

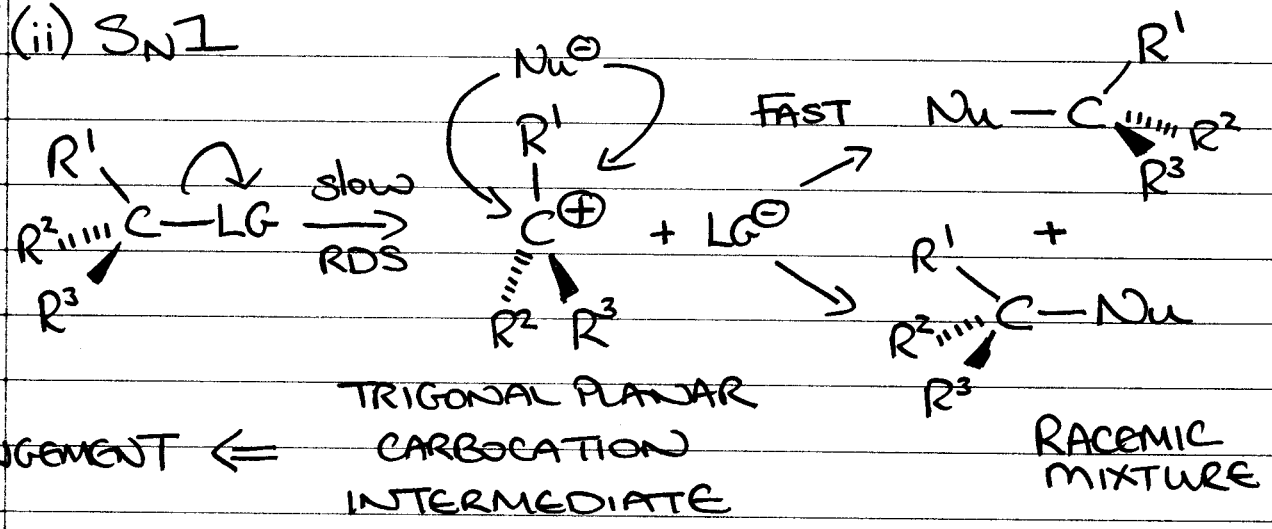
S_N2 = SUBSTITUTION, NUCLEOPHILIC, BIMOLECULAR

BIMOLECULAR - Rate of reaction is dependant upon the concentrations of both the NUCLEOPHILE and the ELECTROPHILE

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

↑ 2nd order rate constant

(ii) S_N1



REARRANGEMENT ←

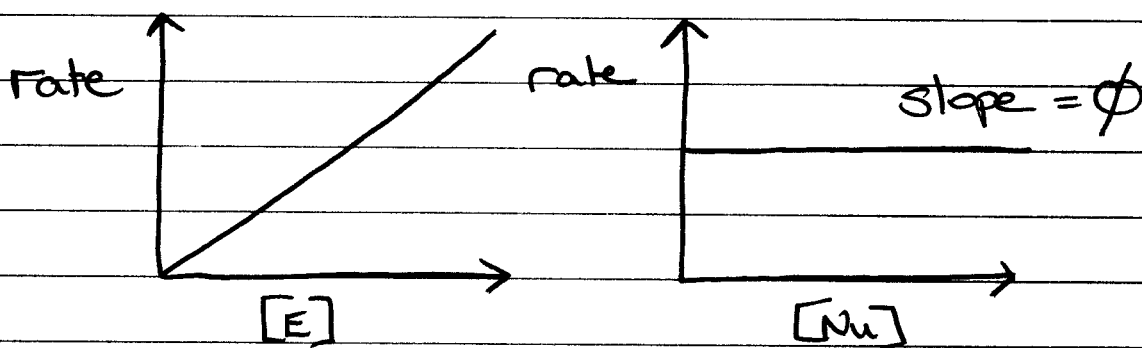
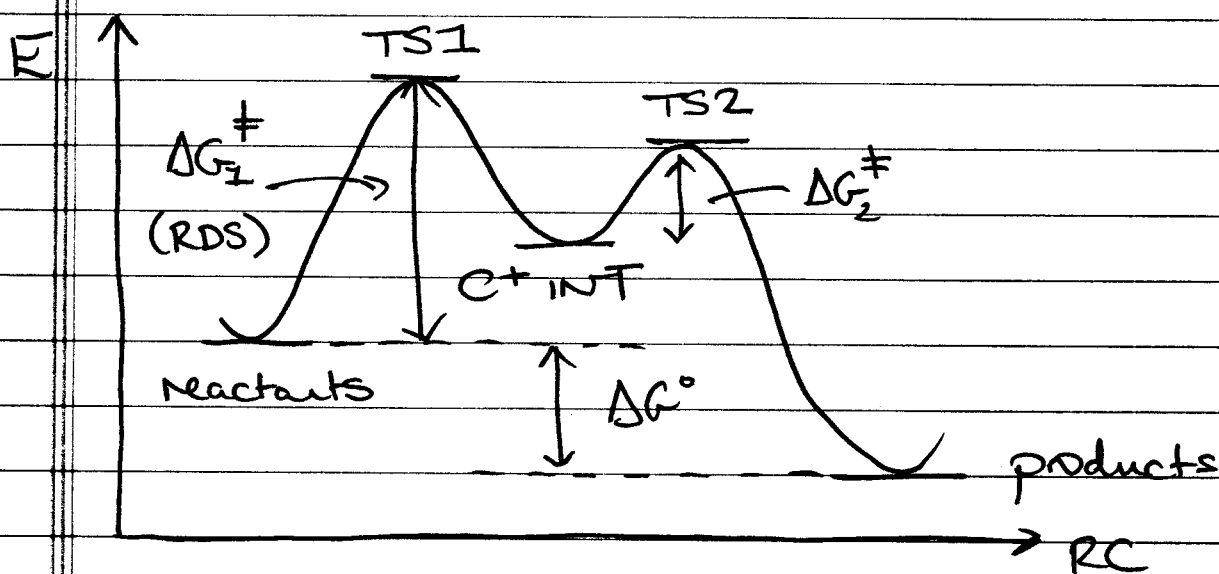
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ANY STEREOCHEMICAL INFORMATION IN THE STARTING MATERIAL IS LOST

S_N1 - SUBSTITUTION, NUCLEOPHILIC, UNIMOLECULAR

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

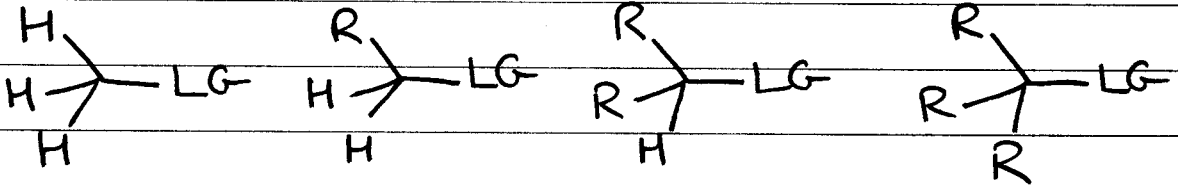
first order rate constant



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

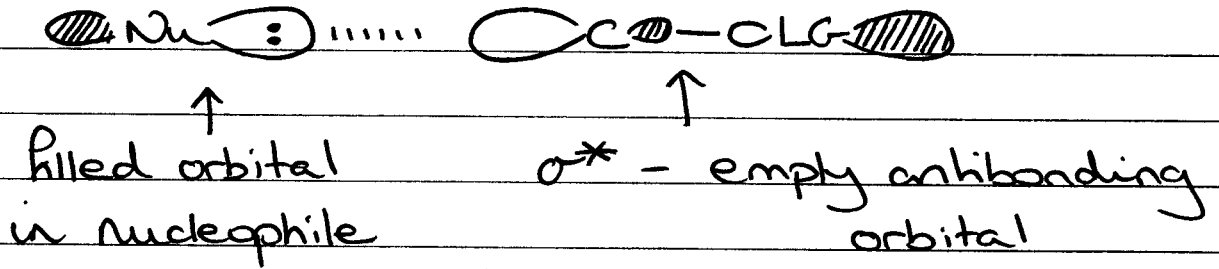
What decides S_N1 vs S_N2 ?

③ THE ELECTROPHILE

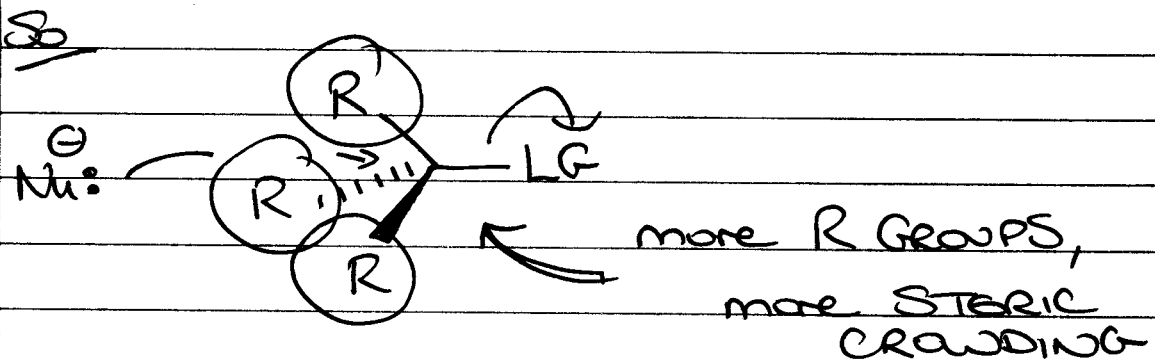
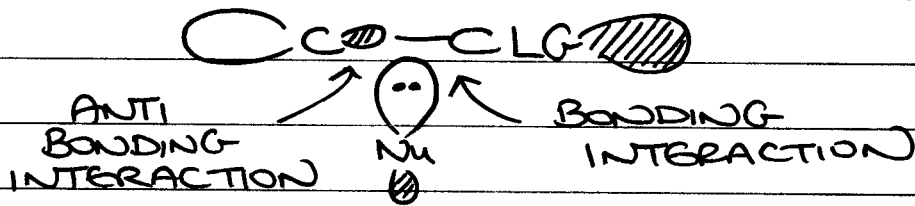


methyl primary secondary tertiary

S_N2 - BACKSIDE ATTACK

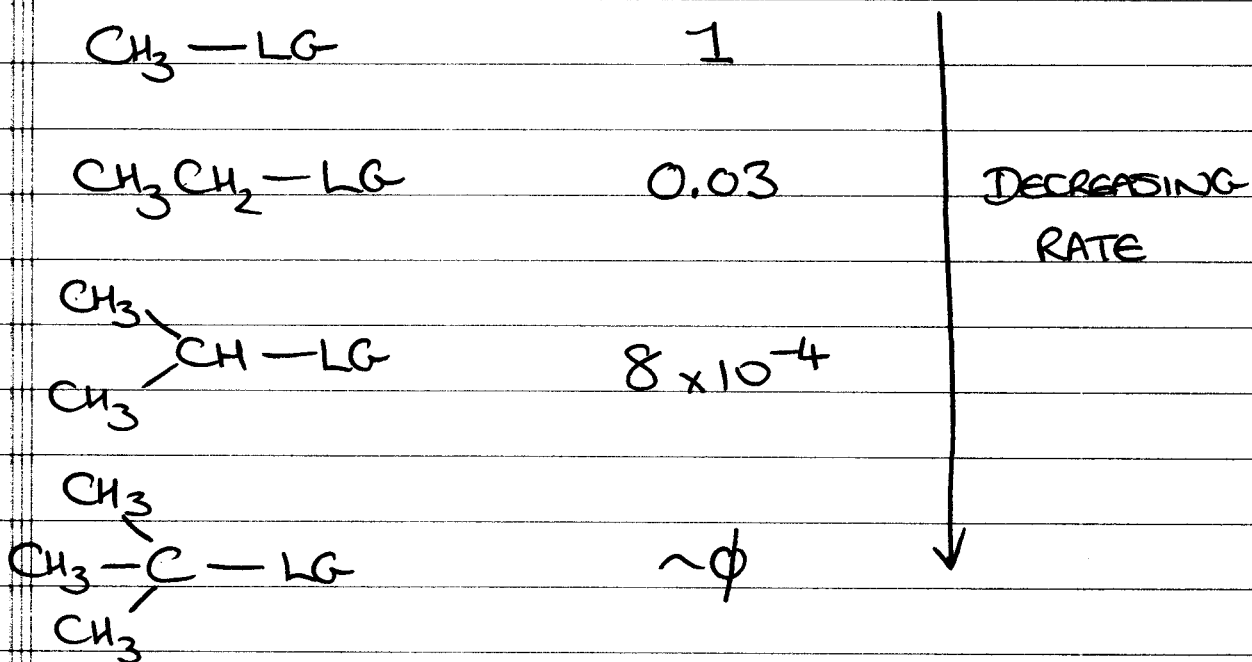


FRONTSIDE ATTACK?



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Relative rates of S_N2 reactions

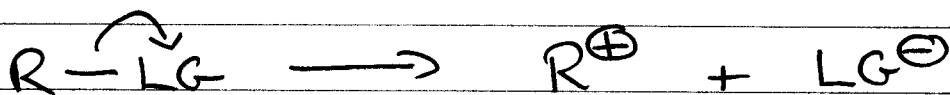


Some 1° groups also slow things down:

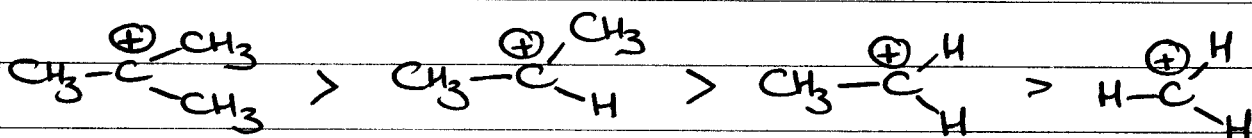


neo-pentyl

CONSIDER S_N1 REACTIONS: OPPOSITE



C^{\oplus} STABILITY



So, 1° and CH_3 electrophiles S_N2

3° electrophiles S_N1 (WHAT ABOUT SECONDARY?)

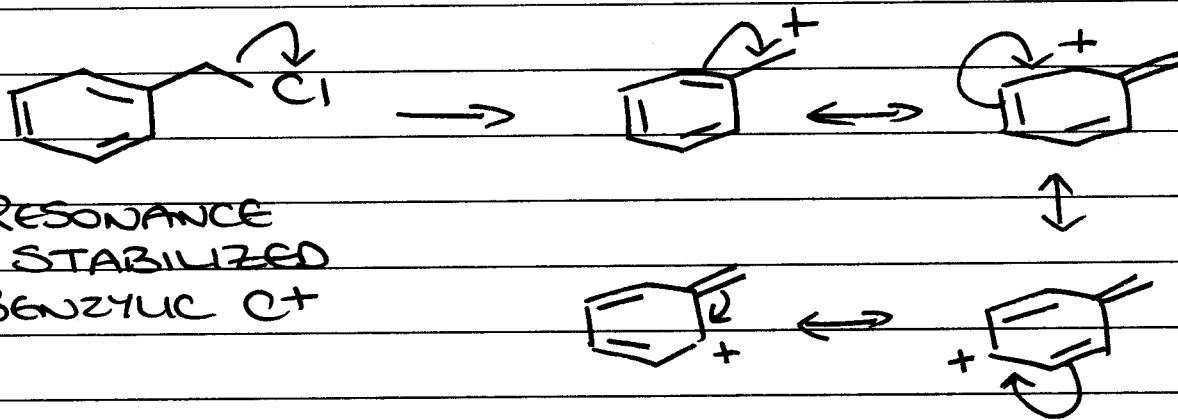
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2° C^+ can react either way - depending on other factors

- other types of C^+



RESONANCE STABILIZED
 1° ALLYLIC

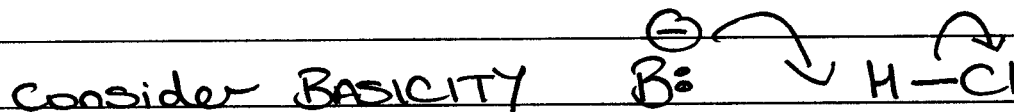


RESONANCE
STABILIZED
BENZYLIC C^+

1° ALLYLIC/BENZYLIC electrophiles
 S_N1 vs S_N2 (other factors, Nu, LG, solvent)
STERICS favors S_N2 ELECTRONICS favors S_N1

$2^\circ/3^\circ$ ALLYLIC/BENZYLIC electrophiles
almost exclusively S_N1

④ NUCLEOPHILE



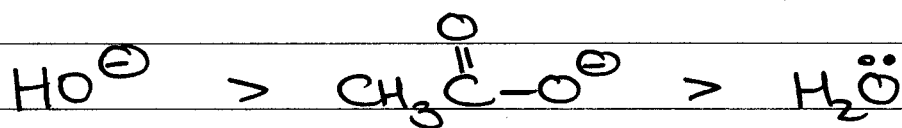
Nucleophilicity is similar $\text{Nu}^{\ominus} \curvearrowright \text{C}-\text{LG}$

- affinity for C atom
- KINETIC rather than THERMODYNAMIC effect

IMPRECISE QUANTITY - for any given species can vary depending upon other factors (Solvent/ELECTROPHILE)

- General trends

(i) Same Nucleophilic atom (parallels BASICITY)



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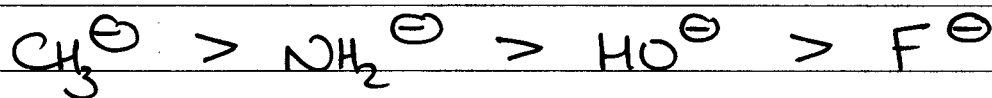
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-2

pKa of
HX

consider CHARGE & RESONANCE

(ii) Nucleophiles in the same row (parallels basicity)

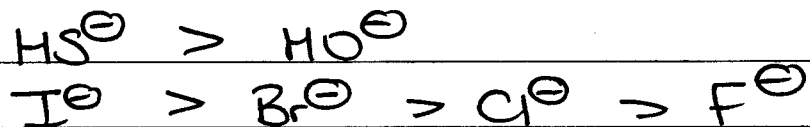


consider ELECTRONEGATIVITY

(iii) Nucleophiles in the same group (COMPLICATED)

All comes down to size.

In general nucleophilicity increases going down a group...



- opposite to BASICITY - why?

(i) ENERGY LEVELS

- higher energy of lone pair electrons as you go down the periodic table \rightarrow better overlap w/ σ^*

(ii) POLARISABILITY

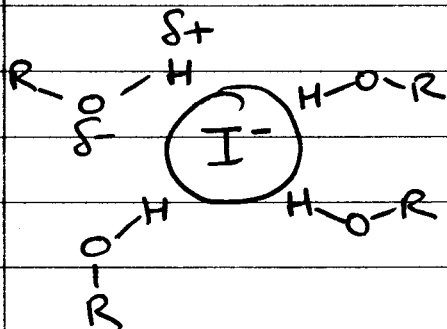
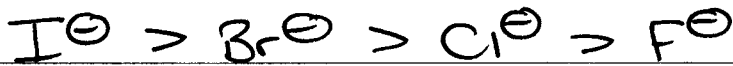
Larger atoms, more diffuse electron clouds \Rightarrow greater polarisability \rightarrow BONDS can begin to form at greater INTERATOMIC DISTANCES.

(iii) SOLVENT (large effect)

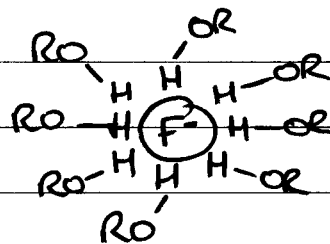
- POLAR PROTIC (H_2O , MeOH , EtOH , $\text{H}-\overset{\text{O}}{\parallel}-\text{OH}$)

- POLAR APROTIC (DMSO , DMF , MeCN , Acetone)

POLAR PROTIC SOLVENTS

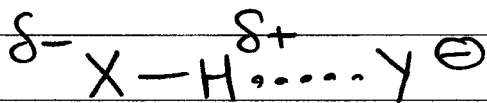


LOW CHARGE DENSITY
(weak solvent cage)



HIGH CHARGE DENSITY
(strong solvent cage)

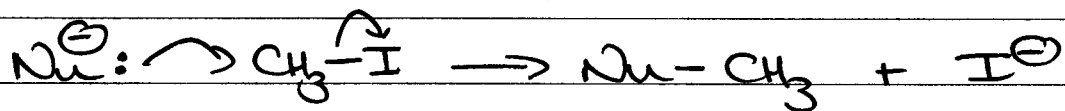
HYDROGEN BONDING - noncovalent interaction



So, smaller Nu = higher charge density
 \Rightarrow more solvated LESS NUCLEOPHILIC

BUT IN POLAR APROTIC SOLVENTS

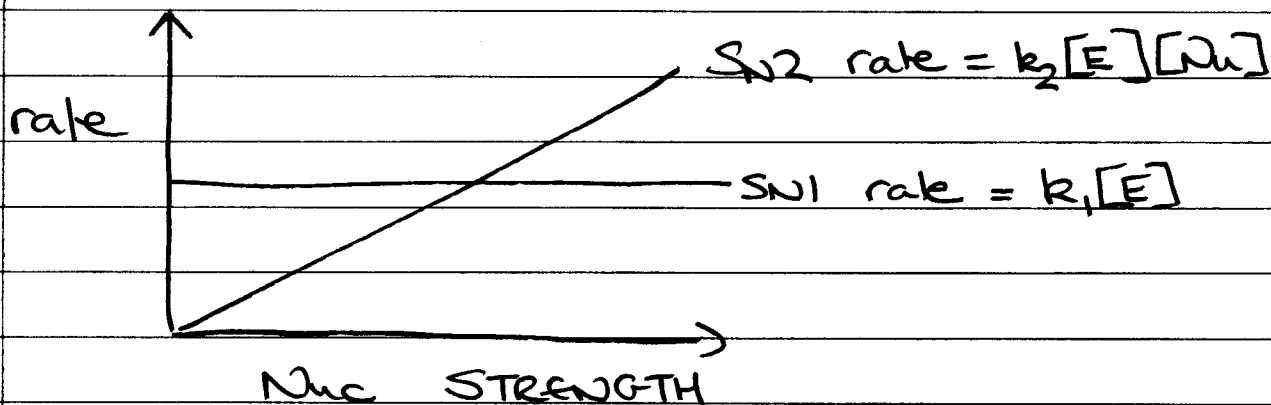
\Rightarrow ANIONS WEAKLY SOLVATED, trend is reversed and correlates w/ BASICITY



Nu	pKa	MeOH (time to complete reaction)	DMF \rightarrow (time to complete reaction)	equiv polarities
I ⁻	-10	17 min	8.7s	OVERALL MESSAGE
Br ⁻	-8	12h	8.7s	POLAR PROTIC SOLVENTS ARE GOOD
Cl ⁻	-6	13d	1.4s	
F ⁻	3	>2yrs	<1.2s	

(10)

S_N1 vs S_N2



No effect on S_N1 , but stronger Nu favors S_N2 reactions.