

Free radical substitution

Free radical = very reactive species with unpaired e⁻
 → H atoms on halogenoalkanes/alkenes replaced by halogen atoms (F/Cl/Br/I)

X.S F₂/Cl₂/Br₂/I₂ needed

Initiation: molecule → radical
 F₂ $\xrightarrow{\text{UV light}}$ 2F• / Cl₂ $\xrightarrow{\text{UV light}}$ 2Cl•

Propagation: molecule + radical → molecule + radical

Every replaced H = 1 propagation step

CH₄ + Cl• → •CH₃ + HCl

CH₃ + Cl₂ → CH₃Cl + Cl•

Termination: radical + radical → molecule

Steps chain reactⁿ

2 • CH₃ → CH₃-CH₃

2 • CCl₃ → CCl₃-CCl₃

Depletion of Ozone O₃:

Cl₂ $\xrightarrow{\text{UV light}}$ 2Cl•

Cl• + O₃ → ClO• + O₂

ClO• + O₂ → Cl• + 2O₂

Overall: Cl₂ → 2Cl• (Cl regenerates)

Nucleophilic addition

Reduction of aldehyde/ketones

NaBH₄ (aq) - source of H⁻

Primary alcohol

Secondary alcohol

Ketone

Nucleophilic addition-elimination

Acylation: Insertion of acyl group R-C(=O)
 by replacing H on nucleophile.
 Nucleophiles: RNH₂ > NH₃ > ROH > H₂O

Best L.P most available

Products: N substituted R-C(=O)-N-R'

amide R-C(=O)-NH₂

ester R-C(=O)-OR'

H₂O → Carboxylic acid R-C(=O)-OH

mechanism

amine/ammonia

Alcohol/alcohol

SALT + RNH₃⁺

Example with acid anhydride + amine

Example with acid anhydride + water

* Only 1 product

Electrophilic substitution

Nitration: H atom on benzene ring replaced by NO₂ (nitro) group.
 Conditions: conc H₂SO₄ & HNO₃ 50°C
 2 steps:

1 Generation of electrophile:
 HNO₃ + 2H₂SO₄ → NO₂⁺ + 2HSO₄⁻ + H₂O

2 Nitration: Nitronium ion

Nitro Benzene

3 steps: Friedel crafts acylation

Conditions: Acyl chloride or Acyl chloride or Anhydrous

1 Generation of electrophile

2 Acylium ion

3 Regeneration of catalyst

AlCl₄⁻ + H⁺ → AlCl₃ + HCl

Example with acid anhydride + methyl benzene

1 HC(=O)-O-C(=O)-CH₃ + AlCl₃ → HC(=O)⁺ + [AlCl₃-O-C(=O)-CH₃]⁻

2 Aromatic ketone

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