Draw The Major Product(s) Obtained When Each Of The Following Compounds Is Treated With Fuming Sulfuric

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Understanding the chemical reactions involving fuming sulfuric acid—also known as oleum—is essential for students and professionals in organic chemistry. Fuming sulfuric acid is a highly concentrated form of sulfuric acid containing free sulfur trioxide (SO_3), which makes it a powerful reagent capable of inducing various reactions such as sulfonation, oxidation, and dehydration. When specific organic compounds are treated with fuming sulfuric acid, they undergo characteristic transformations leading to distinct major products. This article provides a comprehensive overview of the major products formed when different compounds are subjected to fuming sulfuric acid, supported by detailed explanations, reaction mechanisms, and illustrative examples.

Introduction to Fuming Sulfuric Acid and Its Reactivity

Fuming sulfuric acid (oleum) is a mixture of sulfuric acid (H_2SO_4) and free sulfur trioxide (SO_3). Its strong electrophilic nature makes it a potent reagent in organic synthesis. It is commonly used for:

- Sulfonation: Introducing sulfonic acid groups (–SO_3H) into aromatic compounds.
- Dehydration: Removing water from alcohols and other compounds.
- Oxidation: Altering oxidation states of certain functional groups.
- Chlorosulfonation and other substitution reactions.

The exact product depends on the structure of the starting compound and the reaction conditions, such as temperature and concentration.

Reactions of Fuming Sulfuric Acid with Aromatic Compounds

Aromatic compounds, especially benzene and its derivatives, undergo sulfonation when treated with fuming sulfuric acid. This process introduces sulfonic acid groups onto the aromatic ring, often resulting in the formation of sulfonic acids.

1. Benzene

Reaction: When benzene reacts with fuming sulfuric acid, the major product is benzene sulfonic acid (benzenesulfonic acid).

Mechanism: The SO_3 component acts as an electrophile, attacking the aromatic ring to form a sigma complex, which then loses a proton to restore aromaticity, resulting in sulfonation.

Major Product:

- Benzenesulfonic acid ($C_6H_5SO_3H$):

Notes:
- The sulfonation is an electrophilic aromatic substitution.
- Usually occurs at room temperature.
- The product increases the water solubility of benzene.

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2. Toluene

Reaction: Fuming sulfuric acid sulfonates toluene primarily at the methyl group or the ring, depending on reaction conditions.

Major Product:

- Toluene-4-sulfonic acid (p-toluenesulfonic acid):

- Often the predominant product due to the activating effect of the methyl group.

Additional Products:
- Sometimes ortho- and para-sulfonic acids are formed in a mixture.

Mechanism:
- Similar electrophilic substitution as benzene, with increased reactivity because of the methyl group’s activating effect.

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3. Naphthalene

Reaction: Naphthalene undergoes sulfonation, predominantly at the more reactive alpha (1-position).

Major Product:

- Naphthalene-1-sulfonic acid

Significance:
- Used in dye manufacturing and as a precursor for various organic syntheses.

Reactions of Fuming Sulfuric Acid with Alkyl and Aryl Halides

Fuming sulfuric acid can also react with halides, leading to sulfonation or chlorosulfonation, depending on the substrate.

1. Alkyl Halides

Reaction: Under certain conditions, alkyl halides can undergo sulfonation or chlorosulfonation, replacing halogen atoms with sulfonic groups.

Major Product:

- Usually, the formation of sulfonic acids from alkyl halides is less common; instead, reactions tend to involve substitution of halogen atoms by sulfonic groups when possible.

2. Aryl Halides

Reaction: Aromatic halides such as chlorobenzene can be sulfonated to produce sulfonic acids.

Major Product:

- Sulfonated chlorobenzene derivatives, such as chlorobenzenesulfonic acid.

Reactions of Fuming Sulfuric Acid with Alcohols and

Phenols

Fuming sulfuric acid exhibits dehydration properties, especially with alcohols and phenols, leading to aromatic sulfonation or dehydration products.

1. Phenol

Reaction: Phenol reacts with fuming sulfuric acid to form phenolsulfonic acids, predominantly ortho and para isomers.

Major Product:

- Phenol-2-sulfonic acid (ortho-sulfonic acid derivative)

- Phenol-4-sulfonic acid (para-sulfonic acid derivative)

Notes:
- Due to the activating nature of the hydroxyl group, sulfonation occurs mainly at ortho and para positions.

2. Alcohols (Primary and Secondary)

Reaction: Alcohols generally undergo dehydration to form alkenes when treated with fuming sulfuric acid.

Major Product:

- Alkenes: e.g., ethanol gives ethene and ethyl hydrogen sulfate as intermediates.

Additional Note:
- When heated, dehydration is favored, with the major product being the corresponding alkene.

Reactions of Fuming Sulfuric Acid with Unsaturated Compounds

Unsaturated compounds such as alkenes and alkynes react with fuming sulfuric acid via addition reactions, leading to sulfonation or addition products.

1. Alkenes

Reaction: Under controlled conditions, alkenes undergo addition with SO_3, forming alkyl hydrogen sulfates.

Major Product:

- Alkyl hydrogen sulfate (e.g., ethyl hydrogen sulfate from ethene)

Application:
- These intermediates are valuable in manufacturing detergents and surfactants.

2. Alkynes

Reaction: Alkynes can undergo addition reactions forming sulfonated derivatives.

Reactions of Fuming Sulfuric Acid with Other Functional Groups

Fuming sulfuric acid also reacts with various functional groups, often leading to oxidation, sulfonation, or dehydration.

1. Carboxylic Acids

Reaction: Generally, carboxylic acids are stable under sulfonation conditions; however, oxidizable groups may undergo oxidation.

2. Amines and Amino Compounds

Reaction: Amines tend to undergo sulfonation to produce sulfonamide derivatives.

Summary of Major Products for Key Compounds

Compound	Major Product(s)	Notes
Benzene	Benzene sulfonic acid (benzenesulfonic acid)	Electrophilic aromatic substitution
Toluene	Toluene-4-sulfonic acid (p-toluenesulfonic acid)	Activating methyl group, para isomer favored
Naphthalene	Naphthalene-1-sulfonic acid	More reactive at alpha position
Phenol	Phenol-2-sulfonic acid and phenol-4-sulfonic acid	Ortho and para sulfonation
Alkyl halides	Corresponding sulfonic acids (if substituted)	Usually via nucleophilic substitution
Alcohols	Alkenes (via dehydration), alkyl hydrogen sulfates	Dehydration to alkenes, sulfonation intermediates
Unsaturated hydrocarbons	Alkyl hydrogen sulfates (addition products)	Addition across double bonds

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Conclusion

Treating compounds with fuming sulfuric acid results in a variety of major products depending on the structure and functional groups present. Aromatic compounds mainly undergo sulfonation to produce sulfonic acids, which are valuable in dyes, detergents, and pharmaceuticals. Alkyl and aryl halides can be sulfonated or chlorosulfonated, while

alcohols and phenols often undergo dehydration or sulfonation at specific positions.

Understanding these reactions enables chemists to design synthetic pathways for desired compounds, optimize reaction conditions, and harness the reactivity of fuming sulfuric acid effectively. Always remember that the conditions—such as temperature, concentration, and duration—play a crucial role in determining the major products formed in these reactions.

Note: For detailed reaction mechanisms and structural illustrations, consulting organic chemistry textbooks or peer-reviewed articles is recommended.

Frequently Asked Questions

What is the major product formed when an alkene is treated with fuming sulfuric acid?

The major product is an alkyl hydrogen sulfate, formed by the addition of hydrogen sulfate (HSO_4^-) across the double bond of the alkene.

When phenol reacts with fuming sulfuric acid, what is the main product obtained?

Phenol reacts with fuming sulfuric acid to produce phenol sulfate, an aryl sulfate derivative resulting from electrophilic substitution.

What major product is formed when an alcohol is treated with fuming sulfuric acid?

The primary product is an alkyl hydrogen sulfate, formed via sulfonation of the alcohol's hydroxyl group.

How does fuming sulfuric acid react with aromatic compounds like benzene?

It can lead to sulfonation, producing benzene sulfonic acid as the major product.

What is the major product when an alkene with a tertiary carbon is treated with fuming sulfuric acid?

The major product is typically an alkyl hydrogen sulfate, with regioselectivity favoring more stable carbocation intermediates.

Does treatment of alkynes with fuming sulfuric acid lead to addition products? If so, what are they?

Yes, alkynes generally undergo electrophilic addition with sulfuric acid, resulting in dihydroxyalkyl sulfates initially, which can further sulfonate to produce sulfate derivatives.

What is the difference in products obtained from treating primary versus secondary alcohols with fuming sulfuric acid?

Primary alcohols mainly form alkyl hydrogen sulfates, while secondary alcohols can form similar products but may also undergo sulfonation at different positions, depending on the structure.

Can fuming sulfuric acid cause sulfonation of heterocyclic compounds? What is the typical product?

Yes, heterocyclic compounds can undergo sulfonation, leading to heteroaryl sulfonic acids as the major products.

Additional Resources

Draw The Major Product(s) Obtained When Each Of The Following Compounds Is Treated With Fuming Sulfuric

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Introduction

Fuming sulfuric acid, also known as oleum, is a highly concentrated form of sulfuric acid containing free sulfur trioxide (SO_3). It is a powerful sulfonating agent, capable of introducing sulfonyl groups into organic molecules with high efficiency. Due to its reactivity, treatment of various organic compounds with fuming sulfuric acid often results in distinctive sulfonation products, which are of significant interest in both industrial applications and organic synthesis. This article delves into the mechanisms, typical products, and detailed pathways involved when specific compounds are

subjected to fuming sulfuric acid.

Understanding Fuming Sulfuric Acid and Its Reactivity

Fuming sulfuric acid is a mixture of sulfuric acid (H_2SO_4) and free SO_3. Its strong electrophilic nature enables it to add sulfonyl groups ($-SO_3H$) to aromatic and some aliphatic compounds. The key features influencing the outcome include:

- Electrophilic sulfonation: The SO_3 acts as an electrophile, attacking electron-rich sites.
- Reaction conditions: Typically carried out at controlled temperatures to prevent over-sulfonation or degradation.
- Position selectivity: For aromatic compounds, sulfonation usually occurs at the most activated positions—ortho or para—depending on existing substituents.

General Principles of Sulfonation with Fuming Sulfuric Acid

- Aromatic Sulfonation: Typically proceeds via an electrophilic aromatic substitution mechanism.
- Aliphatic Sulfonation: Less common; when it occurs, it often involves oxidation or insertion into C-H bonds.
- Multiple sulfonations: Can happen if excess acid or prolonged reaction times are used, leading to disulfonates or polysulfonates.

Treatment of Specific Compounds with Fuming Sulfuric Acid

In this section, we analyze the major products obtained upon sulfonation of various representative compounds. For each compound, we examine the reaction mechanism, the position of sulfonation, and the structural features influencing the product distribution.

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1. Benzene

Expected Major Product: Benzenesulfonic acid (or sulfonic acid benzene)

Mechanism and Pathway

Benzene undergoes electrophilic aromatic substitution with SO_3, facilitated by fuming sulfuric acid. The process involves:

- Formation of the sigma complex (arenium ion), where SO_3 attacks the aromatic ring.
- Deprotonation restores aromaticity, resulting in sulfonic acid.

Product Details:

- Product: Benzenesulfonic acid ($C_6H_5SO_3H$)
- Position: Para and ortho isomers may form, but usually, the para isomer predominates due to steric considerations in the reaction environment.

Significance:

Benzenesulfonic acid is widely used as a surfactant, in dye manufacturing, and as a precursor for various sulfonate derivatives.

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2. Toluene

Expected Major Product: p-Toluenesulfonic acid (p-TS)

Mechanism and Pathway

Toluene's methyl group is an activating and ortho/para-directing substituent, increasing electron density at these positions. When treated with fuming sulfuric acid:

- The electrophile (SO_3) preferentially reacts at the para position due to steric hindrance at ortho positions.
- The methyl group stabilizes the sigma complex, favoring sulfonation at the para position.

Product Details:

- Major product: p-Toluenesulfonic acid (para-isomer)
- Minor product: ortho-toluenesulfonic acid, but in smaller amounts.

Industrial Relevance:

p-Toluenesulfonic acid is a strong acid used as a reagent in organic synthesis, especially in the preparation of sulfonate esters and as a catalyst.

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3. Aniline

Expected Major Product: p-Aminobenzenesulfonic acid (sulfanilamide)

Mechanism and Pathway

Aniline is an aromatic amine with a strongly activating amino group. When sulfonated:

- The amino group directs sulfonation to the ortho and para positions.
- Under mild conditions, sulfonation predominantly occurs at the para position due to less steric hindrance and less electrostatic repulsion.

Product Details:

- Major product: p-Aminobenzenesulfonic acid
- Additional notes: The amino group can be sulfonated further under harsher conditions, leading to disulfonation.

Industrial and Pharmaceutical Use:

p-Aminobenzenesulfonic acid is used in dyes, pharmaceuticals, and as a precursor to sulfonamide antibiotics.

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4. Naphthalene

Expected Major Product: Naphthalenesulfonic acid (primarily 1- or 2-naphthalenesulfonic acid)

Mechanism and Pathway

Naphthalene, being polycyclic and aromatic, undergoes sulfonation at the most reactive site:

- Typically at the 1-position (α-position) due to higher electron density.
- The sulfonation occurs via electrophilic attack, forming a sigma complex stabilized by the aromatic system.

Product Details:

- Major isomer: 1-Naphthalenesulfonic acid
- Minor isomer: 2-Naphthalenesulfonic acid (less reactive site)

Applications:

Used in dye manufacturing, as a surfactant, and in the production of naphthalene derivatives.

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5. Phenol

Expected Major Product: Phenol sulfonic acids (ortho- and para-)

Mechanism and Pathway

Phenol is activated toward electrophilic substitution due to

the lone pair on oxygen:

- Sulfonation occurs predominantly at the ortho and para positions.
- Under controlled conditions, para is usually favored due to steric factors.

Product Details:

- Main products: ortho- and para-phenolsulfonic acids
- Predominance: p-phenolsulfonic acid tends to be the major product.

Uses:

Phenol sulfonic acids serve as intermediates in dye synthesis and as surfactants.

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6. Acetanilide

Expected Major Product: p-Acetanilidesulfonic acid

Mechanism and Pathway

Acetanilide, with an amino substituent, directs sulfonation ortho and para. However, the acyl group reduces the activating effect of the amino group, making the reaction milder:

- The para position is favored.
- Sulfonation occurs at the para position relative to the

acetanilide group.

Product Details:

- Major product: p-Acetanilidesulfonic acid
- Application: Used in dye manufacturing and as intermediates.

Factors Influencing Sulfonation Outcomes

- Substituents on aromatic rings: Electron-donating groups activate and direct sulfonation to ortho and para positions; electron-withdrawing groups deactivate.
- Reaction temperature: Elevated temperatures can lead to multiple sulfonations or degradation.
- Concentration of fuming sulfuric acid: Excess promotes poly-sulfonation; milder conditions favor mono-sulfonation.
- Presence of directing groups: Functional groups like amino, hydroxyl, or methyl influence regioselectivity.

Industrial Significance and Applications

The products obtained from sulfonation with fuming sulfuric acid are crucial in various sectors:

- Dye industry: Many dyes are sulfonated aromatic compounds.
- Surfactants: Sulfonates are key surfactants in cleaning agents.
- Pharmaceuticals: Sulfonated derivatives serve as

intermediates in drug synthesis.
- Polymer industry: Sulfonated materials enhance properties such as ion exchange capacity.

Concluding Remarks

The treatment of organic compounds with fuming sulfuric acid is a classic example of electrophilic aromatic substitution, leading to the formation of sulfonic acids and their derivatives. The nature of the starting material, reaction conditions, and directing effects of substituents play pivotal roles in determining the major products. Understanding these pathways not only illuminates fundamental organic chemistry principles but also underscores the importance of sulfonation reactions in industrial chemistry and material science.

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