Propose A Synthesis Of Each Of The Following Compounds Using The Indicated Starting Material. You May

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Introduction

The synthesis of organic compounds is a fundamental aspect of organic chemistry, with applications spanning pharmaceuticals, materials science, and chemical research. When designing synthetic routes, chemists often start from readily available or easily prepared starting materials, aiming to transform them into complex target molecules efficiently and selectively. This article explores various synthetic strategies for converting specific starting materials into desired compounds, illustrating the principles of retrosynthesis, functional group transformations, and strategic reagent choice. The focus will be on proposing viable, step-by-step synthetic routes for each compound, considering reaction conditions, intermediate stability, and overall yield.

General Principles for Designing Synthetic Routes

Before diving into specific examples, it is essential to understand some core principles:

Retrosynthetic Analysis

- Break down the target molecule into simpler, more accessible precursors.
- Identify key disconnections that simplify the synthesis.
- Consider functional group interconversions that facilitate subsequent transformations.

Functional Group Compatibility

- Choose reagents and conditions that do not interfere with existing functional groups.
- Protect groups if necessary to mask reactive sites.

Strategic Use of Reactions

- Utilize classical reactions such as substitutions, additions, eliminations, and rearrangements.
- Employ modern techniques like cross-coupling, oxidation, and reduction reactions.

Yield and Selectivity

- Optimize conditions to maximize yield.
- Control stereochemistry and regioselectivity where applicable.

Proposing Synthesis Routes for Selected Compounds

1. Synthesis of Aniline from Nitrobenzene

Starting Material: Nitrobenzene

Retrosynthetic Analysis

- The target compound, aniline, can be obtained by reducing nitro groups to amino groups.
- The most straightforward pathway involves catalytic hydrogenation or metal reduction.

Proposed Synthetic Route

1. Reduction of Nitrobenzene to Aniline

Reaction Conditions and Reagents

- **Catalytic Hydrogenation:** Use hydrogen gas (H_2) with a metal catalyst such as Pd/C or PtO_2 under mild conditions.
- **Chemical Reduction:** Alternatively, employ iron powder or zinc dust in acidic conditions (e.g., Fe/HCl or Zn/HCl).

Summary

- The reduction process converts the nitro group ($-NO_2$) to an amino group ($-NH_2$), yielding aniline efficiently.

2. Synthesis of Benzaldehyde from Benzene

Starting Material: Benzene

Retrosynthetic Analysis

- Benzaldehyde contains an aldehyde functional group attached to a benzene ring.
- Synthesis involves introducing a formyl group onto benzene.

Proposed Synthetic Route

1. Friedel–Crafts formylation of benzene to produce benzaldehyde.

Reaction Conditions and Reagents

- Reagent: Formaldehyde source, typically paraformaldehyde or formyl chloride.
- Catalyst: Aluminum chloride ($AlCl_3$).
- Conditions: Reflux in an inert solvent like dichloromethane or nitrobenzene, under controlled temperature.

Summary

- The electrophilic formylation attaches the -CHO group to the benzene ring, giving benzaldehyde.

3. Synthesis of Acetic Acid from Ethylene

Starting Material: Ethylene

Retrosynthetic Analysis

- Ethylene can be oxidized to produce acetic acid via various pathways, including carbonylation reactions.

Proposed Synthetic Route

1. Ethylene Carbonylation (Monsanto process):
2. Use of carbon monoxide (CO) and a catalyst such as rhodium or iridium complexes to convert ethylene into acetic acid.

Reaction Conditions and Reagents

- Reagents: Ethylene gas, carbon monoxide, metal catalyst (e.g., Rhodium complex).
- Conditions: Elevated temperature and pressure in a reactor designed for hydrocarbon carbonylation.

Summary

- The process involves inserting a carbonyl group into ethylene, ultimately producing acetic acid with high efficiency.

4. Synthesis of Ethanol from Ethene

Starting Material: Ethene

Retrosynthetic Analysis

- Ethene can be hydrated to give ethanol via addition of water across the double bond.

Proposed Synthetic Route

1. Electrophilic hydration of ethene to form ethanol.

Reaction Conditions and Reagents

- Reagents: Water (H_2O).
- Catalyst: Acid catalyst such as sulfuric acid (H_2SO_4).
- Conditions: Acid-catalyzed hydration under mild temperature and pressure.

Summary

- The process adds water across the double bond, yielding ethanol efficiently.

5. Synthesis of Toluene from Benzene

Starting Material: Benzene

Retrosynthetic Analysis

- Toluene can be synthesized via alkylation of benzene with methyl groups.

Proposed Synthetic Route

1. Friedel–Crafts alkylation of benzene with methyl chloride (CH_3Cl).

Reaction Conditions and Reagents

- Reagents: Methyl chloride (CH_3Cl).
- Catalyst: Aluminum chloride ($AlCl_3$).

- Conditions: Reflux in an inert solvent, typically in the presence of the Lewis acid catalyst.

Summary

- The electrophilic methylation introduces a methyl group onto benzene, forming toluene.

Advanced Considerations and Optimizations

For each synthetic route, considerations such as yield optimization, stereochemical control, and environmentally benign reagents are crucial. For example:

Protecting Groups

- Protect sensitive functional groups during multi-step syntheses to prevent side reactions.

Catalyst Selection

- Use of heterogeneous vs. homogeneous catalysts impacts reaction efficiency and separation.

Green Chemistry Principles

- Employing less toxic reagents and minimizing waste aligns with sustainable practices.

Conclusion

Proposing synthetic routes from simple or readily available starting materials requires a strategic combination of retrosynthetic analysis, functional group transformations, and reaction condition optimization. Whether converting nitrobenzene to aniline or benzene to benzaldehyde, each pathway exemplifies foundational principles of organic synthesis. By carefully selecting reagents, catalysts, and reaction conditions, chemists can efficiently construct complex molecules from simple precursors, advancing both scientific understanding and practical applications. Future developments in catalysis, green chemistry, and automation will continue to refine these synthetic strategies, making chemical synthesis more sustainable and versatile.

Frequently Asked Questions

What is a common approach to synthesize an alcohol from an alkene as the starting material?

You can perform an acid-catalyzed hydration of the alkene, typically using dilute H_2SO_4, to produce the corresponding alcohol.

How can you synthesize a carboxylic acid starting from a primary alkyl halide?

React the primary alkyl halide with a strong oxidizing agent like potassium permanganate (KMnO4) under controlled conditions to oxidize it to the corresponding carboxylic acid.

What method is used to synthesize an amine from a nitrile as the starting material?

Reduce the nitrile using a reducing agent such as lithium aluminum hydride (LiAlH4) to obtain the primary amine.

How can a ketone be synthesized from a secondary alcohol as the starting material?

Oxidize the secondary alcohol using an oxidizing agent like PCC or Jones reagent to form the corresponding ketone.

What is the typical synthesis route for an ester from a carboxylic acid as the starting material?

React the carboxylic acid with an alcohol in the presence of an acid catalyst (usually H2SO4) to perform esterification, forming the ester.

How can an alkyl halide be converted into an alkene?

Use a dehydrohalogenation reaction, typically by treating the alkyl halide with a strong base like KOH or NaOH to eliminate HX and form the alkene.

What is a common synthesis method for a phenol from a benzene derivative?

Subject benzene to hydroxylation conditions, such as with NaOH and oxygen, or via electrophilic aromatic substitution using reagents like Fe or Cu catalysts with oxygen.

How can a primary amine be synthesized from an aldehyde as the starting material?

Perform reductive amination by reacting the aldehyde with ammonia and a reducing agent like sodium cyanoborohydride (NaBH3CN).

What is the typical pathway to synthesize an alkyl thiol from an alkyl halide?

React the alkyl halide with thiourea to form a thiouronium salt, then hydrolyze it to obtain the alkyl thiol.

How can a conjugated diene be synthesized from a monoalkene?

Use dehydrohalogenation or elimination reactions on appropriate alkyl halides or alcohols to introduce additional double bonds, forming the conjugated diene system.

Additional Resources

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Introduction

Organic synthesis is the cornerstone of chemical innovation, enabling the construction of complex molecules from simpler starting materials. The ability to efficiently and selectively synthesize target compounds is essential for pharmaceuticals, agrochemicals, materials science, and academic research. This comprehensive guide will focus on proposing synthetic routes for various compounds starting from specified materials, emphasizing the strategic choices, reaction mechanisms, and practical considerations involved.

In this discussion, we will explore each compound individually, outlining possible synthetic pathways, reagents, conditions, and rationales for each step. The goal is to provide a deep understanding of how to approach such syntheses, considering stereochemistry, yield optimization, environmental factors, and overall feasibility.

General Principles in Planning Organic Synthesis

Before delving into individual cases, it’s important to recall some foundational principles:

- Retrosynthetic Analysis: Starting from the target molecule, work backwards to identify simpler precursor structures.
- Functional Group Compatibility: Choose reactions that do not interfere with existing groups.
- Chemoselectivity and Regioselectivity: Favor reactions that selectively modify desired sites.
- Stereochemistry: Maintain or establish stereocenters with control over stereochemistry.
- Step Economy: Minimize the number of steps to improve overall yield and reduce waste.
- Availability of Reagents: Opt for commercially available and cost-effective reagents.

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1. Synthesis of an Aromatic Amine from Nitrobenzene

Starting Material: Nitrobenzene

Target Compound: Aniline (Phenylamine)

Proposed Synthetic Route:

Step 1: Reduction of Nitrobenzene to Aniline

- Reaction Type: Catalytic hydrogenation
- Reagents & Conditions:
- Catalyst: Palladium on carbon (Pd/C), Raney nickel, or platinum
- Hydrogen gas (H_2) at atmospheric or elevated pressure
- Solvent: Ethanol, ethanol-water mixture, or acetic acid
- Mechanism:
- The nitro group undergoes stepwise reduction:
- Nitro → Nitroso → Hydroxylamine → Amine
- Catalytic hydrogenation facilitates the transfer of hydrogen atoms to reduce the nitro group efficiently.
- Considerations:
- Avoid over-reduction of aromatic ring (generally not an issue here)
- Control temperature and pressure to optimize yield

Alternative Methods:
- Metallic Reduction:
- Using Fe/HCl or Sn/HCl under reflux
- Suitable for small-scale syntheses
- Chemical Reducing Agents:
- Tin(II) chloride ($SnCl_2$)
- Sodium dithionite

Summary:

This straightforward reduction transforms a nitro group into an amine, yielding aniline with high purity and efficiency.

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2. Synthesis of a Primary Alcohol from Alkene via Hydroboration-Oxidation

Starting Material: 1-Butene

Target Compound: 1-Butanol

Proposed Synthetic Route:

Step 1: Hydroboration-Oxidation

- Reaction Type: Syn addition of boron and hydrogen across the alkene
- Reagents & Conditions:
- Reagents: diborane (B_2H_6) or borane (BH_3) complex
- Oxidant: Hydrogen peroxide (H_2O_2) in the presence of sodium hydroxide (NaOH)
- Solvent: Tetrahydrofuran (THF)
- Mechanism:
- The boron adds to the less substituted carbon (anti-Markovnikov addition)
- Oxidation replaces boron with hydroxyl group

- Outcome:
- Converts terminal alkene into primary alcohol with anti-Markovnikov selectivity

Alternative:
- Markovnikov addition: Using acid-catalyzed hydration, but yields secondary or tertiary alcohols depending on the alkene structure.

Summary:

Hydroboration-oxidation provides a regioselective synthesis of primary alcohols from terminal alkenes, offering high stereoselectivity and minimal rearrangements.

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3. Synthesis of a Ketone from an Alkyl Halide via Oxidation

Starting Material: 2-Bromopropane

Target Compound: Acetone (Propanone)

Proposed Synthetic Route:

Step 1: Formation of a Grignard Reagent

- Reagents & Conditions:
- Magnesium turnings
- Anhydrous diethyl ether
- Reaction: 2-bromopropane + Mg → Propylmagnesium bromide (Grignard reagent)

Step 2: Nucleophilic Addition to Carbon Dioxide

- Reagents & Conditions:
- Pass CO_2 gas through the Grignard solution
- The Grignard adds to CO_2, forming a carboxylate intermediate

Step 3: Acid Work-up

- Reagents & Conditions:
- Acidic aqueous solution (e.g., HCl)
- Converts carboxylate to carboxylic acid

Step 4: Decarboxylation to Ketone

- Alternative Path:
- Instead, directly oxidize the Grignard reagent with suitable oxidants (e.g., CuO) to produce ketones
- Or, perform oxidation of secondary alcohols derived from Grignard addition

Alternative Route:

- Oxidation of secondary alcohols:
- Synthesize isopropanol via Grignard addition to acetaldehyde

- Oxidize isopropanol using PCC or CrO_3 to acetone

Summary:

Starting from an alkyl halide, forming a Grignard reagent enables addition to suitable carbonyl compounds or oxidation steps to produce ketones.

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4. Synthesis of a Carboxylic Acid from an Alkene via Oxidation

Starting Material: Ethene

Target Compound: Ethanoic acid (Acetic acid)

Proposed Synthetic Route:

Step 1: Ozonolysis of Alkene

- Reaction: Breaks the double bond, generating aldehyde intermediates

Step 2: Oxidation of Aldehyde

- Reagents & Conditions:
- Use of potassium permanganate ($KMnO_4$) or potassium dichromate ($K_2Cr_2O_7$) under acidic or neutral conditions
- Conversion of aldehyde to carboxylic acid

Alternatively:

- Direct oxidative cleavage:
- Using strong oxidants to cleave the double bond directly into carboxylic acids

Summary:

Oxidation of alkenes through ozonolysis followed by acidification provides an efficient route to carboxylic acids.

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5. Synthesis of an Ether from Alcohols via Williamson Ether Synthesis

Starting Material: Ethanol

Target Compound: Ethyl methyl ether

Proposed Synthetic Route:

Step 1: Preparation of Alkoxide Ion

- Reagents & Conditions:

- Sodium metal or sodium hydride (NaH)
- Ethanol reacts with NaH to form sodium ethoxide

Step 2: Nucleophilic Substitution

- Reagents & Conditions:
- Methyl iodide (CH_3I)
- Reacts with sodium ethoxide via SN2 mechanism

- Outcome:
- Formation of ethyl methyl ether

Considerations:

- Use of primary halides favors SN2 reactions
- Avoiding steric hindrance enhances yield

Summary:

Williamson ether synthesis provides a straightforward method for constructing ethers from alcohols and alkyl halides.

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6. Synthesis of an Amide from a Carboxylic Acid and Amine

Starting Material: Benzoic acid

Target Compound: Benzamide

Proposed Synthetic Route:

Step 1: Activation of Carboxylic Acid

- Reagents & Conditions:
- Convert to acyl chloride using thionyl chloride ($SOCl_2$) or oxalyl chloride

Step 2: Nucleophilic Attack by Amine

- Reagents & Conditions:
- Benzylamine
- Reaction with acyl chloride under basic or neutral conditions

- Outcome:
- Formation of benzamide via nucleophilic acyl substitution

Alternative:

- Direct amidation using coupling agents like DCC or EDC if starting with the acid

Summary:

Conversion of carboxylic acids to acyl chlorides followed by reaction with amines is a reliable pathway to amides.

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7. Synthesis of a Thiol from an Alkyl Halide

Starting Material: 1-Chloropropane

Target Compound: Propanethiol

Proposed Synthetic Route:

Step 1: Nucleophilic Substitution

- Reagents & Conditions:
- Thiourea (NH_2CSNH_2)
- Reacts with alkyl halide to form an isothiouronium salt

Step 2: Hydrolysis

- Reagents & Conditions:
- Basic aqueous solution (NaOH)
- Hydrolyzes the isothiouronium salt to release the thiol

Alternative Route:

- Direct nucleophilic substitution using thiourea or thiolate ions

Summary:

Thiolation via nucleophilic substitution provides an

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