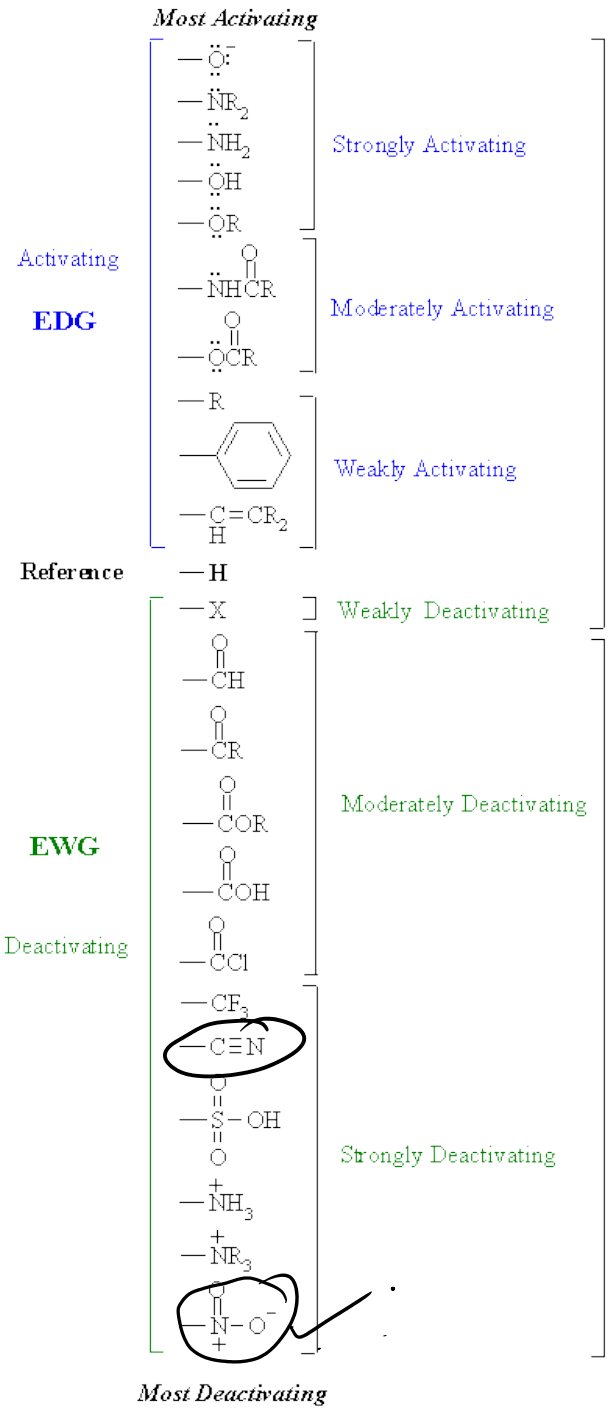
IMPORTANT NAMED REACTIONS

Electrophilic Substitution Reactions



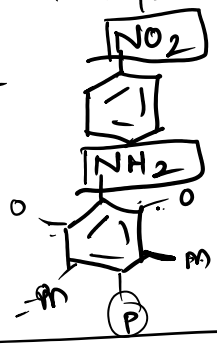
3. types
1. Addition
2. Substitution
3. Elimination.

Aromatic.

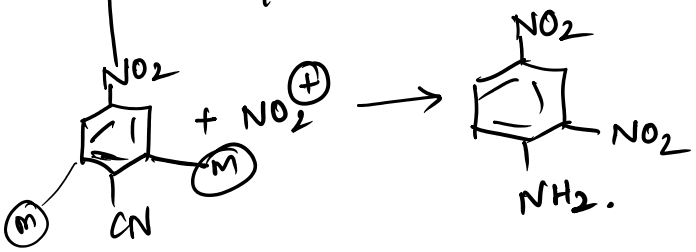
1. Electrophile - e⁻ loving
2. Nucleophile - e⁻ hating (or) e⁻ rich

Aromatic — nitration, Sulphonation, F.CA/Alky, Halogenation.

1. EWG -



① EWG ⇒ meta position
② EDG ⇒ "O, P" position.
③ both are present "go with Strength"



Nucleophilic Substitution Reactions: SN1 / SN2

Feature	SN1 (Substitution Nucleophilic Unimolecular)	SN2 (Substitution Nucleophilic Bimolecular)
1. Mechanism	Two-step mechanism: 1. Formation of carbocation (slow) 2. Nucleophilic attack (fast)	Single-step mechanism: Simultaneous bond breaking and formation
Rate Law	Rate = k[RX] (First order)	Rate = k[RX][Nu^-] (Second order)
Rate Determining Step	Carbocation formation	Complete reaction
Substrate Preference	3° > 2° > 1° Best: $(CH_3)_3C$-X	1° > 2° >> 3° Best: CH_3-X
Stereochemistry	Racemization (usually) Some retention possible due to ion pairs	Inversion of configuration (always) Walden inversion
Solvent Preference	Polar protic solvents (H_2O, ROH, HCOOH)	Polar aprotic solvents (DMF, DMSO, acetone)
Nucleophile Strength	Not important Even weak nucleophiles work	Very important Strong nucleophiles needed
Temperature Effect	Higher temperature favors reaction	Less dependent on temperature
Leaving Group	Good leaving groups required Order: $I^- > Br^- > Cl^- > F^-$	Same order of preference $I^- > Br^- > Cl^- > F^-$

	$Cl^- > F^-$	
Competitive Reactions	Competes with E1 Higher temperature favors E1	Competes with E2 Strong base favors E2
Rearrangement	Possible through carbocation	Not possible
Examples	$(CH_3)_3C\text{-}Br + H_2O \rightarrow (CH_3)_3C\text{-}OH$	$CH_3CH_2\text{-}Br + CN^- \rightarrow CH_3CH_2CN$
Concentration Effect	$[Nu^-]$ doesn't affect rate	$[Nu^-]$ directly affects rate
Energy Diagram	Two-humped curve (shows intermediate)	Single-humped curve (shows transition state)
Kinetic Evidence	Rate independent of $[Nu^-]$	Rate dependent on both [RX] and $[Nu^-]$
Activation Energy	Generally higher (due to carbocation formation)	Generally lower (single concerted step)

Nucleophilic Substitution Reactions

Finkelstein Reaction :

$R\text{-}Cl + NaI \rightarrow R\text{-}I + NaCl$

Mechanism: SN2 displacement

Swarts Reaction:

$R\text{-}Cl + AgF \rightarrow R\text{-}F + AgCl$

Mechanism: SN2 nucleophilic substitution

Elimination & Addition:

Saytzeff's Rule :

$R\text{-}X + KOH \rightarrow$ More substituted alkene

Mechanism: E2 elimination

Hofmann Rule:

$R_4N^+OH^- \rightarrow$ Less substituted alkene

Mechanism: E2 elimination

Markovnikov's Rule

$R\text{-}CH{=}CH_2 + HBr \rightarrow R\text{-}CHBr\text{-}CH_3$

Mechanism: Electrophilic addition — -ve addenum go to more Substituted. (or) less no. of Hydrogen.

Anti-Markovnikov's Rule:

$R\text{-}CH{=}CH_2 + HBr/ROOR \rightarrow R\text{-}CH_2\text{-}CH_2Br$ *Mechanism: Free radical addition*

Coupling Reactions

Wurtz Reaction

$2R\text{-}X + 2Na \rightarrow R\text{-}R + 2NaX$ → higher alkanes.

Mechanism: Free radical coupling

Wurtz-Fittig Reaction

$R\text{-}X + Ar\text{-}X + 2Na \rightarrow R\text{-}Ar + 2NaX$

Mechanism: Free radical coupling

Fittig Reaction

$2Ar\text{-}X + 2Na \rightarrow Ar\text{-}Ar + 2NaX$

Mechanism: Free radical coupling

Alcohols & Ethers

Williamson Synthesis

$R\text{-}X + R'O^-Na^+ \rightarrow R\text{-}O\text{-}R' + NaX$

Mechanism: SN2 substitution

Lucas Test :

$R\text{-}OH + ZnCl_2/HCl \rightarrow R\text{-}Cl + H_2O$ (1°/2°/3°-OH)

Mechanism: SN1/SN2 depending on alcohol

Aldehydes & Ketones

Aldol Condensation :

$2RCHO \rightarrow RCH(OH)CH_2CHO \rightarrow RCH{=}CHCHO$ (Aldol. → Alkene.) *Mechanism:*

Aldol Condensation :

$2RCHO \rightarrow RCH(OH)CH_2CHO \rightarrow RCH=CHCHO$ Aldol. Alkene. Mechanism: Nucleophilic addition-elimination

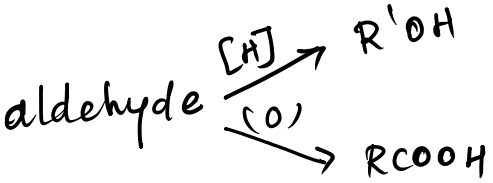
Cross Aldol Condensation :

$RCHO + R'CHO \rightarrow RCH=CHCOR'$

Mechanism: Nucleophilic addition-elimination

Cannizzaro Reaction :

$2RCHO + OH^- \rightarrow RCH_2OH + RCOO^-$



Mechanism: Hydride transfer

Crossed Cannizzaro :

$RCHO + R'CHO + OH^- \rightarrow RCH_2OH + R'COO^-$ Mechanism: Hydride transfer

Clemmensen Reduction :

$RCOR' + Zn(Hg)/HCl \rightarrow RCH_2R'$ Acid.

Mechanism: Reduction via organometallic intermediate

Wolff-Kishner Reduction :

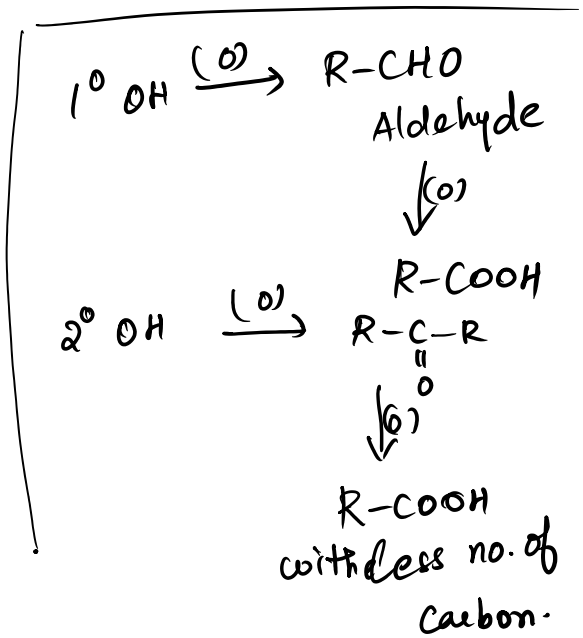
$RCOR' + NH_2NH_2/KOH \rightarrow RCH_2R'$ base.

Mechanism: Hydrazone formation followed by decomposition

MPV Reduction :

$RCOR' + Al(OiPr)_3 \rightarrow RCH(2^{o}OH)R'$

Mechanism: Hydride transfer



Carboxylic Acids

Hell-Volhard-Zelinsky :

$RCOOH + X_2/P \rightarrow RCHXCOOH$ HVZ.

Mechanism: α-halogenation via acid halide

Kolbe Electrolysis :

$2RCOO^- \rightarrow R\text{-}R + 2CO_2 + 2e^-$

Mechanism: Decarboxylation followed by radical coupling

Aromatic Substitution

Friedel-Crafts Alkylation :

$ArH + RX + AlCl_3 \rightarrow ArR + HX$

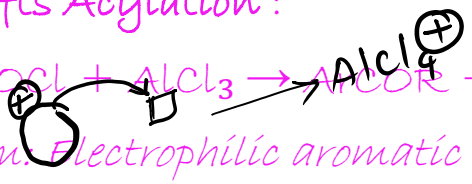
EDG ⇒ "o, p"

EWG ⇒ meta.

Mechanism: Electrophilic aromatic substitution

Friedel-Crafts Acylation :

$ArH + RCOCl + AlCl_3 \rightarrow ArCOR + HCl$



Mechanism: Electrophilic aromatic substitution

Reimer-Tiemann :

$ArOH + CHCl_3 + NaOH \rightarrow Ar\text{-}CHO$

Intermediate. $\ominus CHCl_2$

"Mechanism"

Mechanism: Carbene addition

Kolbe-Schmidt:

$ArONa + CO_2 \rightarrow ArOH\text{-}COOH$

Mechanism: Electrophilic substitution

Diazonium Reactions

Sandmeyer Reaction :

$ArN_2^+X^- + CuX \rightarrow ArX + N_2$

Mechanism: Single electron transfer

Gattermann Reaction

$ArN_2^+Cl^- + Cu/HCl \rightarrow ArCl + N_2$

Mechanism: Single electron transfer

Amine Reactions

Hoffmann Bromamide :

$RCONH_2 + Br_2/NaOH \rightarrow RNH_2 + CO_2$

Amide ⟶ Amine.

Mechanism: Rearrangement

Gabriel Phthalimide

$C_8H_4O_2NK + RX \rightarrow RNH_2$

1° amine.

Mechanism: SN2 followed by hydrazinolysis

Rearrangements

Mechanism: SN2 followed by hydrazinolysis

Rearrangements

Carbylamine Reaction :

$RNH_2 + CHCl_3 + KOH \rightarrow RNC$

Mechanism: α-elimination — Alkyl isocyanide

Pinacol-Pinacolone :

$R_2C(OH)\text{-}C(OH)R_2 + H^+ \rightarrow R_3CCOR$

Mechanism: 1,2-rearrangement

Beckmann Rearrangement :

$R_2C{=}NOH + H^+ \rightarrow RCONHR$

Mechanism: Migration with N departure

Hofmann Rearrangement :

$RCONH_2 + Br_2/NaOH \rightarrow RNH_2$

Mechanism: Migration to electron-deficient nitrogen

Important Tests

Hinsberg Test :

$RNH_2 + C_6H_5SO_2Cl \rightarrow$ Different products for 1°, 2°, 3° amines

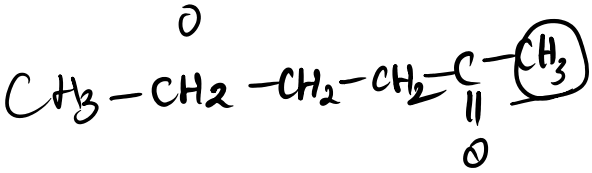
dif. 1°, 2°, 3°.

Mechanism: Nucleophilic substitution

Iodoform Test :

$CH_3COR + I_2/NaOH \rightarrow CHI_3 + RCOONa$

CH_3 must be there in α position.



Mechanism: Base-catalyzed halogenation

Polymer Formation:

Free Radical Polymerization:

$nCH_2{=}CHX \rightarrow -(CH_2\text{-}CHX)n-$

Mechanism: Initiation, propagation, termination

Condensation Polymerization :

$nA\text{-}A + nB\text{-}B \rightarrow -(A\text{-}B)n-$

Mechanism: Step-growth

Rearrangement Reactions

Benzidine Rearrangement :

$C_6H_5-N=N-C_6H_5 \rightarrow H_2N-C_6H_4-C_6H_4-NH_2$

Mechanism: [1,2]-sigmatropic rearrangement

Wagner-Meerwein Rearrangement:

$R_3C^+ \rightarrow$ Migration of H or R

Mechanism: Carbocation rearrangement

Claisen Rearrangement :

Allyl phenyl ether → o-allylphenol

Mechanism: [3,3]-sigmatropic rearrangement

Addition Reactions:

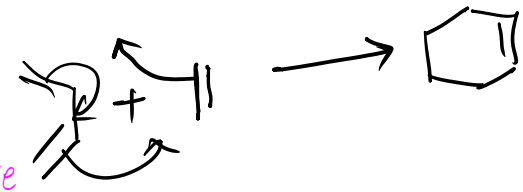
Birch Reduction

ArH + Na/NH_3 → 1,4-dihydroArH

Mechanism: Radical anion formation

Diels-Alder Reaction

Diene + dienophile → cyclohexene derivative



Mechanism: [4+2] cycloaddition

Oxidation Reactions

Etard Reaction

$ArCH_3 + CrO_2Cl_2 \rightarrow ArCHO$

$-CH_3 \rightarrow$ benzaldehyde.

Mechanism: Oxidation of toluene derivatives

Oppenauer Oxidation

Secondary alcohol + $Al(OiPr)_3$ → Ketone

Mechanism: Hydride transfer (reverse of MPV)

Substitution Reactions

Von Richter Reaction

$ArNO_2 + CN^- \rightarrow$ m-carboxylic acid

Mechanism: Nucleophilic aromatic substitution

Bucherer Reaction

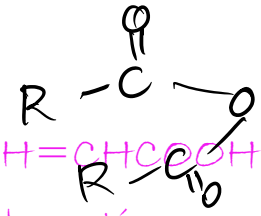
$ArOH \rightleftharpoons ArNH_2$ (interconversion)

Mechanism: Nucleophilic aromatic substitution

Condensation Reactions

Perkin Reaction :

$ArCHO + (RCO)_2O \rightarrow ArCH=CHCOOH$



unsat. Carboxylic.

Mechanism: Aldol type condensation

Knoevenagel Condensation :

$RCHO + CH_2(COOR')_2 \rightarrow RCH=C(COOR')_2$ Mechanism: Base-catalyzed condensation

Elimination Reactions

Cope Elimination : $R_3N^+O^- \rightarrow$ Alkene + R_2NOH Mechanism: syn-elimination

Important Name Reactions with Reagents

Reformatsky Reaction $RCHO + BrCH_2COOR' + Zn \rightarrow$ β-hydroxy ester Mechanism: Organozinc addition

Stephen Reaction $RCN + SnCl_2/HCl \rightarrow RCHO$ Mechanism: Reduction of nitrile

Additional Test Reactions

Beilstein Test For halogens (green flame) Mechanism: CuX formation

Tollens' Test $RCHO + [Ag(NH_3)_2]^+ \rightarrow RCOO^- + Ag\downarrow$ Mechanism: Oxidation of aldehyde

Special Mention

Fischer Esterification $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$ Mechanism: Nucleophilic acyl substitution

Grignard Reaction $RMgX$ + various substrates Mechanism: Nucleophilic

addition

JEE Advanced 2018:

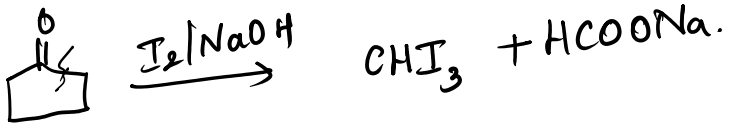
1. The product formed when cyclopentanone reacts with $I_2/NaOH$ is:

a) $HCO_2Na + CHI_3$

b) Only CHI_3

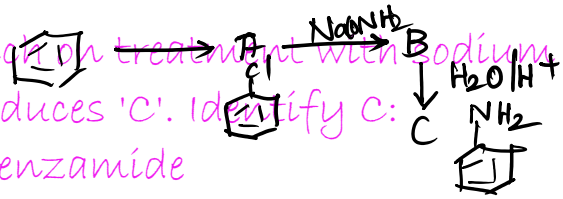
c) No reaction

d) Ring opening doesn't occur



2. Benzene on monochlorination gives 'A' which on treatment with sodium amide yields 'B'. 'B' on acid hydrolysis produces 'C'. Identify C:

a) Phenol b) Aniline c) Chlorobenzene d) Benzamide



JEE Main 2019:

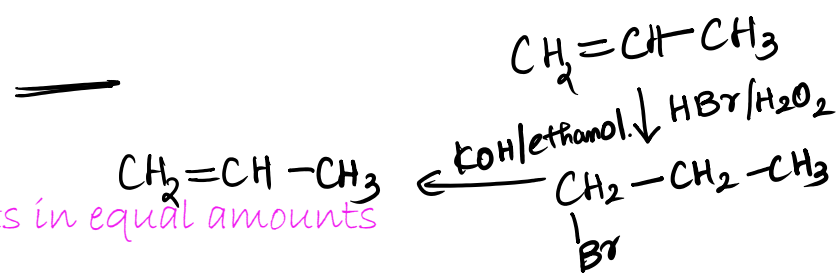
3. In Friedel-Crafts acylation of anisole with acetyl chloride and $AlCl_3$, the major product is:

a) o-methoxyacetophenone

b) p-methoxyacetophenone

c) m-methoxyacetophenone

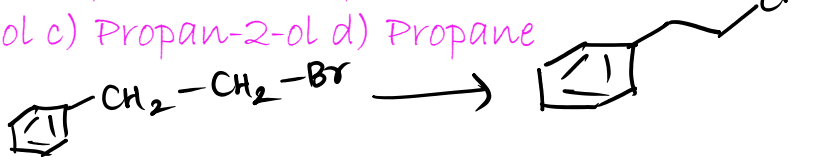
d) mixture of o- and p-products in equal amounts



JEE Advanced 2017:

4. The major product in: Propene → HBr/peroxide → KOH/ethanol → X is:

a) Propene b) Propan-1-ol c) Propan-2-ol d) Propane



JEE Main 2016:

5. Which compounds give positive iodoform test?

a) Only acetone b) Acetone and 2-pentanone c) All ketones d) Only aldehydes

JEE Advanced 2016:

6. Major product in: $PhCH_2CH_2Br + KCN \rightarrow ?$

a) $PhCH_2CH_2CN$ b) $PhCH=CHCN$ c) $PhCN$ d) $Ph\text{-}CH(CN)\text{-}CH_3$

JEE Main 2015: 7. Identify A: $C_6H_5NH_2 \rightarrow C_6H_5N_2Cl \rightarrow A$

a) C_6H_5Cl b) C_6H_5F c) C_6H_5OH d) C_6H_5CN

JEE Advanced 2015:

8. Product when benzaldehyde reacts with concentrated KOH:

a) Only benzyl alcohol b) Only potassium benzoate c) Benzyl alcohol + Potassium benzoate d) Rosenmund Redn.

Catalyst

JEE Main 2014:

9. Reagent to convert acid chlorides to aldehydes:

a) $LiAlH_4$ b) $Pd/BaSO_4 + H_2$ c) Na/ethanol d) Zn-Hg/HCl

JEE Advanced 2014:

10. Product of: $CH_3COCH_2COOC_2H_5 + NaOH + I_2 \rightarrow$

a) Only CHI_3 b) Only CH_3COONa c) $CHI_3 + CH_3COONa + CO_2$ d) No reaction

H.W

JEE Main 2013:

11. Decreasing order of reactivity towards nucleophilic addition:

a) $HCHO > CH_3CHO > PhCHO > CH_3COCH_3$ b) $CH_3COCH_3 > PhCHO > CH_3CHO > HCHO$ c) $PhCHO > HCHO > CH_3CHO >$

HCHO

a) PhCHO > CH_3CHO > HCHO b) PhCHO > HCHO > CH_3CHO > CH_3COCH_3 c) PhCHO > HCHO > CH_3CHO > CH_3COCH_3

d) CH_3CHO > HCHO > CH_3COCH_3 > PhCHO

JEE Advanced 2013:

12. In: $PhCH_2Br \rightarrow PhCH_2MgBr \rightarrow PhCH_2CH_2OH$, second step uses:

a) H_2O b) CH_2O c) CO_2 d) O_2

JEE Main 2012:

13. Major product in Reimer-Tiemann reaction of phenol:

a) p-hydroxybenzaldehyde b) m-hydroxybenzaldehyde c) o-hydroxybenzaldehyde d) mixture of all isomers

JEE Advanced 2012:

14. Acetophenone with Zn(Hg)/HCl gives: a) Ethylbenzene b) Acetaldehyde c) Ethanol d) Benzyl alcohol

JEE Main 2011:

15. Best sequence for benzene → benzoic acid:

a) $CH_3Cl/AlCl_3 \rightarrow KMnO_4/OH^-$ b) Direct oxidation c) $CO_2/AlCl_3$ d) $CH_3OH/AlCl_3$