GOC - Reaction Mechanism - 1

1. stability of an intermediate $\propto \frac{1}{|\text{charge on species}|}$.

2. Electrophile = e^- loving = Lewis acides
Nucleophile = nucleus loving = Lewis bases
Ambident nucleophile = nucleophile with 2 or more e^- rich centres.

3. Carbocation = $CH_3^{\oplus}$ = sp^2, 6 e^- (deficient), diamagnetic
Carbanion = $CH_3^{\ominus}$ = sp^3, 8 e^- (rich), diamagnetic
Carbon free radical = $CH_3^{\bullet}$ = sp^2, 7 e^- (deficient), paramagnetic.
Carbene = $:CH_2$ = 6 e^- (deficient)
Nitrene = $:\ddot{N}-$ = 6 e^- (deficient).
I effect — applicable till 4th C, distance dependent

4. -I groups ⇒ $OR_2^{\oplus} > NR_3^{\oplus} > NH_3^{\oplus} > NO_2 > SO_3H > CN > COOH > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$.
($C=C$ or sp^2 C shows -I).
+I groups ⇒ $H < D < T < CH_3 < C_2H_5 < C_3H_7 < \ldots\ldots < COO^{\ominus} < O^{\ominus} < NH^{\ominus}$.
Distance is more dominant than strength of the I group.

5. In nitrogen containing compounds, more the e^- density on Nitrogen, more is the basic strength. (3° amine > 2° > 1° > NH_3).
But in aqueous sol., NR_3 NHR_2 NH_2R
If R = CH_3 — $2^\circ > 1^\circ > 3^\circ$
If R = C_2H_5 — $2^\circ > 3^\circ > 1^\circ$
Methanol is more acidic than water due to higher pKa.

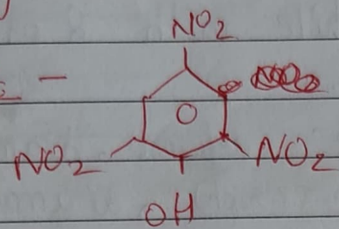
6. Symmetrical resonating structures are more stable than a number of asymmetrical resonating structures.

7. +M groups = Activating groups = o/p directing groups
Eg - OH, OCH_3, NH_2, CH_2, C_2H_5, $:\ddot{F}:$.
stability of resonating structures

Due to intramolecular H-bonding, acidic strength decreases (by 1 position)

-M groups = Deactivating groups / m-directing groups.
Eg - Cl, Br, I, NO_2, COOH, SO_3H, CN,
$-HC=CH_2$, $-C\equiv CH$
M effect not applicable at meta position.
Carboxylic acids are always more acidic than alcohols/phenols.

Except -



2,4,6 - trinitrophenol / picric acid
↓
one of the most acidic organic compounds.

8. Ortho effect - ortho substituent of COOH or NH_2
- any ortho substituent (big groups)
with COOH - acidic strength is most
- big group with NH_2. - least basic strength.

9. Hyperconjugation - α H must be present
- not shown by $C^{\ominus}$.
more α H ⇒ more stability.

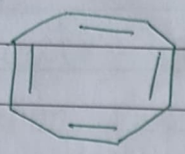
10. Stability of alkenes ∝ α-H ∝ $\frac{1}{\text{Heat of hydrogenation (HOH)}}$,
(HOH ∝ reactivity) reactivity

11. Aromatic compounds - (i) cyclic compound
(ii) sp^2 or sp C must only be present
(iii) complete conjugation
(iv) $(4n+2)\pi$ e^- or
$(2n+1)\pi$ bonds.

Anti-aromatic compounds - (i), (ii), (iii) same
(iv) $4n$ π e^- or
$2n$ π bonds.

If (i), (ii) or (iii) - not applicable
⇒ Non-aromatic

Stability = Aromatic > Non-aromatic > Anti-aromatic.

Exception  – structure becomes non planar due to presence of 8c in same plane (steric hindrance).
∴ non-aromatic.

12. Acidic strength ∝ $-M\ \alpha\ -H\ \alpha\ -I\ \alpha\ \perp\ \alpha\ \perp\ \alpha\ \perp$.
$+I \quad +H \quad +M$

Basic strength ∝ $+M\ \alpha\ +\overset{H}{\underset{H}{N}}\ \alpha\ +I\ \alpha\ \perp\ \alpha\ \perp\ \alpha\ \perp$.
$-I \quad -H \quad -M$

(+ is stabilized by + effects.
– is stabilized by – effects.
charge.

Distance is more dominant than strength of groups in these effects.

→ Stability of RS
① octet should be complete or max. no. of bonds.
② non-polar structures are more stable than polar ones.
③ In polar structures, –ve charge should be on more electro –ve atom and +ve charge on more electro +ve atom.
④ Unlike charges should be near while like charges should be far apart.

→ c+ / c· rearrangement.
→ ring expansion / contraction.

GOC - Reaction Mechanism - 2

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(1) Substitution

(a) Free Radical - alkanes and allylic/benzylic alkenes

→ 3 steps - initiation, propagation, termination.

(i) Halogenation (F_2 / Cl_2 / Br_2 / I_2)

(ii) Nitration (conc. HNO_3, 400°c) - breaking of C-C bonds also takes place - mixture of nitroalkanes is formed.

(iii) Sulphonation (direct - $H_2S_2O_7$ or fuming H_2SO_4)

(iv) Reed reaction (chlorosulphonation) (indirect (i) $SO_2 + Cl_2$ (ii) NaOH or H_2O ← hydrolysis)

(v) Allylic/Benzylic substitution (NBS/hν or Br_2 (low conc.)/hν)

(b) Electrophilic - benzene and its derivatives

→ 2 steps - (i) Lewis acid is used
(ii) sigma complex formation.

(i) Halogenation (X_2 and $FeCl_3$ or $AlCl_3$)

(ii) Nitration (conc. HNO_3 + conc. H_2SO_4) NO_2^+ = attacking species

(iii) Sulphonation (conc. H_2SO_4) SO_3 = attacking species.

(iv) Friedel Craft Alkylation

(v) Friedel craft Acylation

(vi) Gatterman's Koch Reaction (CO + HCl)

(vii) Gatterman's Aldehyde Synthesis (HCN + HCl)

(c) Nucleophilic - alkyl halides and acid derivatives

SN^1	SN^2
- 3° alkyl halides and more stable 2° alkyl halides	- less stable 2° and all 1° alkyl halides
- racemic mixture obtained.	- Walden inversion (100% inversion)
	(DMF = dimethyl formamide favours SN^2)

Lewisite gas = 2-chlorovinyl dichloro arsine (4 times more poisonous than mustard gas).

(2) Addition (shown by unsaturated and carbonyl compounds)

(a) Electrophilic (alkenes) (Markownikov, Modified Markownikov)

→ Case 1 = E^+ has no lone pair. Rearrangement ✓

Case 2 = E^+ has lone pair. Rearrangement X. (cyclic mechanism)

(i) Halogen (X_2)
(ii) Halogen acid (HX)
(iii) Hypohalous acid (HOX)
(iv) water (H_2O)
(v) Tilden reagent (NOCl)
(vi) Hydroboration oxidation (i) BH_3 / THF (ii) H_2O/H^+ or H_2O/OH^-.
(vii) Oxymercuration demercuration
(i) $Hg(OAc)_2$ / H_2O
(ii) $NaBH_4$.

(b) Free Radical (alkenes)

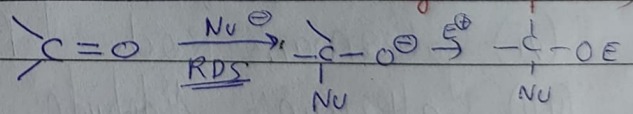
(i) catalytic hydrogenation (Ni/Pd/Pt/Δ)
(ii) Peroxide/Kharasch effect/Anti-markovnikov (HBr, peroxide)

(c) Nucleophilic (Alkynes and carbonyl compounds)

C_1 (alkynes)

(i) Water (1% $HgSO_4$ + 40% H_2SO_4)
(ii) Alcohol (HgO and BF_3)
(iii) $AsCl_3$ ($AlCl_3$ or $HgCl_2$)
acetylene + $AsCl_3$ → Lewisite gas ★

C_2 (carbonyl compounds)



Reactivity of CO $\propto$ $\frac{1}{\text{Stability of } C^+}$

(3) Elimination

α elimination / 1,1 elimination

$CHCl_3 \xrightarrow{KOH} :CCl_2$ (di-chloro carbene)

β Elimination / 1,2 Elimination

E_1

(i) Dehydration of alcohol (-HOH). (Saytzeff)
↳ ($H_2SO_4 \rightarrow H^+$).

E_2

(i) Dehydrohalogenation of halides (alcoholic KOH / $NaNH_2$)
(Saytzeff)

(ii) Pyrolysis of tetra alkyl ammonium ion (OH^-)
- Hoffmann

(4) Isomerization

in presence of $AlCl_3$ / HCl or $Al_2(SO_4)_3$ / H_2SO_4

$CH_3-CH_2-C\equiv H \xrightarrow{\text{alc. KOH}} CH_3-C\equiv C-CH_3$ (internal alkyne formed.)

$NaNH_2 \rightarrow$ terminal alkyne formed