COLLEGE OF EDUCATION FOR PURER SCIENCE
CHEMISTRY DEPARTMENT
CLASS 4
ELECTIVE ORGANIC CHEMISTRY

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INTRODUCTION TO NITRO COMPOUNDS

CHEMISTRY OF ORGANIC FUNCTIONAL GROUPS

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LECTURE 1

– WHAT ARE NITRO COMPOUNDS?

- ORGANIC COMPOUNDS CONTAINING ONE OR MORE **–NO_2 GROUPS** BONDED DIRECTLY TO CARBON ATOMS
- EXAMPLES: NITROMETHANE, NITROBENZENE
- SOME ARE NATURALLY OCCURRING; MOST ARE SYNTHETIC
- USED IN INDUSTRIAL SOLVENTS AND EXPLOSIVES

– Structure of the Nitro Group

- Resonance hybrid of two equivalent structures

- sp^2 hybridization at nitrogen

- Delocalized π orbital over N and O atoms

- - Bond length ~121 pm (between single and double bond)

CLASSIFICATION

- **ALIPHATIC NITRO COMPOUNDS** (NITROPARAFFINS): E.G., NITROMETHANE
- **AROMATIC NITRO COMPOUNDS** (NITROARENES): E.G., NITROBENZENE
- BASED ON CARBON ATTACHMENT:
  - PRIMARY, SECONDARY, TERTIARY NITRO COMPOUNDS

– Isomerism

- Nitro compounds vs. alkyl nitrites (isomers)
- Carbon bonded to oxygen in nitrites
- Structural isomerism due to position of nitro group

– Nomenclature

- IUPAC rules: prefix “nitro” + parent hydrocarbon
- Numbering gives lowest possible number to nitro group
- Examples:
  - 1-nitropropane
  - p-nitrotoluene

- Nitro compounds contain the –NO_2 functional group
- Classified as aliphatic or aromatic
- Resonance-stabilized nitro group
- Important in industrial and explosive applications

PREPARATION OF NITRO COMPOUNDS

LECTUR 2

From Saturated Hydrocarbons

- Vapour phase nitration using HNO_3 or N_2O_4
- Free radical mechanism
- Products: mixtures of nitroalkanes
- Industrial use: solvents

From Unsaturated Hydrocarbons

- Alkenes react with N_2O_4/O_2 → vic-dinitro compounds
- Base-catalyzed elimination → nitroalkenes

From Alkyl Halides

- Ambident nucleophile: nitrite ion (attacks via O or N)

- Reactions with $NaNO_2$ or $AgNO_2$

- Yields: nitro compounds (N attack) or nitrites (O attack)

From Halocarboxylic Acids

- Chloroacetic acid + nitrite → nitroacetic acid → decarboxylation → nitromethane

From Amines

- Oxidation of primary amines → hydroxylamine → nitroso compound → nitro compound

- $KMnO_4$ in aqueous acetone → high yield of nitro compounds

Preparation of Aromatic Nitro Compounds

- Nitration of benzene using nitrating mixture (HNO_3 + H_2SO_4)
- Electrophilic substitution mechanism
- Formation of nitronium ion (NO_2^+) as electrophile

Summary

- Methods include nitration of alkanes/arenes, reaction of halides/nitrite, oxidation of amines
- Each method has specific conditions and reagents
- Understanding mechanisms helps predict products

PHYSICAL PROPERTIES AND ACIDIC NATURE OF NITRO COMPOUNDS

LECTUR 3

Physical Properties

- Highly polar with large dipole moments (~3–4 D)

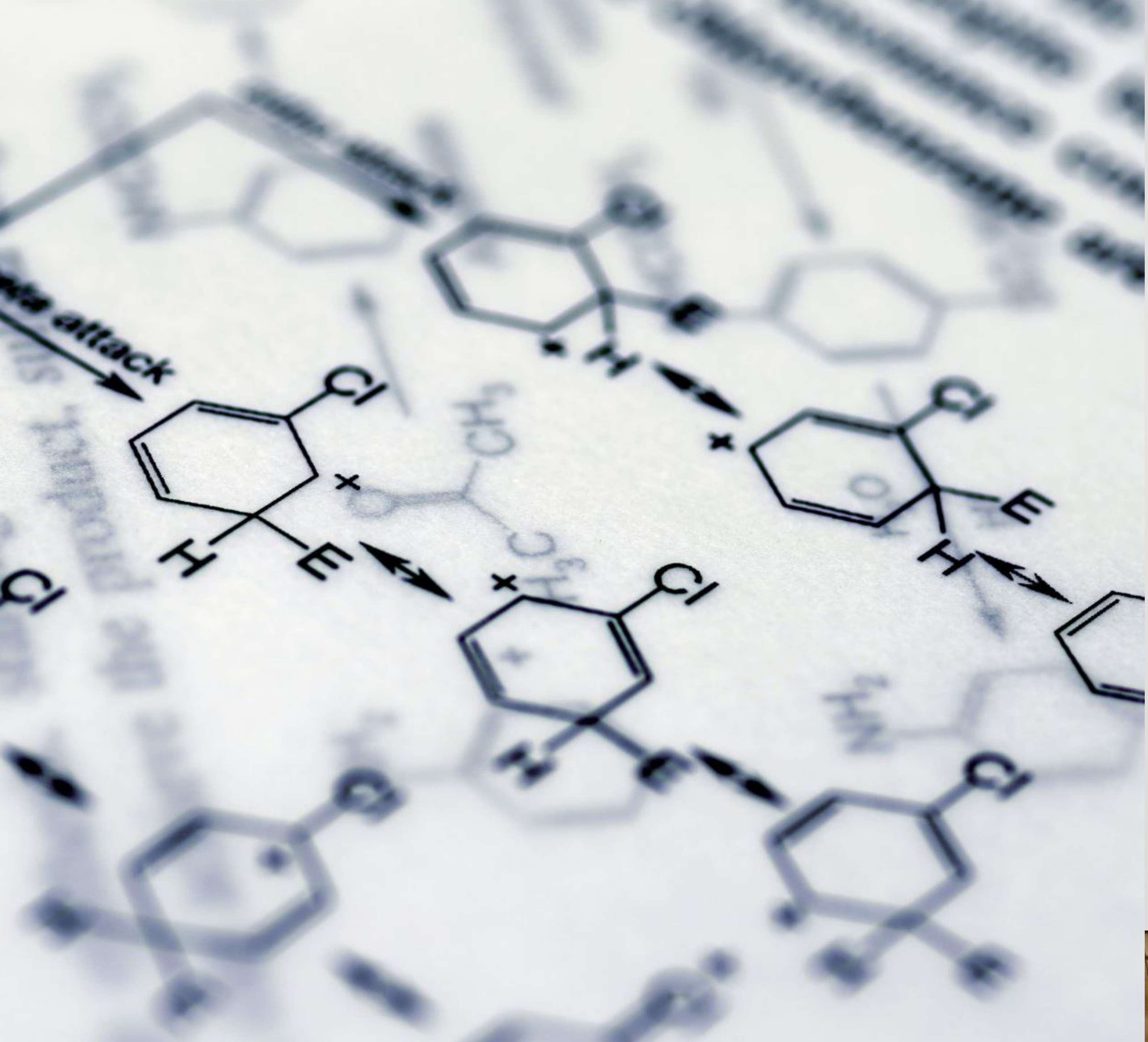
- Boiling points higher than isomeric nitrites

- Solubility: lower members sparingly soluble in water

- Explosive nature (especially polynitro compounds

Comparison with Nitrites

- Nitro compounds vs. alkyl nitrites
- Differences in polarity, boiling point, solubility
- Stability: nitroalkanes stable; nitroarenes unstable



- **Acidic Character of α-Hydrogens**
- **- Electron-withdrawing effect of nitro group**
- **- Stabilization of conjugate base (nitronate ion) by resonance**
- **- Dissolves in strong bases like NaOH**

Aci-Nitro Form

- Tautomer of nitro compound
- More acidic and reactive
- Can act as nucleophile or electrophile in reactions

Pseudo-Acidity

- Slow back conversion from aci-form to nitro form
- Makes nitro compounds appear only weakly acidic
- Applications in organic synthesis

Summary

- Nitro compounds are highly polar and have unique physical behavior

- α-Hydrogens show acidic character due to resonance stabilization

- Aci-nitro form plays key role in many reactions

CHEMICAL REACTIONS OF NITROALKANES

LECTUR 4

HENRY REACTION

- CARBON-CARBON BOND FORMATION
- REACTION BETWEEN NITRO COMPOUND (ACI-FORM) AND ALDEHYDE/KETONE
- PRODUCT: B-NITRO ALCOHOL OR A-NITROALKENE

Michael Addition

- With α,β-unsaturated esters/carbonyl compounds
- Base-catalyzed addition
- Product: Michael adducts

Halogenation

- Chlorination/bromination of α-hydrogens
- All α-H replaced under basic conditions
- Example: chloropicrin from nitromethane

Alkylation

- Deprotonation → nitronate ion → reaction with alkyl halides

- Butyllithium used for deprotonation

- Useful for creating new C–C bonds

– Nef Reaction

- Hydrolysis of nitro compounds → aldehydes/ketones + nitrous oxide
- Two-step process: salt formation + acid hydrolysis

Mannich Reaction

- With formaldehyde and amine
- Forms nitroamines
- Used in pharmaceutical synthesis

Hydrolysis of Nitroalkanes

- Cleavage of C–N bond under acidic conditions

- Primary nitroalkanes → carboxylic acids + hydroxylamine

- Secondary nitroalkanes → ketones + nitrous oxide

Summary

- Nitroalkanes undergo diverse reactions due to aci-form
- Many reactions involve nucleophilic/electrophilic behavior
- Useful in forming new C–C and C–N bonds

REDUCTION AND SUBSTITUTION REACTIONS OF NITRO COMPOUNDS

LECTUR5

OVERVIEW OF REDUCTION PATHWAYS
- STEPWISE REDUCTION: NITRO → NITROSO → HYDROXYLAMINE → AMINE
- FINAL PRODUCT: PRIMARY AMINE IF FULLY REDUCED

CATALYTIC REDUCTION
- H_2 WITH CATALYSTS (NI, PT, PD/C)
- CLEANEST ROUTE TO ANILINE-TYPE COMPOUNDS

ACIDIC MEDIUM REDUCTION
- METALS (FE, SN, ZN) + HCL
- TRANSFER OF ELECTRONS AND PROTONS
- SIDE PRODUCTS POSSIBLE WITH SNCL$_2$

NEUTRAL AND ALKALINE REDUCTION

- NEUTRAL: ZN + NH_4CL → HYDROXYLAMINES
- ALKALINE: NAOH/GLUCOSE → AZOXYBENZENE
- ZN + NAOH → AZOBENZENE

ELECTROLYTIC AND LIALH$_4$ REDUCTION - PH-DEPENDENT ELECTROLYTIC REDUCTION - LITHIUM ALUMINUM HYDRIDE GIVES PRIMARY AMINES (ALIPHATIC) OR AZO COMPOUNDS (AROMATIC)

– ELECTROPHILIC SUBSTITUTION
- META-DIRECTING EFFECT OF NITRO GROUP
- DEACTIVATES RING → ONLY META POSITIONS REACT
- NO FRIEDEL-CRAFTS REACTION DUE TO STRONG ELECTRON WITHDRAWAL

– NUCLEOPHILIC SUBSTITUTION
- ORTHO/PARA POSITIONS ATTACKED BY NUCLEOPHILES
- EXAMPLE: KOH → O-NITROPHENOL
- PRESENCE OF SECOND NITRO GROUP ENHANCES DISPLACEMENT

– BENZIDINE REARRANGEMENT
- MECHANISM: [5,5] SIGMATROPIC REARRANGEMENT
- IMPORTANCE IN DYE CHEMISTRY

SUMMARY

- NITRO COMPOUNDS CAN BE REDUCED TO VARIOUS NITROGEN-CONTAINING PRODUCTS
- REDUCTION PATHWAY DEPENDS ON MEDIUM AND REAGENT
- NITRO GROUP INFLUENCES SUBSTITUTION REACTIONS SIGNIFICANTLY
- REARRANGEMENT REACTIONS OPEN PATHWAYS TO COMPLEX MOLECULES