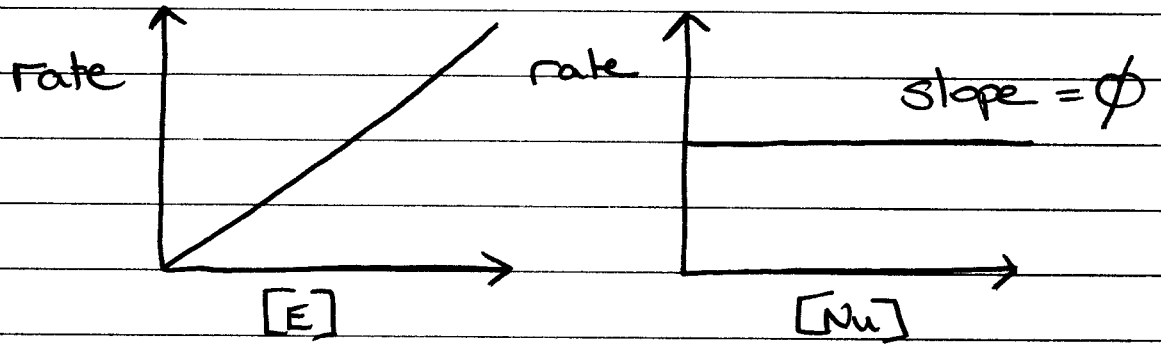
ANY STEREOCHEMICAL INFORMATION IN THE STARTING MATERIAL IS LOST

S_N1 - SUBSTITUTION, NUCLEOPHILIC, UNIMOLECULAR

Rate depends only on [E] rate = k_1[E]

first order rate constant

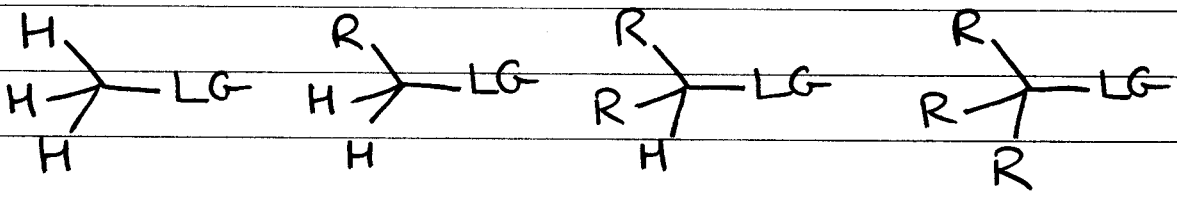




RDS does NOT involve the nucleophile, so adding more of it to the reaction does not alter the rate ⇒ Also, reactivity of the NUCLEOPHILE does not matter

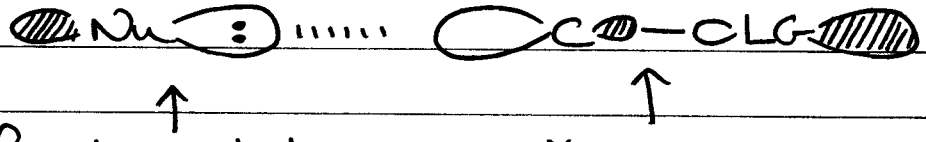
What decides S_N1 vs S_N2 ?

(3) THE ELECTROPHILE



methyl primary secondary tertiary

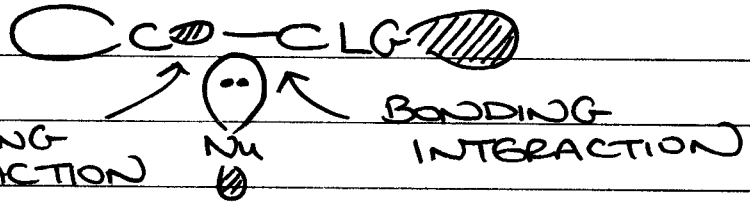
S_N2 — BACKSIDE ATTACK



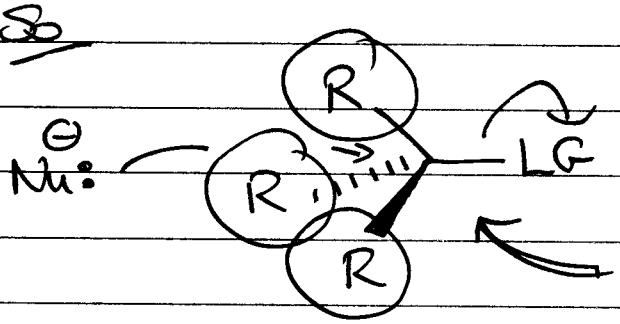
filled orbital in nucleophile

σ^* - empty antibonding orbital

FRONTSIDE ATTACK?



So



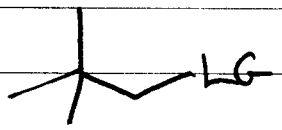
more R GROUPS, more STERIC CROWDING

Relative rates of S_N2 reactions

CH_3-LG	1
CH_3CH_2-LG	0.03
$(CH_3)_2CH-LG$	8×10^{-4}
$(CH_3)_3C-LG$	~0

DECREASING RATE ↓

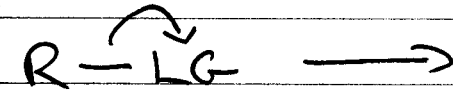
Some 1° groups also slow things down:



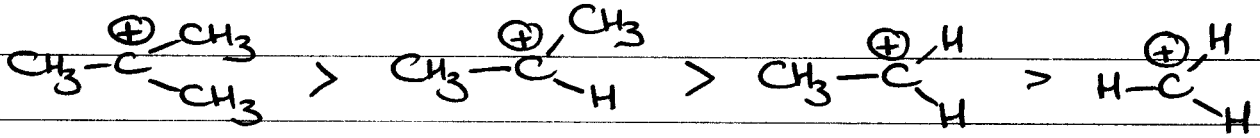
2×10^{-7}

neo-pentyl

CONSIDER S_N1 REACTIONS : OPPOSITE



C^+ STABILITY

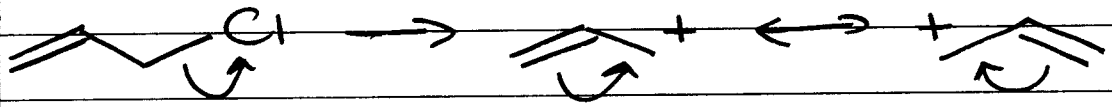


So, 1° and CH_3 electrophiles S_N2

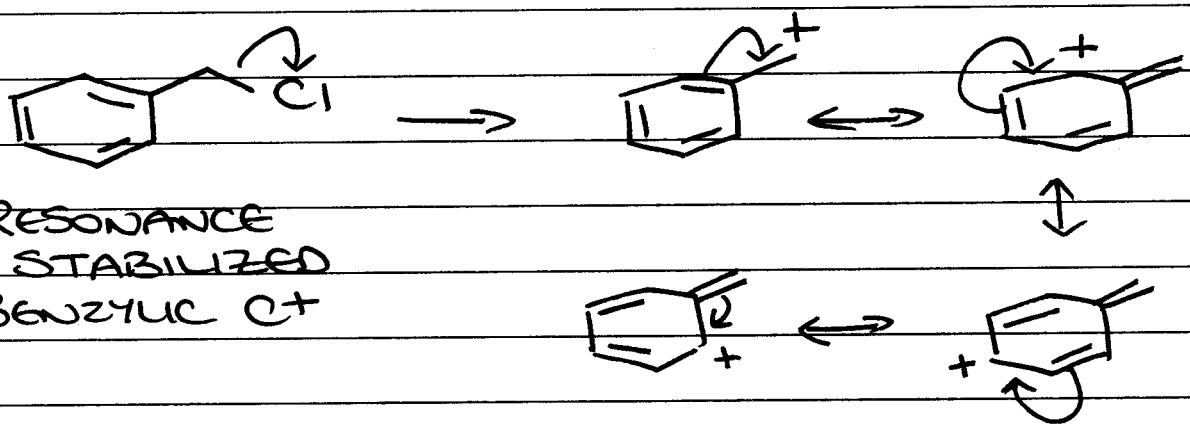
3° electrophiles S_N1 (WHAT ABOUT SECONDARY?)

2° C+ can react either way – depending on other factors

- other types of C+



RESONANCE STABILIZED
1° ALLYLIC



RESONANCE
STABILIZED
BENZYLIC C+

1° ALLYLIC / BENZYLIC electrophiles
SN1 vs SN2 (other factors, Nu, LG, solvent)
STERICS favors SN2 ELECTRONICS favors SN1

2°/3° ALLYLIC / BENZYLIC electrophiles
almost exclusively SN1

(4) NUCLEOPHILE

Consider BASICITY